The experimental evidence of the role of surface restructuring during catalytic reactions

G.A. Somorjai

Department of Chemistry and Materials Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, U.S.A.

Changes of surface structure of transition metals, and oxides were observed to occur on three different time scales. Chemisorption induced restructuring is localized to the proximity of the adsorption site and is likely to take place within less than 10^{-6} sec. In this regime the coverage dependence of restructuring can also be detected. Surface reconstruction has also been found to occur on the catalytic turnover time scale (10^{-2}–10^2 sec) and is detectable readily during oscillatory and partial oxidation reactions. Structural changes also occur at oxide-metal interfaces in this time scale under reaction conditions. Surface atom transport controlled restructuring takes place during longer time-periods, 10^2–10^4 sec. These diffusion controlled processes can be correlated with catalyst activation and deactivation that are detectable on a similar time scale. Oxidation and reduction of catalyst particles, sulfur or alkali metal adsorption can all lead to restructuring of this type. The results of experiments are reviewed and the need for developing time resolved techniques to detect surface structural changes at high pressures and temperatures is discussed.

Keywords: Surface restructuring; evidence for restructuring; adsorption induced restructuring

1. Introduction

Surface science studies lead to the evolution of simplified models of surfaces that are used to explain or rationalize complex surface phenomena. In the 1930's the accepted model of a surface was one of structureless discontinuity [1] that worked well in the absence of experimental techniques that would explore surfaces on the atomic scale. Such model explains the existence of the surface space charge and its behavior during electrochemical reactions and the variation of work function from crystal face to crystal face. Because of the discontinuity at the surface the electrons spilled over by tunneling into vacuum or into another medium (liquid or solid) with a different dielectric constant on the other side of the interface leaving behind a net positive charge. When an atom or molecule adsorbs on a surface with such a space charge it becomes more polarized thereby altering the work function at that particular surface. In the 1950's

surface studies by electron microscopy and field ion microscopy revealed the presence of atomic scale surface irregularities, steps and kinks and point defects (adatoms, atom vacancies). The development of the heterogeneous surface-rigid lattice model [1,2] followed as a result of these findings. This model displays surface atoms at various sites (terrace, step, kink, ad-atom, vacancy) where they are distinguishable from other surface atoms by their number of nearest neighbors. In such surfaces the atoms assumed to maintain their bulk-like equilibrium positions. Thus, by knowing the bulk crystal structure the positions of surface atoms could be predicted.

However, the heterogeneous surface-rigid lattice model did not stand up to the scrutiny of modern surface science studies. Surface crystallography experiments indicate that the surface atoms relax inward, they contract by a large fraction of the interlayer distance. This inward contraction is larger the more open or rougher the surface is [3] (roughness defined as 1/the packing density). Relaxation at the surface often leads to reconstruction [2] as atoms that have directional bonding are seeking new equilibrium positions to optimize their bond strengths to other atoms in the surface and under the surface. The relaxation is particularly large at surface irregularities at steps and kinks as these atoms moved inward to smooth out the surface at the irregularity as much as possible [4]. Thus, atoms in clean surfaces do not occupy bulklike equilibrium positions.

2. Evidence for chemisorption induced restructuring of surfaces

Low energy electron diffraction (LEED)-surface crystallography studies using the recently developed tensor-LEED method of determining the locations of surface atoms permit surface structure determination in the presence of monolayers of ordered or disordered adsorbates. Chemisorption leads to the formation of new surface chemical bonds [4]. As a result, the surface atoms that are relaxed inward when uncovered move again into new equilibrium positions. It was thought that under the influence of chemisorption the relaxed surface atoms of the substrate will move back to bulklike equilibrium positions. This is not the case, however. Chemisorption induces restructuring and the surface atoms move into other sites to optimize their bonding. Table 1 lists the surface structures of metals and semiconductors in the presence of adsorbates that were determined recently. Every substrate surface restructures as a consequence of chemisorption. We shall discuss two examples below to highlight the complexity and diversity of the adsorbate induced surface restructuring phenomenon.

a) Ethylene chemisorption induced restructuring of the rhodium (111) crystal face
    Ethylene at 300 K forms an ethylidyne surface structure, C_2H_3 with the C-C bond perpendicular to the surface [5] and the carbon atom closest to the metal

Table 1
Changes of surface structure induced by chemisorption

Surface-adsorbate system and periodicity	Methode and reference of investigation	Type of restructuring
Cu(100)/O-(2*$\sqrt{2}$ × $\sqrt{2}$)	LEED [1]	Missing-row reconstruction, pairing
	STM/LEED [2]	of Ni-atoms next to row
	Theory (Effective Medium) [3]	"Cu-O-Cu-chains" similar to Cu(110)
Ni(100)/C-p4g(2×2)	LEED [4]	4-fold site
Ni(100)/N-p4g(2×2)	SEXAFS [5,6]	Clockwise rotation of 1st layer atoms
		Buckling of 2nd layer atoms
Ni(100)/Cl-c(2×2)	SEXAFS/XSW [7]	4-fold site
Cu(100)/Cl-c(2×2)	SEXAFS [8]	1st to 2nd layer expansion
Mo(100)/C-c(2×2)	LEED [45]	
Cu(100)/N-c(2×2)	LEED [9]	4-fold site
Cu(100)/S-p(2×2)	XRD [10]	2nd layer buckling (Atom underneath
	MEIS [11]	adsorbate moves down)
	LEED [12]	
Ni(100)/O-c(2×2)	LEED [13,18]	
Ni(100)/O-p(2×2)	LEED [14,18]	
Ni(100)/O-disordered	DLEED [15,18]	
Ni(100)/S-c(2×2)	LEED [16,18]	
Ni(100)/S-p(2×2)	LEED [17,18]	
Ni(100)/S-disordered	DLEED [15,18]	
Cu(110)/K-(1×2)	LEED [19]	Low coverage induced missing-row
Cu(110)/Cs-(1×2)	LEED [19]	reconstruction
Cu(110)/N-(2×3)	PED [20]	Favoring "pseudo-square" model with
	LEIS [21]	square-like 1st layer arrangement
	XPD/AES [22]	Favoring missing-row reconstruction
	STM [23]	with every 3rd ⟨110⟩-row missing
Cu(110)/O-(2×1)	SEXAFS [24]	Missing-row reconstruction
	XRD [25]	Long bridge site
	LEED [26]	"Cu-O-Cu-chains" similar to Cu(100)
	LEED [27]	
	Theory (Effective Medium) [3]	
	ICISS [28]	
Ni(110)/O-(2×1)	LEED [29]	Missing-row reconstruction
		asymmetric long bridge site
Cu(110)/O-c(6×2)	STM/XRD [30]	Cu-adatom c(6×2)-superstructure on
		(3×1) 2 per 3 missing-row
		reconstruction
		2 oxygen sites
Ni(110)/H-(1×2)	LEED [31]	Row-pairing, 2nd layer buckling
Ni(111)/O-(2×2)	LEED [32]	fcc-hollow site
		Clockwise rotation and buckling in 1st layer
Ni(111)/O-p($\sqrt{3}$ × $\sqrt{3}$)	LEED [33]	fcc-hollow site
Ni(111)/S-(2×2)	LEED [34]	fcc-hollow site
		1st to 2nd, 2nd to 3rd layer expansion

Table 1 (continued)

Surface-adsorbate system and periodicity	Methode and reference of investigation	Type of restructuring
Rh(100)/O-(2×2)	LEED [35]	4-fold hollow site, layer contraction
Rh(110)/H	LEED [36-41]	5 superstructure phases
		Local outwards movement of substrate atoms with H-bond
Ru(001)/O-p(2×1)	LEED [42]	3-fold hcp-hollow site
		Buckling and row pairing in 1st and 2nd layer
Ru(001)/O-p(2×2)	LEED [43]	3-fold hcp-hollow site
		Buckling and lateral outwards movement in 1st layer
Cr(110)/N-(1×1)	LEED [44]	4-fold hollow site
		1st layer expansion (24.8%)
Mo(100)/S-c(2×2)	LEED [45]	4-fold hollow site
		2nd layer buckling
Rh(111)/C_2H_3-(2×2)	LEED [47]	Buckling in 1st and 2nd layer
Si(100)/H-(2×1)	STM [47]	Dangling bond adsorption
	LEIS [48]	Dimer relaxation (lengthening)
	Theory (SLAB-MINDO) [49]	
Si(100)/F-(2×1)	ESDIAD [50]	
Si(100)/Cl-(2×1)	SEXAFS [51]	
Si(100)/O-(2×1)	SEXAFS [52]	Dimer insertion (Adsorption into dimer and dimer lengthening)
	Theory (HF-Cluster) [53]	
	Theory (DF-LDA) [54]	
Si(100)/K-(2×1)	LEED [55]	One dimensional Alkali-chains
	SEXAFS [56]	Dimerization nearly removed
	Theory (DF-LDA) [57]	Relaxation of substrate atom distances
Si(100)/Na-(2×1)	LEED [58]	
Si(100)/Li-(2×1)	Theory (DF-LDA) [59]	
Si(111)/Al-($\sqrt{3} \times \sqrt{3}$)R30°	LEED [60]	Removal of (7×7)
	Theory (Total energy) [61]	T4-adsorption site (triangular
Si(111)/Ga-($\sqrt{3} \times \sqrt{3}$)R30°	LEED [62]	site with 4-fold coordination)
	STM [63]	
	XSW, STM [64]	
Si(111)/Sn-($\sqrt{3} \times \sqrt{3}$)	XRD [65]	
Ge(111)/Pb-($\sqrt{3} \times \sqrt{3}$)	LEED [66]	
Si(111)/B-($\sqrt{3} \times \sqrt{3}$)	XRD [67]	Removal of (7×7)
	LEED [68]	T4-"upside down" site (triangular site with 4-fold coordination, B-Si substitution)
Si(111)/Fe-(1×1)	LEED [69]	Removal of (7×7)
Si(111)/As-(1×1)	XSW [70]	Missing top layer in Fe-structure
	MEIS [71]	
	STM, MEIS [72]	
	Theory (GVB) [73]	
Si(111)/GaAs-(1×1)	XSW [74]	
	Theory (DF-LDA) [75]	

Table 1 (continued)

Surface-adsorbate system and periodicity	Methode and reference of investigation	Type of restructuring
Si(111)/Sb-($\sqrt{3} \times \sqrt{3}$)	XPD [76]	Removal of (7×7)
Si(111)/Bi-($\sqrt{3} \times \sqrt{3}$)	XRD [77]	Milk-stool structure, adsorbate trimers
		Si honeycomb layer on top in Bi-structure

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is in a three-fold site (fig. 1a). Forming three metal carbon bonds results in the expansion of the metal atoms [6] around the carbon atom (fig. 1b). This causes the movement of the next nearest neighbor metal atom that has no carbon bond slightly into the surface by about 0.12 Å. In addition, the metal atom in the second layer right under the organic molecule moves upward to bind to the organic species. Thus, there are four metal–carbon bonds instead of three if we include bonding of the adsorbate to the second layer metal atom underneath. The result of chemisorption therefore is the marked restructuring of the metal surface.

b) Oxygen chemisorption induced restructuring of the copper (110) crystal face

Another recent example of adsorbate induced restructuring is the restructuring of the Cu(110) face during the chemisorption of oxygen [7]. The unit cell changes in order to incorporate oxygen atoms into the copper unit cell (fig. 2). The changes occur as a function of time rather slowly at room temperature and can be followed by the scanning tunneling microscope [8]. Fig. 2 shows the evolution of the restructured surface as its domains are forming at the expense of the clean copper domains.

There are not enough systems that have been studied to develop an understanding or to be able to predict the nature of the structural changes that occur when chemisorption takes place. Adsorbate induced restructuring changes with the adsorbate–substrate system, the substrate symmetry, the adsorbate coverage and temperature.

Studies of clean surfaces as well as during chemisorption indicates that the surface atoms are never located at sites predicted by the heterogeneous surface-rigid lattice model either when it is clean or in the presence of adsorbates. The surface atoms move inward when clean and the surface restructures again during chemisorption in order to optimize the bonding of the adsorbate atoms or molecules. Thus, the surface is flexible, it rearranges according to changes of its chemical environments. The surface is dynamic and it is clear that as one adsorbate is substituted by another the surface restructures again to

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optimize its chemical bonding with the new adsorbate. The more open is the surface, the less number of nearest neighbors the surface atoms have, the more marked is the restructuring.

3. Chemisorption induced restructuring during catalytic reactions

Evidence of adsorbate induced restructuring during catalytic reactions has been obtained from studies of carbon monoxide oxidation. This reaction can have an oscillating rate in a given partial pressure and temperature range over several transition metals (Pd, Ir, Pt, ...) [9]. Ertl and his co-workers have
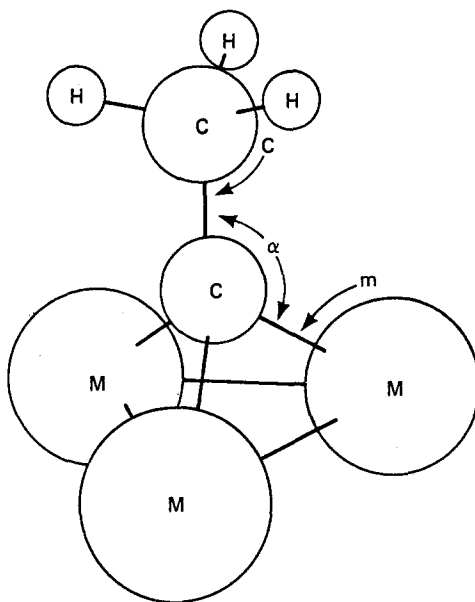
	C [Å]	m	r_M	r_C	α [°]
Co_3 (CO)$_9$ CCH$_3$	1.53 (3)	1.90 (2)	1.25	0.65	131.3
H$_3$ Ru$_3$ (CO)$_9$ CCH$_3$	1.51 (2)	2.08 (1)	1.34	0.74	128.1
H$_3$ Os$_3$ (CO)$_9$ CCH$_3$	1.51 (2)	2.08 (1)	1.35	0.73	128.1
Pt (111) + (2 × 2) CCH$_3$	1.50	2.00	1.39	0.61	127.0
Rh (111) + (2 × 2) CCH$_3$	1.45 (10)	2.03 (7)	1.34	0.69	130.2
H$_3$C - CH$_3$	1.54			0.77	109.5
H$_2$C = CH$_2$	1.33			0.68	122.3
HC ≡ CH	1.20			0.60	180.0

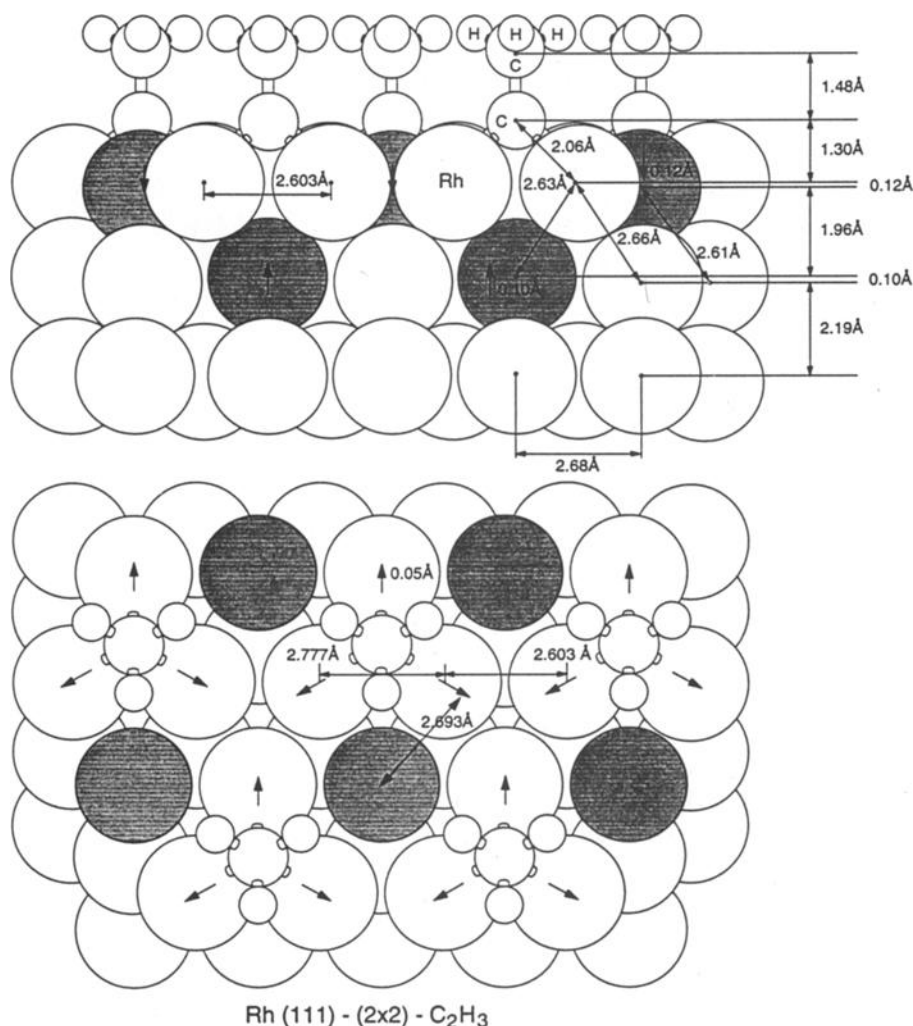Fig. 1a. The ethylidyne molecular surface structure.

Fig. 1b. The restructuring of the rhodium (111) crystal face induced by ethylidyne chemisorption.

studied at low pressures [10], the nature of restructuring during the oscillatory reaction on the (100) crystal face of platinum. The oscillation is caused by two different reaction branches, one involves the carbon monoxide oxidation rate on the CO rich surface the other the reaction rate on the oxygen rich surface. Since the work function changes as the surface becomes enriched with carbon monoxide or oxygen the work function change can be monitored at low pressures by photo-electron emission microscopy (fig. 3). It has been shown that the restructuring rate of the surface is equal to the oscillation rate of the reaction thus the reaction is driven by surface restructuring or conversely surface restructuring is driven by the catalytic chemical reaction. Studies at high pressures carried out in my laboratory on several different surfaces indicated that similar oscillations
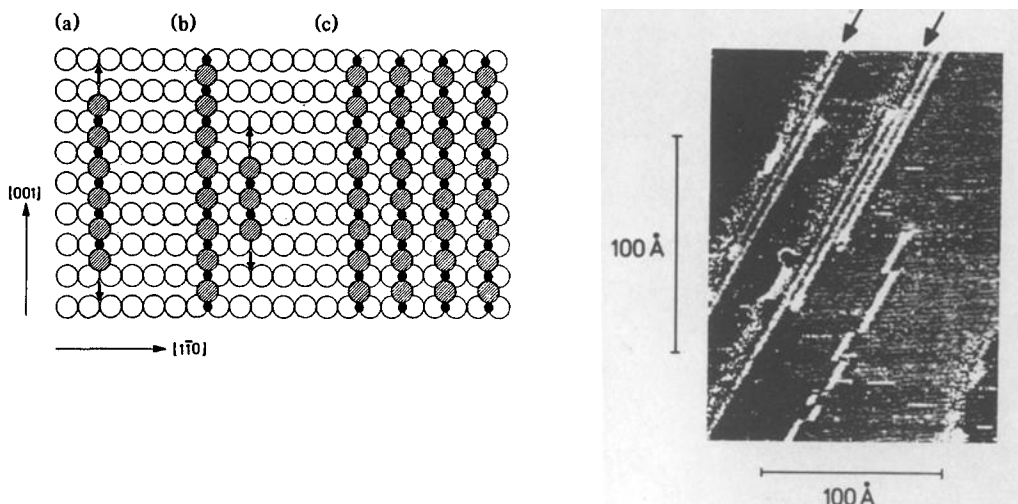
(2x1)-O/Cu(110)

Fig. 2. Oxygen chemisorption induced restructuring of the copper (110) crystal face.

occur [9]. In this circumstance the restructuring is caused by the periodic reduction and oxidation of part of the surface. The oxide-metal interface forms and disappears as the surface concentration becomes more oxygen rich or carbon monoxide rich. Thus there are several mechanisms of oscillations, some involving metal surface restructuring, others involving surface restructuring by the periodic oxidation and reduction of the surface. There are several other oscillatory reactions where surface restructuring may be monitored ($CO + NO$, $NO + NH_3$) and studies of these reactions are in progress in many laboratories.

It is very unlikely that surface restructuring is limited to occur during catalytic reactions that oscillate. It is the contention of this author that surface restructuring drives the turnover of most catalytic reactions since the surface is restructured more readily the lower the coordination of the surface sites. Clusters that are used almost exclusively in heterogeneous catalysis are more likely to show high catalytic reaction rates because their restructuring rate is optimum.

4. Surface restructuring on longer time scales than catalytic reaction turnover times

Restructuring of surfaces also occurs on longer time scales that are controlled by mass transport along the surface. This is one of the mechanisms of catalyst activation or deactivation as the structure of the small chemically active particles is changed due to the presence of additives. Sintering and re-dispersion are among the phenomena that are associated with atom transport and surface restructuring. Fig. 4 shows electron microscopy pictures and schematic diagrams of changes that occur when rhodium particles are heated in hydrogen and then
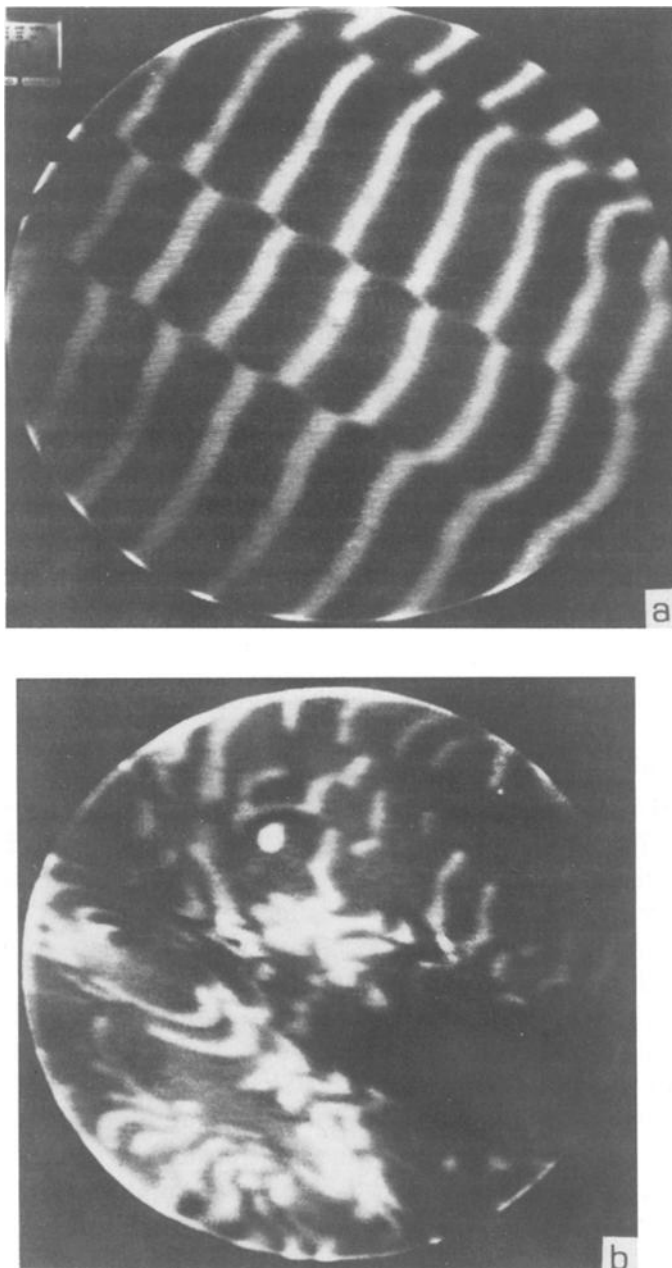
Fig. 3a. Standing-wave-type pattern accompanying harmonic kinetic oscillations. $T = 550$ K, $p_{O_2} = 4.1 \times 10^{-4}$ mbar, $p_{CO} = 1.75 \times 10^{-4}$ mbar.

Fig. 3b. Irregular and rapidly changing pattern reflecting chemical turbulence. $T = 540$ K, $p_{O_2} = 4.0 \times 10^{-4}$ mbar, $p_{CO} = 1.70 \times 10^{-5}$ mbar (G. Ertl, Catal. Lett. 9 (1991) 219.

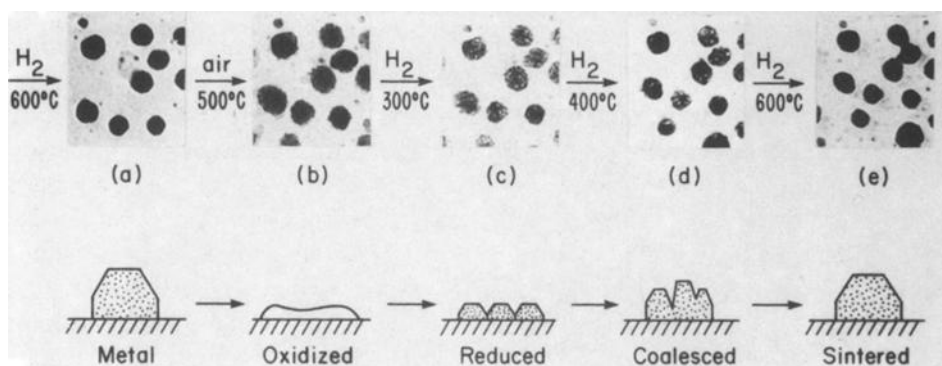Fig. 4. The sintering and redispersion of rhodium particles (ref. [11]).

in oxygen and are again reduced [11]. The growth of the small particles can be reversed by oxidation and subsequent reduction.

Thus the flexible surface restructures on three different time scales; On the time scale of chemisorption involving a slight rotation or movement of the surface atoms to maximize the strength of the surface chemical bonds with the adsorbates; On the time scale of catalytic reaction turnover and on longer time scale involving diffusion controlled atom transport.

5. The catalytic consequences of adsorbate induced surface restructuring

Let us consider that surface restructuring occurs during all catalytic reactions. The dynamical restructuring model can explain the four puzzles of heterogeneous catalysis [1,12]. These are 1) rough surfaces do chemistry; 2) the existence of structure insensitive reactions; 3) the high activity of oxide-metal interfaces; and 4) the high activity of bimetallic interfaces.

1) It is well established by chemisorption studies that low coordination sites, steps and kinks, hold chemisorbed atoms and molecules with higher binding energies than their binding energy on sites on the flat surface [12]. Thermal desorption studies indicate that desorption of atoms such as hydrogen or carbon monoxide from the step sites and the kink sites occur at higher temperatures at a maximum rate indicating their higher binding energies at these sites. Chemisorption of molecules like ethylene or other hydrocarbons lead to CH and C-C bond breaking at much lower temperatures at these defect sites than on the flat surface. High resolution electron energy loss spectroscopy studies on nickel surfaces and on other transition metal surfaces clearly indicate the much higher activity of surface irregularities for bond breaking by the occurrence of these bond scission processes at lower temperatures. Thus, the bond breaking at these defect sites require less activation energy. However, defect sites also prove to be catalytically more active than flat surfaces. Studies of H_2/D_2 exchange at low

pressures, of hydrocarbon conversion reactions on platinum single crystal surfaces revealed that surfaces that have steps and kinks have much higher turnover rates than flat surfaces. The chemisorption activity of these surfaces irregularities that indicate higher binding energies at these sites for chemisorbed atoms and molecules contradict their high catalytic activity that is also observed. High binding energies indicate longer chemisorption residence times. If the atom or molecule occupying the defect sites, remains there for long times its turnover rate must be small yet, higher turnover rates are clearly observed.

One way of explaining this contradiction is the dynamical restructuring model. Under the influence of strong chemisorption the surface restructures. During this restructuring process the catalytically active sites are created. Thus the strongly adsorbed atoms and molecules are responsible for creating the catalytically reactive surfaces which then undergo periodic rapid restructuring as desorption and readsorption occur leading to rapid turnovers. Thus, the chemisorbed atom creates the active sites on which the catalytic reaction occurs by restructuring the substrate surface.

2) One of the most successful classifications in heterogeneous catalysis is the division of reactions into structure sensitive and structure insensitive types [1]. The structure sensitive reactions change their reaction rates as the originally clean surface structure changes. Ammonia synthesis is one example showing extreme structure sensitivity [13]. Structure insensitive reactions maintain their rates the same regardless of the initial surface structure. Hydrogenation reactions especially the well-studied ethylene hydrogenation to ethane have proven to be structure insensitive [14]. While it is not too difficult to rationalize a correlation between the structure of the clean surface and its reactivity since the reaction rate must depend on the nature of bonding of some reaction intermediates that in turn dependent on the surface structure, it is very difficult to understand how structure insensitive reactions could occur.

One explanation is the adsorbate induced restructuring of surfaces during the chemisorption phase of the catalytic reaction as the strongly adsorbed layer forms it restructures the surface thereby creating the active sites. These active sites would not have existed without the chemisorption of the reactants, thus the original clean surface structure has very little to do with the active sites that formed only by adsorbate induced restructuring. Since each crystal face when it restructures yields the same type of active sites, the active site concentration is only coverage dependent but independent of the nature of the clean surface structure and of course the coverage only depends on the applied reactant pressures.

3) Oxide metal interfaces can exhibit very high activity as compared to the metal alone whether the metal is placed on the oxide or the oxide on the metal as shown by Schwab et al. [15] in the 1930's. More recently Touster [16] has reinvestigated this phenomenon using titanium oxide surfaces and found unique high catalytic activity due to oxide metal interfaces and this phenomenon is
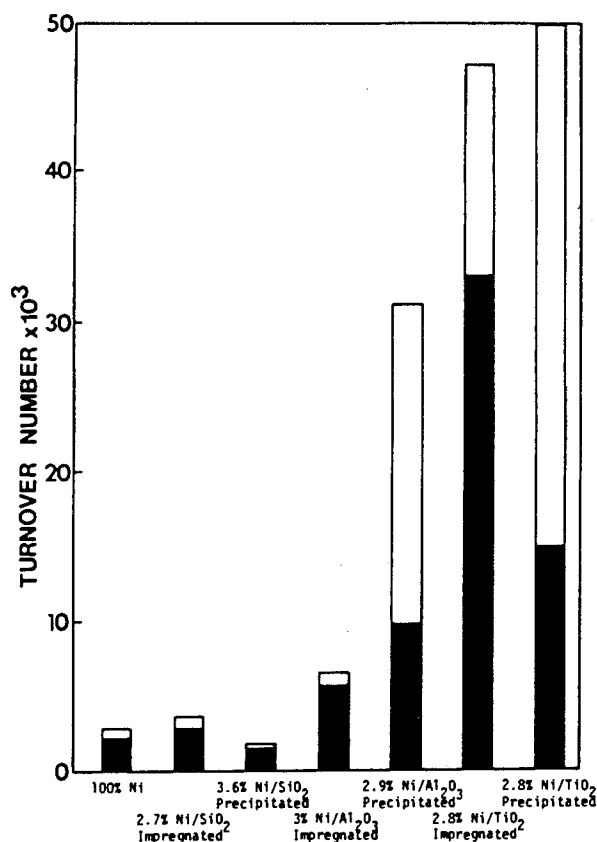
Fig. 5. The effect of various oxide supports on CO hydrogenation over nickel catalysts (ref. [17]).

called strong metal support interaction. The typical oxide induced changes in the metal activity can be readily shown in fig. 5 where Bartholemew and his co-workers [17] have compared the rates for forming methane from carbon monoxide and hydrogen for various nickel catalysts deposited on different oxide supports.

There are orders of magnitude changes in the reaction rate when the nickel particles are deposited on silica as compared to nickel on titanium oxide. The typical activation treatment of catalysts of this type involve reduction in hydrogen during which the oxide encapsulates the metal resulting in much reduced carbon monoxide or hydrogen chemisorption activity followed by oxygen heat treatment that activates the catalysts during which the oxide forms small islands in such a way as to maximize the oxide metal periphery area.

A typical reaction pattern reflecting the behavior of an active oxide metal interface system has been reported for the CO_2/H_2 reaction on Rh on to which a TiO_x is deposited, as a function of TiO_x coverage [18]. The oxide is deposited by condensing the metal from the vapor phase and then oxidized to form TiO_x.

The reaction rate is at a maximum at ~ 0.5 monolayer oxide coverage. The reaction rate increases by 14-fold with respect to the clean metal surface. If we were to give the specific turnover rates by dividing it with the surface area we should use the oxide-metal interface area instead of the total area which is the metal plus the oxide surface area since the oxide is inactive. Since the oxide metal periphery areas is about 10% of the total area, at 50% oxide coverage the specific turnover rate is two orders of magnitude greater as compared to the rate on the clean Rh metal.

Similar behavior is found for CO/H_2 and acetone/H_2 while the hydrogenation of ethylene and the hydrogenolysis of ethane remained unaffected by the presence of TiO_x indicating that the carbon-oxygen bond is being activated at the oxide-metal interface. Thus any molecules that contain CO bonds are benefiting from the presence of the oxide-metal interface catalytic sites. Other oxides deposited on Rh such as vanadium oxide show similar effects, however, the increase in reaction rate is not as large in the presence of vanadium oxide as it is with the TiO_x/Rh interface.

I propose that the increased rate of chemisorption induced restructuring of the metal at the oxide interface is responsible for the increase in reaction rates. The lower coordination metal sites at the periphery of the oxide islands can restructure with higher frequency thereby greatly enhancing the turnover rate. We carried out scanning tunneling microscopy studies to image the TiO_x islands and the oxide-metal interface. Fig. 6 shows the STM picture. The bright rings that appear at the oxide island periphery indicating large charge density associ-
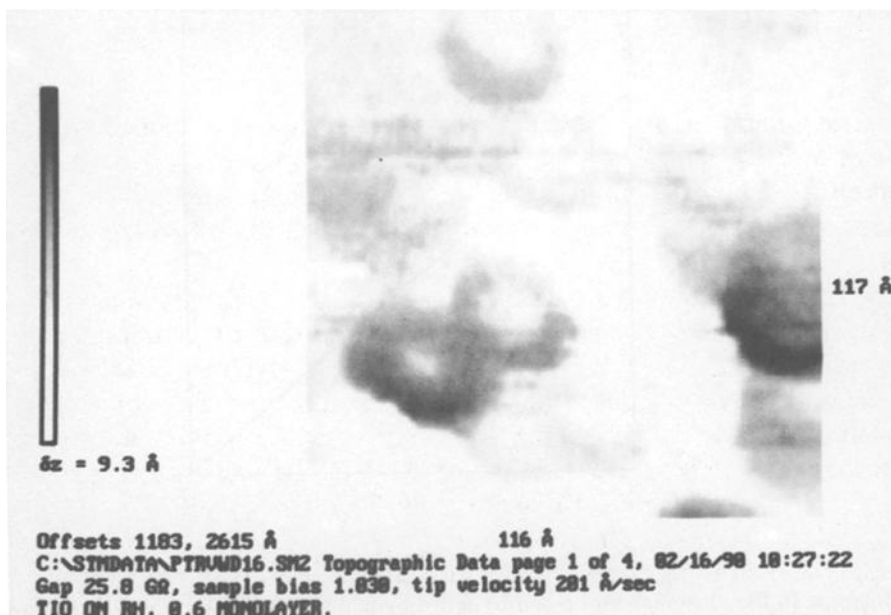

Fig. 6. Scanning tunneling microscope picture of titanium oxide islands on rhodium.

ated with the presence of Ti^{3+} ions in the partially reduced oxide at the metal interface.

4) When gold which is inactive for most reactions as a catalyst, is added to palladium the rate of the hydrogen/oxygen reaction to form water is enhanced by 50-fold [19]. Gold is found to similarly enhance the isomerization [20] and dehydrogenation activity of platinum (figs. 7a and 7b). This effect is difficult to explain unless we invoke again the increased rate of chemisorption induced periodic restructuring of the active transition metal caused by dilution of its site concentration by gold. The formation of lower coordination metal sites at the bimetallic interface, restructure at higher frequencies to cause higher turnover rates.
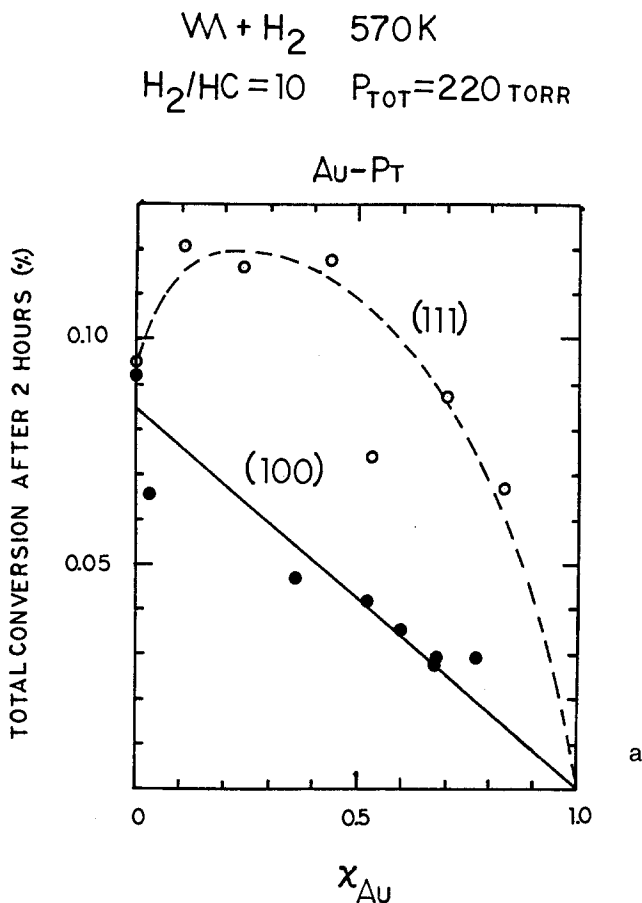
$$\text{\/\/\ + H}_2 \quad 570\,K$$
$$H_2/HC = 10 \quad P_{TOT} = 220\,\text{TORR}$$

Au–Pt

Fig. 7. Increase in the a) isomerization and b) dehydrogenation rates of the Pt(111) crystal face as a function of gold coverage.
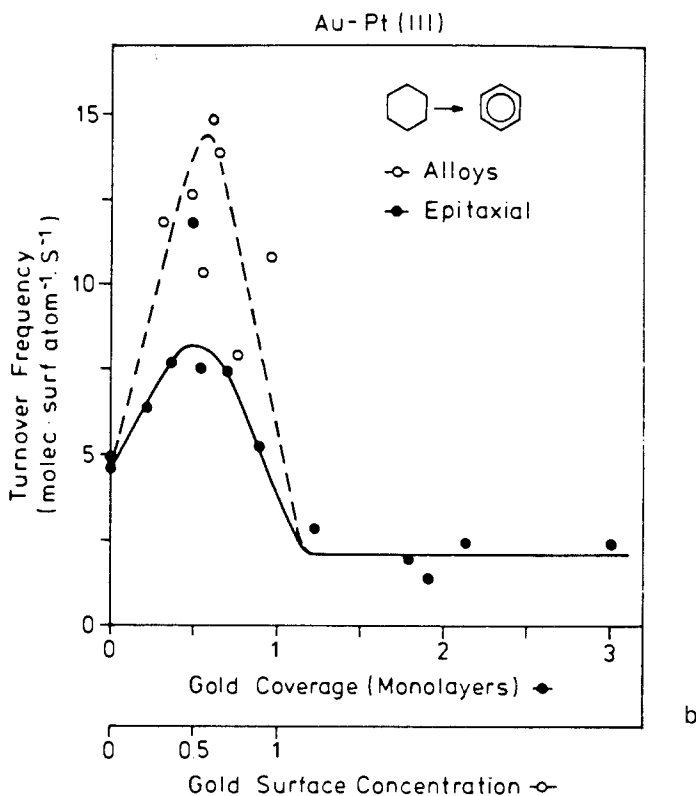
Au‑Pt (III)

Fig. 7. (continued).

6. Conclusion

The recent view of surfaces based on modern surface science studies is one of great flexibility. The surface structure changes in response to its chemical environment to optimize its bonding with the chemisorbed reactants. Restructuring occurs on the time scale of chemisorption and catalytic reactions and also on longer time scales. If we assume the catalytic reaction turnover is driven by the periodic restructuring of the surface, we can explain four of the difficult puzzles of heterogeneous catalysis. 1) why rough surfaces have enhanced chemisorption and catalytic reaction rates, 2) the existence of structure insensitive reactions, 3) highly active oxide‑metal interfaces and 4) highly active bimetallic interfaces with one metal such as gold being inactive.

We need to develop time resolved techniques to monitor simultaneously the dynamic changes that occur on both sides of the surface chemical bonds; the adsorbate and the substrate sides. We need techniques that can determine changes of surface structure on the time scales of 10^{-9}–10^2 sec and at high pressures where the surface is covered with adsorbates and catalytic reactions usually take place. Photon scattering techniques [non linear laser optics that

provide sum frequency generation (SFG) or synchrotron radiation induced extended X-ray absorption fine structure (EXAFS)] appear promising along with the application of the scanning tunneling microscope (STM). Once the technique is available pressure jump or temperature jump studies that alter the surface concentration of intermediates in a time-dependent way can yield information that would elucidate the roles of adsorption induced restructuring of surfaces.

Acknowledgement

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