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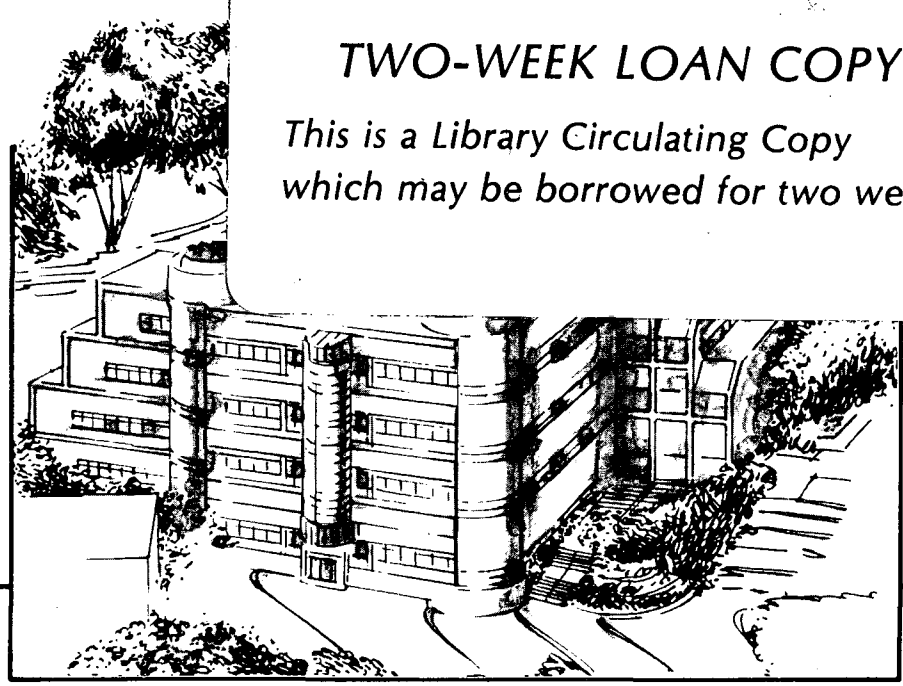

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CONCEPTS IN SURFACE SCIENCE AND HETEROGENEOUS CATALYSIS

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Abstract

The development and application of surface sensitive techniques over the last two decades has greatly improved our understanding of surface phenomena at the molecular level. From this newly acquired vast data base new concepts have emerged and it is the purpose of this paper to review those that relate most directly to the chemical properties of surfaces. Concepts concerned with the structure of clean and adsorbate-covered surfaces, the nature of the surface chemical bond, the dynamics of gas–surface interactions, surface chemical reactions and catalytic processes are presented and illustrated with examples from the recent literature.

1 Introduction

The study of surface phenomena is a multi-disciplinary science, utilizing a wide spectrum of experimental and theoretical techniques. The field encompasses research not only on the chemical properties of interfaces but also the mechanical, optical, electrical and magnetic properties. During the past twenty years there has been an explosive growth in the study of surfaces and interfaces because it is one of the intellectual frontiers of the physical sciences and is also of immense technological importance. From the results of these molecular level studies, new concepts have emerged which have markedly altered many of our views of surface phenomena. The purpose of this paper is to review some of the more general concepts that have emerged from this research in the field of surface science and to present examples that both illustrate the phenomena and demonstrate their role in more complex systems. We shall, however, concentrate on those particular features of surface structure and molecular behaviour at interfaces which are most directly related to the chemical properties of the surface.

One field which has benefitted greatly from the advances in our fundamental understanding of chemical phenomena at surfaces is that of catalysis science. Indeed, as a subfield of surface science, the study of heterogeneous catalysis has undoubtedly been of unique importance. For this reason we have, in many cases, chosen examples that show how these concepts relate to catalytic phenomena and catalyst systems that are of major importance in the chemical and petroleum industries. In addition, we include a section which summarizes concepts that have emerged from studies directed specifically at the catalytic properties of surfaces.

2 The Experimental Approaches and Techniques of Modern Surface Science

There are two main approaches to the study of surfaces. The first utilizes high surface area materials to enhance the contribution of the surface to the overall properties and characterizable features of the solid. One class of solids that fall into this category are the microporous crystalline zeolites[1,2] and related materials which may have surface areas in the range 200-700 m^2/g: an example of a zeolite structure is shown in Fig.1. This particular zeolite is a naturally occurring mineral but, since the discovery that these materials possess unique properties in the role of both catalysts and selective adsorbents (molecular sieves) several hundred such structures have been synthesized in the laboratory; many of which have no analogue in nature. Indeed, the progress in this field has been such that novel structures tailored to the needs of particular chemical processes have been prepared . The zeolite illustrated in Fig.1 contains only silicon, aluminum and oxygen framework atoms but in recent years compositions including many other elements (eg Ga, Ge, Fe, P) have been prepared and new classes of compounds, such as the aluminum phosphates[3], have also been synthesized in microporous, crystalline forms. Microporous, crystalline solids may be studied by electron microscopy , solid state NMR, EXAFS, X-ray and neutron diffraction in order to determine the location, coordination number and chemical environment of each atom - many of which, by the very nature of the materials, are surface atoms. This information can then be used, for example, to relate molecular structure to catalytic behaviour.

The second approach involves the use of model low surface area specimens. These consist of single crystal or polycrystalline samples with a surface area typically of the order of $1cm^2$. Well defined surfaces can be prepared by the careful orientation, cutting and polishing of single crystals which may then be cleaned by ion sputtering and other techniques in a high vacuum system. It is much easier to control and determine the cleanliness, structure and composition of these $1cm^2$ samples than high surface area materials and thereby more

definitive measurements of relevant atomic and molecular level parameters may be obtained.

A wide range of techniques have been developed that are capable of specifically probing the properties of interfaces[4]. A selection of these experimental techniques is presented in Table I - they predominantly involve the use of photons, ions and low energy electrons to probe the immediate and near surface regions. The combined use of several of these techniques provides complimentary information on different aspects of the interface including composition (AES, XPS, ISS), geometric structure (LEED, XRD, ISS, TEM[HREM], XPD, STM), electronic structure (UPS, XPS, BIS) and adsorbate bonding (HREELS, LEED, TPD, XANES). Some of these techniques can also be used to look at the surfaces of high surface area solids but, in many cases, readily interpretable information can only be extracted from single crystal studies. Furthermore, most of these probes can only be used in a high vacuum environment.

In the study of catalytic surface phenomena low surface area specimens have proved to be a very valuable tool, especially as models for supported metal catalysts. This very important class of catalysts consist of small (10-1000Å) metal particles dispersed on a support; typically, but not exclusively, an oxide. The metallic surface areas of such materials generally fall in the range 1-100 m^2/g. The study of such systems using surface sensitive techniques is restricted in part, as mentioned above, by the inherent limitations of many of the experimental probes but more fundamentally by the complex, heterogeneic nature of the materials themselves. Judiciously chosen, single crystal model samples allow fundamental studies of reaction mechanisms and the effects of surface structure and bonding to be performed under well defined conditions. It is undoubtedly in this area of catalysis that modern surface science has contributed the most.

The challenge to the surface scientist working in applied technological fields such as catalysis is to relate the properties of these low surface area samples to those of real systems under their operating conditions. The problem revolves around the "pressure gap" - the application of most surface sensitive techniques is restricted to high vacuum conditions

and typically involves measurements at relatively low temperatures and coverages. In contrast, the process that is being modelled often occurs under conditions of high pressure, temperature and coverage. One approach to this problem involves the use of UHV apparatus equipped with environmental cells in which conditions much closer to those actually employed can be attained. This has been successfully applied to the study of both electrochemical and catalytic phenomena. In the latter case, the low area single crystal specimen may, after preparation and characterization under high vacuum conditions, be enclosed in an isolation cell and then exposed to reactant gases at elevated pressures[5-8](Fig.2). The rate and kinetic parameters of the reaction, along with the selectivity, can be ascertained from the product distribution which is in turn determined using mass spectrometry or gas chromatography. After reaction the sample is transferred back into high vacuum and the surface composition and structure redetermined. Therein lies a method for correlating high pressure catalytic behaviour with specific surface properties. A few examples of this powerful technique will be presented later, but first we will review some of the more classical concepts of surface chemistry as well as concepts that have emerged from fundamental studies in modern surface science.

3 Classical Concepts in Surface Science

Three of the classical concepts in surface chemistry are:

- the surface free energy and surface segregation.
- the surface space charge.
- the unique properties of curved surfaces.

The fact that **the surface free energy** is always positive means that any condensed phase will preferentially minimize its surface area and/or place on the surface that material which

has the lowest free energy. As a general guideline[9], metals have higher surface free energies than oxides, so oxides usually cover the metals. Since water has an even lower surface energy than oxides, it covers the oxides, while organic molecules such as benzene have a lower surface energy still and will cover the aqueous phase. Finally, fluorocarbons have the lowest surface energy of all and are therefore the most specific to surfaces. Those materials that segregate to surfaces because of their low surface energy are called surface active agents. Their behaviour, for example, underlies the principle of operation of detergents.

The theoretical foundations for the thermodynamic description of **surface segregation** were developed by Gibbs[10]. In dilute alloy systems, for example, segregation is driven predominantly by the lowering of the surface free energy and relief of bulk strain energy[11-13], although other factors (eg heat of mixing of alloy phases) can modify the extent of segregation. The important conclusion, however, is that the driving force to minimize the total free energy of the system may give rise to surface compositions very different from the bulk even in what are nominally single phase systems and, in doing so, may impart to the surface superior mechanical or chemical properties. Modern surface science studies on alloy systems have not only confirmed the basic premise of surface segregation on an atomic scale but have also allowed a detailed and quantitative test of the various theoretical models (eg. ref.14).

The next figure (Fig.3) shows how a **space charge** may buildup at any interface due to the extension of the electronic wavefunctions out of the solid into the vacuum or other medium - the electrons 'spill out' leading to a surface dipole and a space charge whose thickness decreases with increasing initial charge density[15]. The resulting charge separation provides a static electric field that is an important property of any surface and a face specific contribution to the work function. Furthermore, the adsorption of atoms or molecules that donate or accept electrons can drastically modify this surface dipole. Adsorbate bonding and diffusion, as well as surface ionization are all influenced by this surface electric field.

Curved surfaces have vapor pressures that are different internally and externally in order to maintain the surface curvature (Fig.4A). Particles with different radii of curvature also have different vapor pressures and solubilities[16,17]; more specifically, the smaller the particle, the higher its vapor pressure or solubility Fig.4B). As a result, in a system containing a mixture of small and large particles the small particles will dissolve preferentially. Similarly, large particles will grow at the expense of small ones (Ostwald ripening) thus leading to phenomena such as sintering. Nature has a way of preventing this by providing systems where all the particles have very similar radii. Examples of these include colloidal systems (eg milk and blood) in which the particles can also stabilized against coalescence by electrostatic repulsion between electrical double layers induced by the surface charge separation described above.

We can therefore expect the behavior of surface systems to be markedly dependent on their surface energies, surface charge and size; indeed these concepts are used in areas such as catalysis science (to prepare, stabilize and regenerate catalyst particles), the paint industry and separation technology.

4 Modern Concepts in Surface Science

Modern surface science has provided many new concepts, some intimately related to those already mentioned, and brought our understanding of the properties of surfaces down to the molecular and even atomic levels.

4.1 Relaxation, Reconstruction and Atomic Scale Structure (Terraces, Steps and Kinks) of Clean Surfaces

Since the 3D periodicity of a solid is terminated at the surface, it is possible for the interlayer spacing of atomic layers near the surface to differ from that found throughout the bulk ("**relaxation**"). Surface crystallography studies[18] have shown that in vacuum virtually all

clean metal surfaces relax and that the spacing between the first and second atomic layers is significantly (ca.1-20 %) reduced from that which characterizes the bulk. The lower the atomic packing and density of the surface, the larger is the relaxation.

The forces which lead to relaxation of surfaces and result in a change in the equilibrium position and bonding of surface atoms can give rise to more drastic **reconstruction** of the outermost layers; that is, the surface can assume an atomic structure which differs more fundamentally from that expected from termination of the bulk structure. One example is shown in Fig.5. The gold, platinum and iridium (100) surfaces all show reconstruction: the surface unit cell which would be square in the absence of reconstruction is, instead, pseudo-hexagonal[19]. The surface structure assumed involves not only closer packing but also buckling of the surface layer. Many other surfaces of monatomic solids also exhibit reconstruction and this can lead to unique electronic and chemical properties. The reconstruction of semiconductor interfaces is generally more dramatic than is the case for metals. An example is shown in Fig.6 which illustrates the (2x1) surface reconstruction of the Si(100) face. Extensive analysis of LEED and ion scattering data[20,21] has led to the structure shown, in which the outermost atomic plane consists of buckled but untwisted dimers, and relaxation extends down to the fourth or fifth layer.

The phenomena of relaxation and reconstruction are both microscopic expressions of the minimization of the surface free energy of the system.

The presence of **atomic steps and kinks**, even on nominally perfect low index crystal faces, has been revealed by several imaging techniques (eg low energy electron microscopy[22], photoelectron microscopy[23], reflection and transmission electron microscopy[24]) but recent developments in Scanning Tunnelling Microscopy (STM) in particular have greatly increased our atomic-level understanding of local surface structure[25,26]. Fig.7 is an STM image of a rhenium (0001) surface[27] that was passivated by adsorption of half a monolayer of sulphur, thereby making it resistant to oxidation or other chemical attack (by this means it could be

studied by a scanning tunnelling microscope even in air). From this picture, the presence of kinks and steps can clearly be seen. Moreover, it has become clear that the density of step atoms on even the lowest energy surfaces can be relatively high and that such features will be stable under virtually all experimental conditions including those pertaining to heterogeneous catalysis.

The electronic properties of the step atoms differ markedly from those of the terrace atoms. This is reflected in the decrease in the average work function with increasing step density on vicinal surfaces[28] but is more directly illustrated by measurements of the local barrier height using a STM[27]. Intimately related to the change in barrier height are variations in the electric field strength at steps. It is not surprising therefore that such sites are implicated in many aspects of adsorption, desorption, bond dissociation etc.[29-32].

The unusual properties of curved solid surfaces (small particles) are clearly also related to the presence of such atomic-scale structure. Recent work on small metal clusters has shown,however, that in addition to the unusual coordination of surface atoms in this size regime, such particles may also exhibit fluxionality of structure[33], markedly different electronic properties (eg. work function and electronic affinity[34]) and substantially different phase transition temperatures (eg. melting points[35]).

4.2 Adsorption-Induced Changes in Structure and Composition

A related concept that has emerged from modern surface science studies is that of adsorbate-induced restructuring and segregation. In order to demonstrate these phenomena let us consider several examples. When strong bonds are formed between an adsorbate and a surface, the surface atoms may modify their positions to conform to the new chemical environments - this is the phenomenon of **adsorbate-induced surface reconstruction**. For example, low coverages of hydrogen on W(001) induce a c(2x2) surface reconstruction at 300K[36,37]. Similarly, the presence of a quarter monolayer of atomic carbon on Ni(100) induces a reconstruction of the topmost nickel atoms both parallel and perpendicular to the surface, in

such a manner that the four nickel atoms surrounding each carbon atom are rotated with regard to the underlying layers[38] (Fig.8). The importance of adsorbate induced restructuring such as this in heterogeneous catalysis should not be underestimated since the catalytically active surface may only exist in the presence of certain adsorbates. The time scale for the reconstruction may be much shorter than catalytic turnover times or, in other cases, may even be determined by the reaction mechanism. There have been numerous investigations of kinetic oscillations in the catalytic oxidation of CO on Pt surfaces[39]. These self-sustained reaction rate oscillations may be accompanied by large temperature changes as shown in Fig.9 and have been observed over a wide range of conditions. One of the mechanisms shown to operate under low pressure, isothermal conditions[40] involves the restructuring of the Pt(100) surface in the manner described in the previous section. In the presence of a high concentration of adsorbed carbon monoxide the primitive (1x1) surface structure with a square unit cell is preferred, whereas in the presence of atomic oxygen the reconstructed hexagonal surface structure is more stable. Variations in the surface concentration of the adsorbed species during the oxidation, oscillations in the reaction rate and restructuring of the platinum surface are all intimately coupled and occur on the same time scale thereby yielding the observed behaviour. This, however, is only one of several mechanisms that can lead to oscillatory behaviour and the nature of the driving force at higher pressures is still under debate[41-43].

If reconstruction occurs very slowly, on a time scale that is much longer than that of the reaction, there may be long term changes in the catalytic reaction rates (ie either a gradual increase in activity or a slow poisoning of the catalytic reaction). One such example of a slow diffusion-controlled reconstruction is the coalescence of atomic surface steps into multi-atomic steps that ultimately leads to facetting[44]. This type of behaviour is likely to be irreversible under reaction conditions but might be reversed by thermal restructuring upon desorption of the reaction intermediates. A related phenomenon is the change in shape, structure and size of small supported metal particles upon oxidation or reduction. This

effect is utilized in the regeneration of many aged catalysts where an oxidation/reduction cycle can result in an enhanced dispersion of the active phase[45–47]. Oxidation of the large metal particles formed by sintering generally leads to better wetting of the underlying oxide surface. During subsequent low temperature reduction there is a tendency for the oxidized layer to break up into smaller metal particles: hence the increase in metal surface area and dispersion. In certain systems this procedure may be repeated many times, reproducibly yielding the same catalyst particle structure and therefore the same initial catalytic activity.

The examples above all concern cooperative reconstruction of the substrate surface on a microscopic scale ($\sim$ 50–10000 Å): it can also occur, however, on a very local scale. For example, recent diffuse LEED work[48] has shown that the presence of an adsorbed oxygen atom in a four-fold hollow site on a W(100) surface induces a clustering (or local reconstruction) of the neighbouring tungsten atoms.

It was described earlier how alloy systems may minimize their surface free energy by segregation of one of the components to the surface. The surface composition that satisfies the criterion in the presence of reactive gases will, however, frequently differ from that which holds at a vacuum interface. In certain cases, segregation will result from the preferential reaction of one component to yield a phase insoluble in the alloy. This is well documented for alloys in which selective oxidation of one component can occur; particular examples include alloys of Pt with other Gp.VIII metals[49,50] and alloys of electropositive elements (eg. Zr, Ti, lanthanides and actinides) with more noble metals[51]. A more subtle and surface specific demonstration of this concept is where segregation is induced purely by the different heats of adsorption of a gas phase constituent on the two components of the alloy. This phenomenon is not well documented in the literature although, for example, Bouwman et al.[52] report a reversible surface segregation of Pd in polycrystalline Ag-Pd alloys upon CO chemisorption and a theoretical treatment of such **chemisorption induced segregation**, incorporating some comparisons with experiment, has been carried out by Tomanek et al.[53].

A closely related phenomenon appears to be responsible for at least some aspects of the SMSI (strong metal-support interaction) exhibited by certain metal-oxide systems. In particular, reduction of titania supported catalysts at high temperature can lead to migration of a partially reduced titania species onto the metal particles, thereby blocking the low temperature adsorption of CO and H_2, but not preventing the hydrogenation of CO at higher temperatures[54–56]. The effect may be reversed by annealing in an oxidizing environment.

4.3 Epitaxial Growth and Surface Compound Formation

Fundamental studies of the growth of evaporated films on a multitude of different substrates have led to the concept of **epitaxial growth**. In its broadest interpretation this concept covers all cases where the substrate acts as a 'template' and has a significant influence on the growth mode of the deposited material. A much more restricted definition would include only those examples where the substrate actually imposes its own crystal structure, orientation and lattice parameter on the adsorbed overlayer (ie 'pseudomorphic' growth). The idea is best illustrated by reference to the many studies of ultrathin metal overlayers on metal single crystals[57,58]. There are numerous instances where the growth mode of one metal on another varies according to the orientation and symmetry of the exposed substrate crystal face: a far better illustration of this concept, however, may be obtained from examples such as the Pd/Ag(100) and Fe/Cu(100) systems. In the former case[59], where the two metals have the same bulk structure (fcc), the Pd initially grows in perfect epitaxy with a 5.1% lateral expansion of the interatomic spacing imposed by the substrate. This strained layer-by-layer growth persists to beyond 3 monolayers before relaxation to the bulk structure is seen. In the latter case the effects of the interfacial interaction are more dramatic. The Cu(100) substrate forces the iron to adopt an epitaxial fcc structure (as opposed to the bcc structure of bulk iron) up to film thicknesses of 5ML, after which the epitaxial relationship is unable to sustain the close packed Fe and collapse to a structure more closely approaching that of the bulk occurs[60]. The effect of epitaxial relationships are also evident in more

complex systems in the form of preferential crystallite orientation. For example, electron microscopy studies of Cu/ZnO methanol synthesis catalysts[61] show a strong preference for structural registry of the (211) planes of copper particles with the $(10\bar{1}0)$ plane of ZnO.

Another important concept to consider is that of **surface compound formation**. The studies of Sinfelt and coworkers have shown that when particle sizes become very small and dispersions tend to unity (that is, virtually every atom is present at the surface), alloy systems exhibit very different "phase diagrams" from those that characterize the bulk systems. For example, microclusters containing both Cu and Ru or Cu and Au atoms can be produced despite the elements being completely immiscible in three dimensions[62]. This might have been predicted since the relative importance of the surface and bulk free energy contributions to the total energy of the system changes dramatically at high dispersions. Few studies, however, have directly addressed the influence of particle size on the surface composition of small particles[63]. The application of modern surface sensitive techniques to the study of model bimetallic systems on single crystal substrates has been more extensive. It should be noted that the results of such studies may not necessarily relate to the situation at very high dispersions due to the very different surface:bulk ratios in the two cases. Nevertheless, this work has been very useful in elucidating the properties of interfacial compounds. An example of such a surface compound is shown in the next figure (Fig.10). An α-Cu/Al alloy single crystal with a bulk concentration of 16 at% Al exhibits no long range order in the bulk; the surface, by contrast, is completely ordered as shown in the figure[64]. Furthermore, due to aluminum segregation, the ordered surface phase contains equal numbers of copper and aluminum atoms. Thus the surface has both a very different structure and composition from the bulk.

There is no reason why surface compound formation should be restricted to either metal-metal or gas (vacuum)-solid interfaces. Although substantially less experimental documentation of surface specific metal-oxide or oxide-oxide compound formation is available; disso-

lution of oxide layers into metallic substrates[65,66], chemical interaction of metals with oxide substrates[67,68] and mixed oxide surface compounds[69,70] have all been proposed on the basis of surface science studies of both model and complex systems.

4.4 The Surface Chemical Bond - Bonding Geometries, Thermal Activation and Coadsorption

The next concept of modern surface science to be discussed is that of the **surface chemical bond**. The binding of surface species has been found to be 'cluster-like'; this is a particularly useful concept since it permits one to use localized bonding models in the study of surfaces. It is also an approach frequently adopted in theoretical calculations of molecular adsorption[71,72]. Several organic molecules and molecular fragments that have been identified on metal surfaces by a combination of high resolution electron energy loss spectroscopy and low energy electron diffraction are shown in Figs.11 & 12. These species have the same local structure and similar chemistry to those found in multinuclear organometallic clusters for which good x-ray diffraction information is available. In fact, for virtually every surface species found so far there is a cluster equivalent that has been synthesized by organometallic chemists.

Large organic molecules frequently exhibit distortions when adsorbed on metal surfaces. Benzene and closely related aromatic hydrocarbons generally lie with theirπ-ring parallel to the surface but, as shown by LEED studies, are distorted from their equilibrium gas phase geometry due to the metal-adsorbate interaction. The stronger this interaction, the larger the distortion[73] as shown in Fig.13. Similar distortions are also found in multinuclear organometallic compounds with benzene[74], such as the ruthenium-benzene complex shown in the following figure (Fig.14), although these distortions are not as large as those seen on metal surfaces (presumably because a smaller number of metal atoms are involved in the bonding in a cluster).

In the case of aromatic heterocyclic molecules the situation regarding bonding geom-

etry is not as clear cut[75]. Fig.15 shows one of the structural configurations of pyridine on a Rh(111) surface[76]. For pyridine there exists the possibility of bonding to the surface through the π-system, via the nitrogen alone or through both the N and C2 atoms. Thus, the molecule may assume either flat or upright structures or, as in the case illustrated, with the molecular plane oriented at an angle with respect to the surface. The actual mode of bonding adopted may be dependent upon surface coverage (ie interadsorbate interaction - see below) and temperature as well as the substrate[77–79].

This brings us on to a closely related concept: the **thermal activation of the surface chemical bonds** (also known as temperature dependent bond rearrangement and bond activation). It is found that molecules adsorbed at low temperatures (below ca. 20K) are quite unreactive and assume geometries not unlike those in the gas phase. As the substrate is heated, unique bond breaking processes can occur within well defined temperature ranges - indeed, strong chemical bonds may be broken over very limited ($\sim$10K) temperature ranges as has been shown by temperature programmed spectroscopic studies (eg ref.80). In the case of 'complex' molecules, a progressive increase in temperature can lead to sequential bond breaking, yielding molecular fragments that are very stable within a particular temperature regime. This is demonstrated in Fig.16. Benzene and ethylene assume very different surface structures on Rh(111) at low temperatures: however, as the temperature is increased both molecules decompose and above ca. 450K the molecular fragments remaining on the surface are identical[76,81–83]. In fact, the adsorption of many different hydrocarbons yield surface species that are indistinguishable above a certain temperature[83,85,86].

The mechanisms of these transformations have been studied by both experiment and theory in several molecular systems. For example, studies indicate that the mechanism by which adsorbed ethylene (C_2H_4) is converted into ethylidyne (C_2H_3) involves firstly hydrogenation to a C_2H_5 intermediate with subsequent loss of two hydrogen atoms to give the ethylidyne species, rather than a direct dehydrogenation of C_2H_4 (Fig.17A). The further

fragmentation of C_2H_3 to C_2H_2 and CH species can also be modelled by theory and reasonable agreement between theory and experiment exists (Fig.17B).

The next concept to come from modern surface science studies is that of the **coadsorption** bond. It is frequently found that there are large changes in the isosteric heat of adsorption with increasing coverage which lead to a marked reduction in the average heat of adsorption per molecule. This is commonly caused by a repulsive (predominantly dipolar) adsorbate-adsorbate interaction that becomes increasingly important as the interadsorbate separation decreases at higher coverages and results in a weakening of the bonding of the molecules to the surface. This is but one example of repulsion between 'like' molecules and the behaviour is well illustrated by the CO-metal systems (see eg Fig.18). In these systems there is a delicate interplay between the repulsive interadsorbate forces and structural changes within the adsorbed layer that result in modifications in the CO-substrate bonding strength and geometry. Fig.19 compares the CO/Pt(111) structure at half monolayer coverage[91], in which the CO molecules occupy well defined sites, to that observed at higher coverages on a Rh(111) substrate[92], where, to minimize mutual repulsion, the adsorbed molecules adopt a pseudo-hexagonal structure.

Clearly, because the average heat of adsorption per molecule is smaller at high coverages, the reactivity of molecules under these conditions may be very different from that at low coverages.

Attractive adsorbate-adsorbate interactions upon coadsorption of two different molecules may lead to stronger chemical bonding or pronounced structural effects. An example of the latter type is illustrated in the next figure (Fig.20). LEED and HREELS studies show that benzene molecularly adsorbs at 300K in a disordered manner on a clean Rh(111) surface[76]. It can be readily ordered, however, by coadsorption with other molecules that are electron acceptors, such as CO and NO[93–95]. Like most organic molecules, benzene is a strong electron donor to metal surfaces. Apparently, therefore, the presence of electron acceptor-

donor interactions induces ordering and the formation of surface structures containing both benzene and CO molecules in the same unit cell.

This is not an isolated phenomenon: Table II gives examples of several systems where the coadsorption of an electron donor and an acceptor leads to formation of ordered structures while the coadsorption of two electron donors or two electron acceptors yields disordered surface monolayers. Thus, in these systems at least, it is clear that the attractive forces arising from donor-acceptor interaction are crucially important in determining the stability and structure of the coadsorption system. In the case of the coadsorption of benzene with CO on Rh(111) there is little change in the decomposition/desorption temperatures of either the CO or benzene[93]. By contrast, the coadsorption of CO with alkali metals can have a dramatic influence on the CO binding strength. For example, CO desorbs completely from a clean Cu(110) surface at temperatures below 200K whereas in the presence of coadsorbed potassium two new binding sites are populated yielding CO desorption at 480K and 550K[100]. This corresponds to an increase in the heat of adsorption from around 45kJ/mol to >110kJ/mol. Any such phenomena occurring under catalytic conditions will, of course, play an important role in the reaction concerned and coadsorbed molecules are often used as bonding modifiers, as will be shown later, to change the activity and selectivity of catalysts.

4.5 Surface Dynamics - Adsorption, Diffusion and Reaction

The next concept concerns the dynamics of molecules on surfaces and is sometimes known as the **two dimensional phase approximation**. The basis of the approximation is that the activation energies for diffusion of any adsorbed molecule across a surface are substantially less than the large potential barriers for desorption or, indeed, diffusion into the bulk. It is commonly assumed therefore that at all normal temperatures the adsorbed atoms and molecules can visit all the surface sites within their residence time on the surface and are in equilibrium with each other at the various surface sites. This, for example, explains why attractive inter-adsorbate interactions can lead to the formation of islands of ordered close-

packed structures even at submonolayer coverages. At high coverages[101] and in the presence of certain coadsorbates (see above, and ref.102) the mobility of the species will clearly be reduced; nevertheless, this two dimensional phase approximation is used when developing theories of evaporation[103] or crystal growth[104–106] and has been very useful in modelling many catalytic reactions.

A closely related phenomenon that is very important in heterogeneous catalysis is that of "spillover" of adsorbed species[107,108]. In a multiphasic system such as a supported metal catalyst it is possible for molecules to adsorb, and perhaps even decompose or react, on one component before diffusing over onto a second phase where they may react with a different adsorbed species. This concept underlies the principle of operation of many bifunctional catalysts and has been well demonstrated in surface studies on model systems[109–111].

In molecular beam surface scattering studies, it is possible to separately determine the energy accommodation coefficients for translation, rotation and vibration for molecules incident on a surface by monitoring the kinetic, rotational and vibrational energies of both incident and scattered molecules[112]; a set of results for the scattering of NO from a Pt(111) crystal surface[113] is shown in Fig.21. From such experiments it is apparent that most of these modes equilibrate quite well upon a single collision with the surface, thus giving rise to the concept of **rapid gas-surface energy transfer**. This explains why the desorbed products of even the most exothermic reactions are 'cold'. Nevertheless, the accommodation of a molecule on a surface is not a simple process and surface science studies have given rise to a further concept, namely that of the **precursor state**. It is often proposed that molecules incident on a surface go into a weakly bound state where they spend a residence time that may amount to hundreds of vibrational oscillations before they either desorb or enter into a more stable, strongly chemisorbed state. Furthermore, such precursor states may be subdivided into two categories - namely, "extrinsic" states in which the molecule is physisorbed above a chemisorbed overlayer and "intrinsic" states in which the precursor is

weakly bound to the clean surface itself. The presence of these precursor states has been deduced from atomic and molecular beam scattering experiments as well as desorption and sticking probability studies for many adsorbate surface systems[114,115]. The existence of a second layer physisorbed state has also been well documented by spectroscopic characterization during low temperature adsorption studies: direct and unambiguous spectroscopic characterization of intrinsic precursor states, however, has only recently been reported[116,117]. It should be noted that the term precursor state as used here to describe a weakly bound state which is a precursor to a chemisorbed complex should not be confused with usage relating to the transition from a strongly chemisorbed molecular state to a dissociated one (eg ref.118).

5 Concepts in Heterogeneous Catalysis

Let us now turn to concepts that come directly from studies of catalytic reactions on low area model systems. Useful catalytic processes require a rapid turnover, ie. adsorption, surface diffusion, chemical rearrangement and reaction, and product desorption must all occur in such a manner that the surface can rapidly accommodate new molecules to continue the catalytic conversion. This criterion requires the formation of sufficiently strong chemical bonds between the reactant molecule and substrate to permit bond activation but not so strong as to inhibit interaction with other adsorbed species. The condition is also well illustrated experimentally in the "volcano" shaped plots of activity versus heat of adsorption which are widely found throughout heterogeneous catalysis[119]. Furthermore the binding of the products must not be so strong that the products do not readily desorb since this would lead to stoichiometric as opposed to catalytic reaction.

The first concept to come from studies on well defined surfaces is the existence of two classes of reactions: those that are **structure sensitive** and those that are **structure**

insensitive. Perhaps one of the simplest conceptual reactions is the exchange of hydrogen and deuterium to form HD. This may be studied at low pressures using a mixed molecular beam apparatus in which the H_2 and D_2 are incident on a surface and the HD concentration in the desorbed beam is monitored. Such reactive scattering studies on Pt substrates indicate that atomic steps are the most efficient site for dihydrogen dissociation thereby leading to HD formation[120]. Thus, the reactivity of the close packed (111) surface is about an order of magnitude lower than more open or stepped surfaces since on this face the surface defects are predominantly responsible for hydrogen dissociation[121]. This, therefore, is an example of a structure sensitive reaction and one in which the atomic steps play a unique role.

Many other catalytic reactions have now been studied by modern surface science techniques, some of which are listed in Table III; a few of these examples will now be reviewed in greater detail.

The synthesis of ammonia has been studied over various single crystal surfaces of iron. This is a particularly surface structure sensitive reaction - the (111) and (211) surface orientations are about an order of magnitude more active than the (100) & (210) faces and two orders of magnitude more active than the close packed (110) face; this latter surface being the least active of all those studied[122](Fig.22). Early studies by Boudart[123] led to the suggestion that the seven-fold coordination (C_7) site that is present only on certain iron surfaces is the most active for the dissociation of dinitrogen to atomic nitrogen - the postulated rate determining step in ammonia synthesis. The studies in our own laboratory on the (111) and (211) faces showing these to be the most active in ammonia synthesis seem to confirm this hypothesis since only these two single crystal surfaces contain the C_7 Fe sites in the second layer of the surface (Fig.23).

A somewhat more complicated example of structure sensitivity and insensitivity is the hydrodesulfurization reaction; a very important process used to remove sulphur from an oil feed. This reaction may be modelled by the hydrodesulfurization of thiophene to butane, butenes and butadiene. When this reaction is carried out on molybdenum and rhenium

single crystal surfaces it exhibits structure insensitivity over molybdenum but significant structure sensitivity over rhenium[124](Fig.24). Furthermore, in agreement with results on high surface area materials[125], the specific rates over the rhenium single crystals are 1-5 times higher than over molybdenum. This appears to result from the presence of a stable carbonaceous and/or sulphur overlayer on molybdenum surfaces which not only moderates the highly active surface but also masks the surface structure sensitivity[126,127]. In contrast, rhenium surfaces remain free of irreversibly bound sulphur and carbon under reaction conditions and the different electronic and geometrical properties of the different crystal faces give rise to the observed structure sensitivity[128].

An example of a structure insensitive reaction is ethylene hydrogenation at low temperatures (~300K). This reaction has been extensively studied on Pt(111) and Rh(111) single crystals[129-133]: under these conditions (310K/1 atm.) the metal surfaces are completely covered with a stable adsorbed layer of ethylidyne. The rehydrogenation of this species, and indeed the exchange rate of deuterium into the methyl group, is many orders of magnitude slower than the ethylene hydrogenation rate (Fig.25). The reaction itself appears to occur on top of this ethylidyne overlayer and the purpose of the metal is secondary; more specifically, to dissociate the molecular hydrogen. The ethylidyne deposit can then transfer the hydrogen to weakly bound ethylene adsorbed on top of it resulting in hydrogenation and the formation of ethane (Fig.26).

Another concept in catalysis is the use of **bonding and structural modifiers** - collectively known as 'promoters' - to change the catalytic activity and selectivity. A classic example of a structural modifier is that of alumina in ammonia synthesis over iron catalysts. Model studies have shown that when alumina is added in the form of islands to the inactive Fe(110) surface and the system then heated in water vapor, the ensuing oxidation of the iron is accompanied by migration onto the alumina and substantial restructuring results[134] - various authors have also proposed the formation of an iron aluminate ($FeAl_2O_4$)[135,136].

Subsequent reduction under reaction conditions yields metallic iron crystallites in orientations that are very much more active (Fig.27) than the original surface (ie (111) and (211) as opposed to (110)). The primarily role of the alumina is to stabilise the highly active restructured surface produced by the hydrothermal treatment since transient restructuring and enhanced activity is seen after such treatment even in the absence of alumina. The effect is not restricted to the (110) surface; other inactive surfaces of iron may also be converted to ones containing highly active (111) or (211) crystal faces in the presence of alumina.

Alkali metals are extensively used as promoters in commercial catalyst formulations[137]. The dramatic effect that coadsorption of potassium can have on the strength of molecular CO chemisorption has already been mentioned. A similar increase in binding strength is also observed in the CO/Rh(111) system: furthermore, isotopic scrambling occurs for $\theta_K \geq 0.1$ but not on the K-free Rh(111) surface[138](Fig.28). This is indicative of alkali induced cleavage of the C–O bond and an example of the profound effects that modifiers may have on the chemical bonding of adsorbates.

Similar explanations have been put forward to explain the promoting effect of potassium in ammonia synthesis, ie that the alkali enhances dinitrogen dissociation. Recent work, however, suggests that the primary role of the potassium is to alleviate product inhibition of the reaction[139]. At high conversions (ie high ammonia partial pressures) active sites for the ammonia synthesis are blocked by adsorbed product molecules. Coadsorbed potassium weakens the bonding of the ammonia leading to a lower steady state surface concentration and, hence, increased activity. Thus alkalis may not only promote reactions by activation of the reactant molecules but also by a weakening of the interaction of the product molecules with the surface.

6 Summary

The application of modern surface science techniques has revolutionized our understanding of phenomena occurring at the gas-solid interface and, as we have seen above, led to a number of well defined new concepts. In contrast, progress in developing and applying surface sensitive technology to study other interphasic boundaries (eg gas-liquid and liquid-solid interfaces) has been much slower and this must undoubtedly be one of the greatest challenges that lie ahead. This would open up the way for *in situ* molecular level studies in areas such as electrochemistry, biological surfaces, tribology and corrosion.

Within the field of catalysis, it is also clear that the application of existing surface science techniques and concepts has had a profound influence on the way in which we view the fundamental steps that underly catalytic processes. Whilst much remains to be discovered, and still more subtle nuances lie uncovered, our molecular level understanding of surface and catalytic phenomena has now reached a point where its application may begin to be used to help develop new generations of high technology catalysts. Certainly there are a vast number of areas which could benefit greatly by such developments ; these include chemical energy conversion, low temperature catalysis, pharmaceutical production and the synthesis of complex organic systems. It is the concept of catalyst design, therefore, that is perhaps the most important area in the future of catalytic science.

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Figure Captions

Figure 1: Structure of Faujasite - a naturally occurring Zeolite.

Figure 2: Schematic Illustration of the Design of a Combined UHV/High Pressure Apparatus.

Figure 3: The Electronic State of the Surface: (a) The Fermi Energy (E_F) and Work Function (ϕ), (b) Electron Density Distribution and the Formation of a Surface Dipole, (c,d) The Dipolar Contribution to the local Work Function.

Figure 4: Thermodynamic Properties of Small Spherical Particles (γ - surface tension, r - particle radius, V_m - molar volume).

Figure 5: The (5x1) Reconstruction of Clean Ir(100) Surfaces.

Figure 6: The p(2x1) Reconstruction of Si(100).

Figure 7: 3-D Projection of STM Data for a Sulfur-passivated Re (0001) Basal Plane showing Terraces separated by Steps of 1-10ML (vertical scale x5).

Figure 8: The Ni(100) p(2x2) - C Adsorbate Induced Surface Reconstruction (second layer nickel atoms shown on left).

Figure 9: Self Sustaining Temperature Oscillations in the CO Oxidation Reaction over different Platinum Single Crystal Surfaces (from ref.41).

Figure 10: Surface Compound Formation on the (111) Face of an α-CuAl (16% Al) Alloy.

Figure 11: A Comparison of Proposed Adsorbate Species on Rh Surfaces with the binding of Isostructural Ligands in Cluster Complexes.

Figure 12: Structural Comparison Of Different Ethylidyne Species.

Figure 13: The Bonding Geometry of Benzene in CO-Coadsorption Structures on various Metal Surfaces.

Figure 14: The Distortion of the Benzene Ring in the c(2$\sqrt{3}$x4)rect- C_6H_6 + CO / Rh(111) Structure and $Ru_6C(CO)_{11}(\mu_3\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$ Complex.

Figure 15: The Adsorption of Pyridine on Rh(111): the α-pyridyl species at 310K.

Figure 16: Thermal decomposition Routes of Benzene and Ethylene on Rh (111): Hydrogen Desorption and Adsorbate Interconversion.

Figure 17: Proposed Surface Reaction Mechanisms in the Decomposition of Adsorbed Ethylene (* - from ref.87; # - from ref.88).

Figure 18: Heat of Adsorption for CO on the Pd(100) Crystal Face as a Function of Coverage (from ref.90).

Figure 19: LEED Structures of CO-Metal Systems: A - Pt(111)-c(4x2)-2CO at T = 150K (0.65×10^{15} molecules CO/ cm^2), B - Rh(111)-(2x2)-3CO at T = 240K (1.04×10^{15} molecules CO/ cm^2).

Figure 20: The Rh(111)-$\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$-$C_6H_6$ + CO LEED Structure.

Figure 21: Translational, Rotational and Vibrational Accomodation during the Scattering of NO from Pt(111).

Figure 22: Structure Sensitivity of Ammonia Synthesis over Iron Single Crystals.

Figure 23: Hard Sphere Models of bcc-Fe Surfaces showing Surface Atom Coordination.

Figure 24: Thiophene Hydrodesulfurization over Molybdenum and Rhenium Single Crystal Surfaces.

Figure 25: Hydrogenation Rates over Pt(111) and Rh(111) Single Crystal Surfaces.

Figure 26: Proposed Mechanism for Ethylene Hydrogenation on Group VIII Metal Surfaces at Low Temperatures.

Figure 27: The Effect of Alumina-Induced Reconstruction of Iron Surfaces on the Rate of Ammonia Synthesis.

Figure 28: Number of CO Molecules dissociated per Potassium Atom as a function of Potassium Coverage on Rh(111) (as deduced from $^{13}C^{16}O/^{12}C^{18}O$ scrambling experiments).

Table I

Techniques of Modern Surface Science

- **Electron–Surface Scattering**

Electron Spectroscopy	- Auger Electron Spectroscopy (AES)
	- Ultraviolet Photoelectron Spectroscopy (UPS)
	- X-ray Photoelectron Spectroscopy (XPS)
	- Inverse Photoemission Spectroscopy (BIS)
	- Electron Energy Loss Spectroscopy (HREELS)
Electron Diffraction	- Low Energy Electron Diffraction (LEED)
Electron Microscopy	- Scanning Auger Microscopy (SAM)
	- Scanning Electron Microscopy (SEM,STEM)
	- Transmission Electron Microscopy (TEM,STEM)
	- Reflection Electron Microscopy (REM)
Tunnelling Microscopy	- Scanning Tunnelling Microscopy (STM)

- **Photon–Surface Scattering**

Spectroscopy	- Infra-Red Spectroscopy (IR,FTIR)
	- Raman Spectroscopy
	- Nuclear Magnetic Resonance (NMR)
	- X-Ray Absorption (EXAFS,SEXAFS,XANES)
	- Laser Techniques (SHG,SFG)
X-Ray Diffraction	- Grazing Angle X-Ray Diffraction

- **Molecule/Ion–Surface Scattering**

Molecular Beam Scattering	- Reactive Molecular Beam Scattering (RMBS)
	- Thermal Helium Scattering
Ion Scattering	- Secondary Ion Mass Spectrometry (SIMS)
	- Ion Scattering Spectroscopy (ISS)

- **Other Techniques**

Chemisorption Techniques	- Temperature Programmed Desorption (TPD)
	- Temperature Programmed Reaction Spectroscopy (TPRS)

Work Function Measurements
Radiotracer and Isotopic Labelling

Table II

Coadsorption of Adsorbates on Rh(111)

Adsorbates	Ratio	Coadsorbed LEED Pattern	Ref.
NO + -C.CH_3	1:1	c(4x2)	96
CO + C_2H_2	1:1	c(4x2)	97
CO + -C.CH_3	1:1	c(4x2)	96
CO + C_6H_6	2:1	(3x3)	94
CO + C_6H_6	1:1	c(2$\sqrt{3}$x4)rect	95
CO + C_6H_5F	2:1	(3x3)	97
CO + C_6H_5F	1:1	c(2$\sqrt{3}$x4)rect	97
CO + Na	1:1	c(4x2)	98
CO + NO		Disorder	99
Na + C_2H_2		Disorder	99
Na + -C.CH_3		Disorder	99
Na + C_6H_6		Mixed*	99

* - 2 patterns characteristic of individual adsorbates observed suggesting phase separation into independent domains.

Table III

Surface Science - High Pressure Studies of Catalytic Systems

Hydrogenation of Ethylene (Pt, Rh)

Hydrogenation of Carbon Monoxide (Ni, Fe, Rh, Re, Cu, alloys)

Oxidation of Carbon Monoxide (Pt)

Ammonia Synthesis (Fe, Re)

Ammonia Oxidation (Pt)

Alkane Rearrangements (Pt, Pd, alloys) (Isomerization, Dehydrocyclization & Hydrogenolysis)

Methanol Partial Oxidation (Mo)

Ethylene Partial Oxidation (Ag)

Hydrogenation of Benzene, Cyclohexene (Pt, Pd, Rh, alloys)

Hydrodesulfurization of Thiophene (Mo, Re)

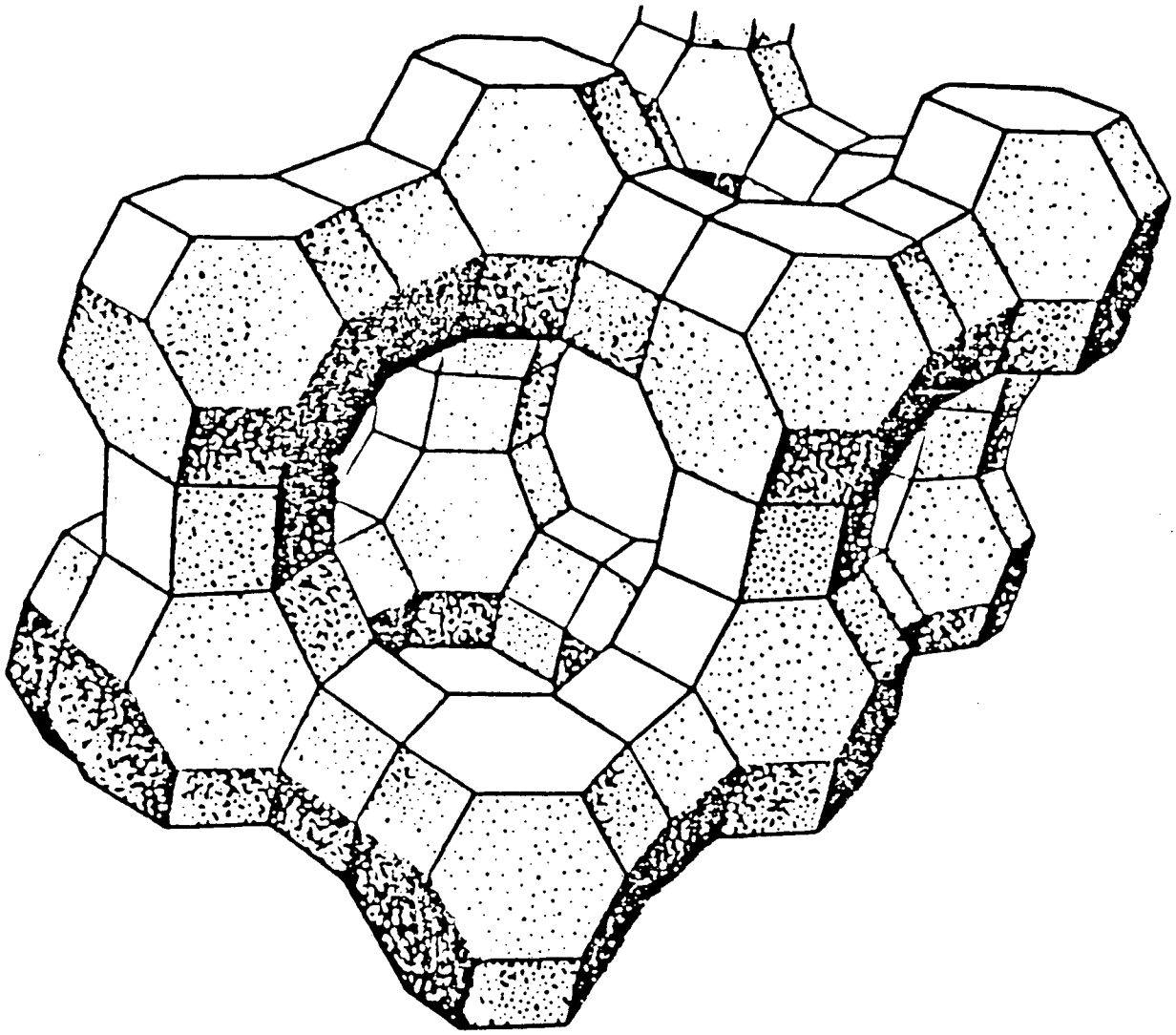
Ammonolysis of Butylalcohol (Rh, Cu)

Hydrogenolysis of Ethane (Pt, Rh)

Steam Gasification of Carbon (Ni, K)

Water Gas Shift Reaction (Cu)

Methane Decomposition (Ni, Rh, Ir)



XBL 886-2253

Fig. 1

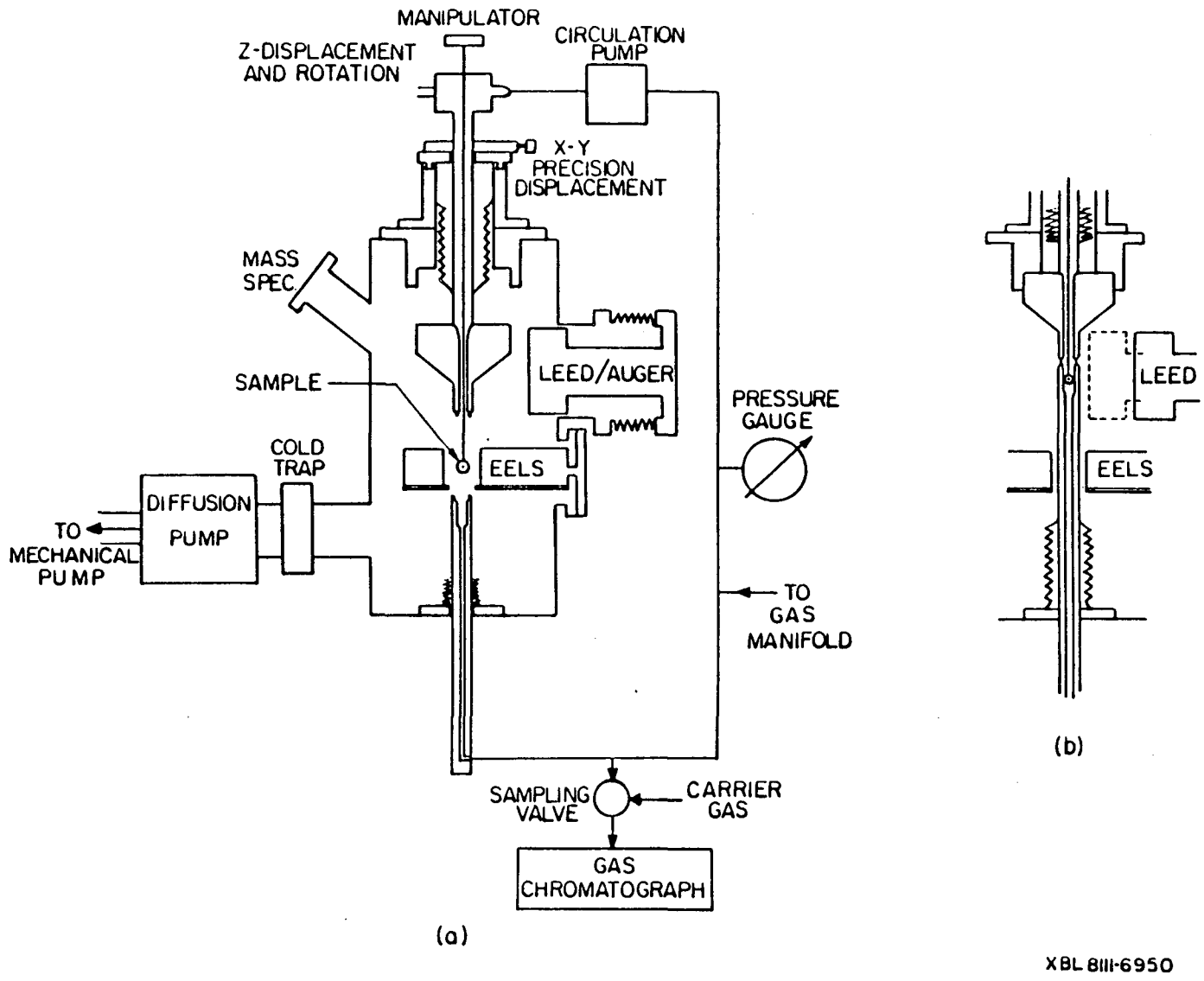

MANIPULATOR
Z-DISPLACEMENT AND ROTATION
CIRCULATION PUMP
X-Y PRECISION DISPLACEMENT
MASS SPEC.
SAMPLE
LEED/AUGER
PRESSURE GAUGE
COLD TRAP
EELS
DIFFUSION PUMP
TO MECHANICAL PUMP
TO GAS MANIFOLD
SAMPLING VALVE
CARRIER GAS
GAS CHROMATOGRAPH
(a)
LEED
EELS
(b)
XBL 8111-6950

Fig. 2

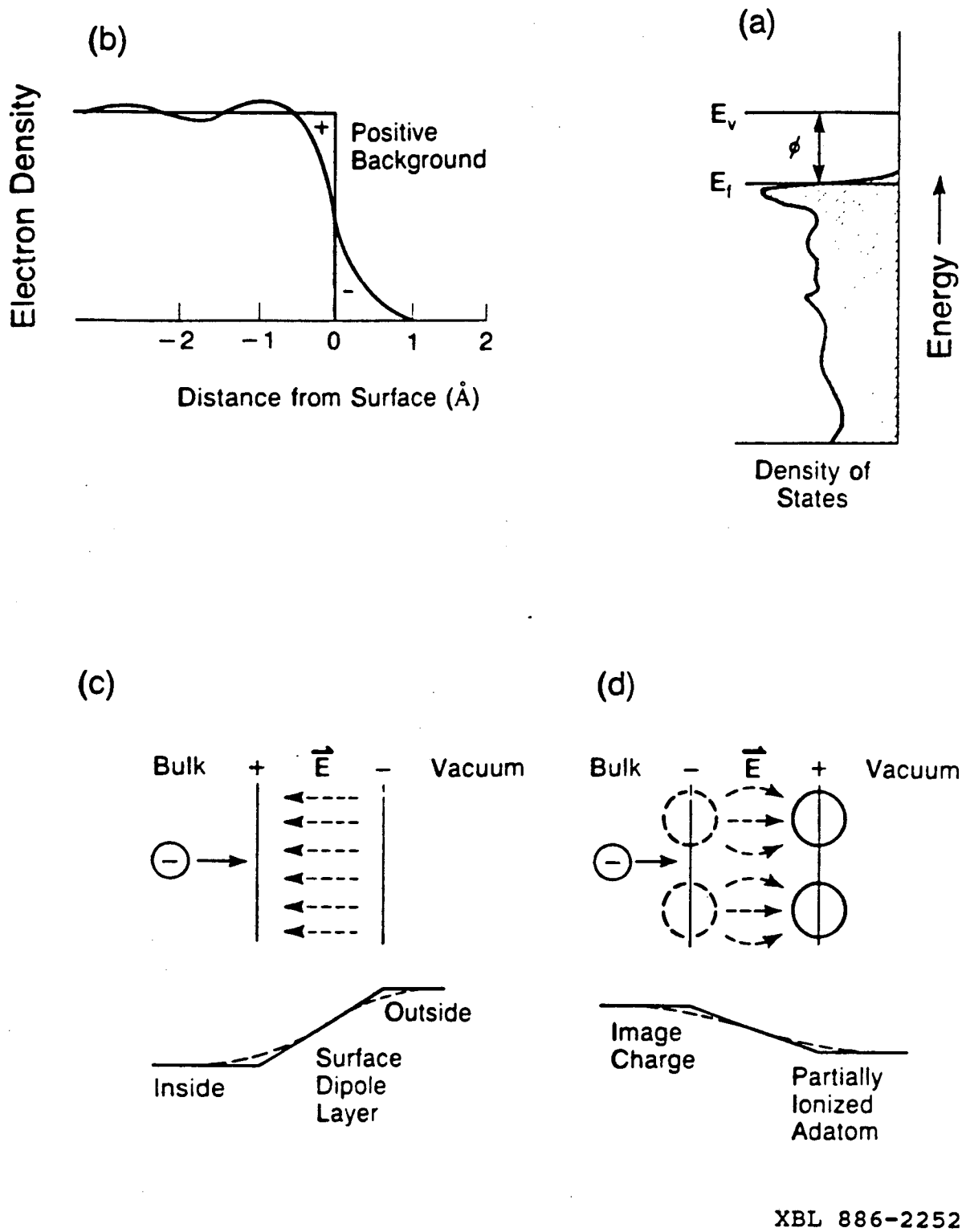
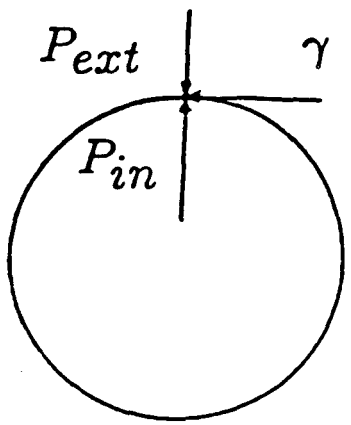
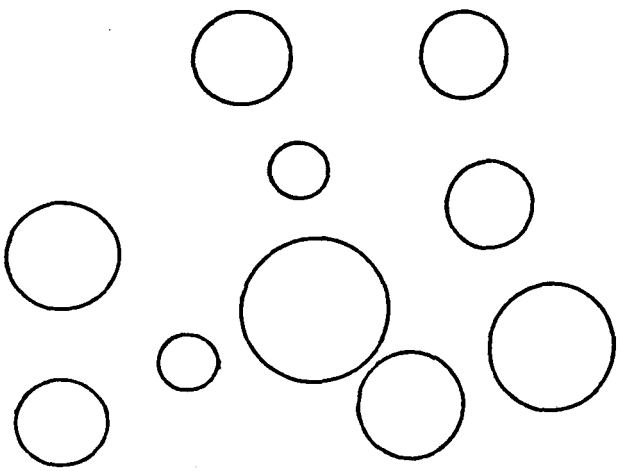

(b)
Electron Density
Positive
Background
+
-
−2
−1
0
1
2
Distance from Surface (Å)
(a)
E_v
ϕ
E_f
Energy
Density of
States
(c)
Bulk
+
$\vec{E}$
−
Vacuum
Outside
Surface
Dipole
Layer
Inside
(d)
Bulk
−
$\vec{E}$
+
Vacuum
Image
Charge
Partially
Ionized
Adatom
XBL 886-2252

Fig. 3



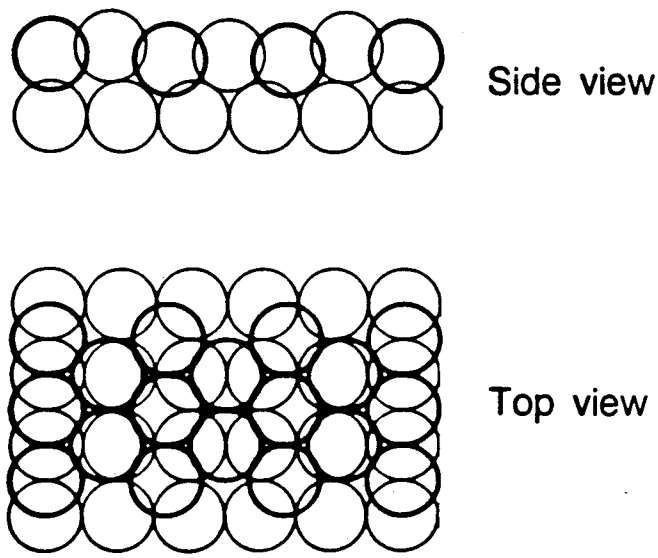
$$(P_{ext} - P_{in}) = \frac{2\gamma}{r}$$



$$ln\frac{P_r}{P_{r=\infty}} = \frac{2V_m\gamma}{rRT}$$

XBL 886-2256

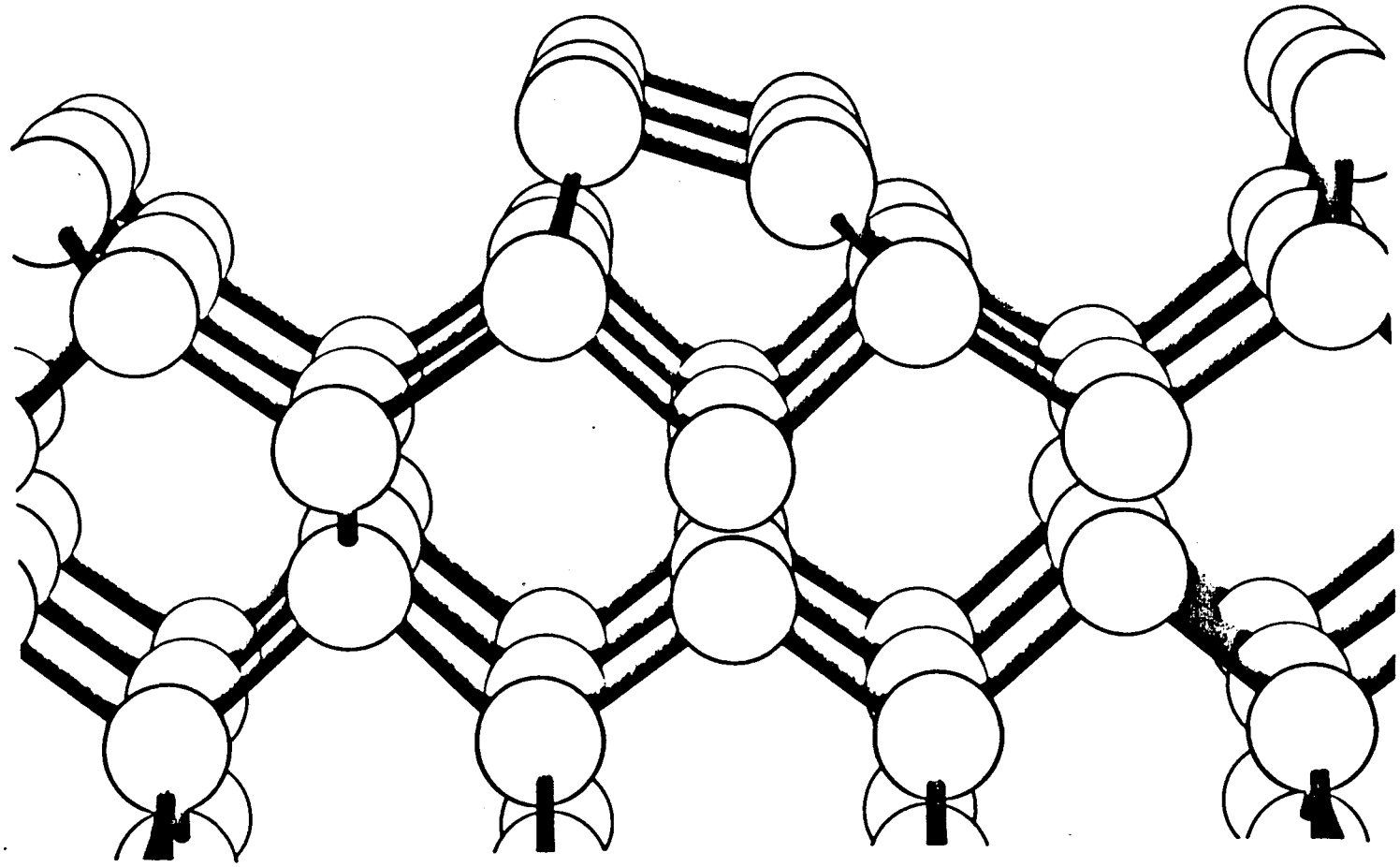
Fig. 4



Ir(100) – (1 × 5)

XBL 8612-9961

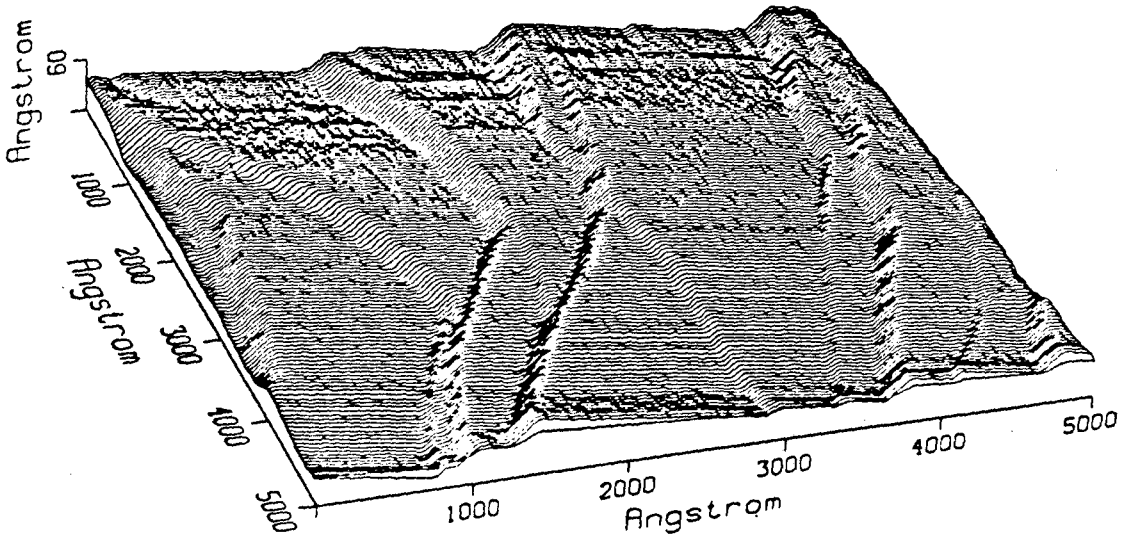
Fig. 5



Si (100) – (2 x 1) buckled dimer

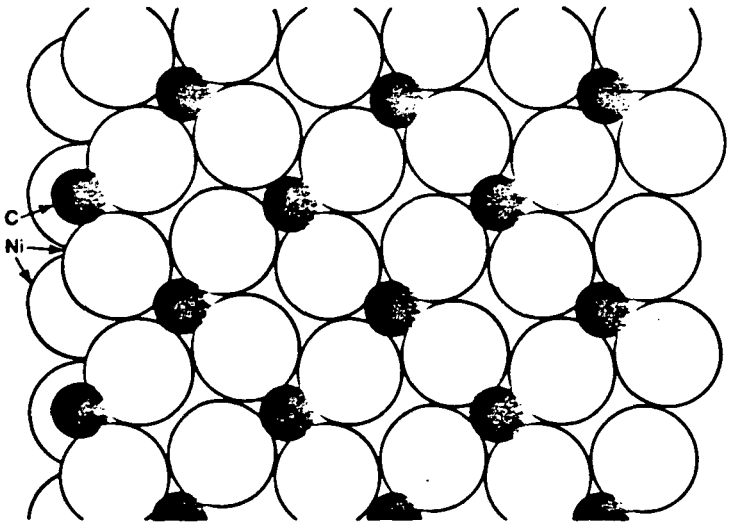
XBL 8611-6535

Fig. 6



XBL 882-364

Fig. 7



Ni (100) – (2 x 2) – 2C

XBL 8611-6513

Fig. 8

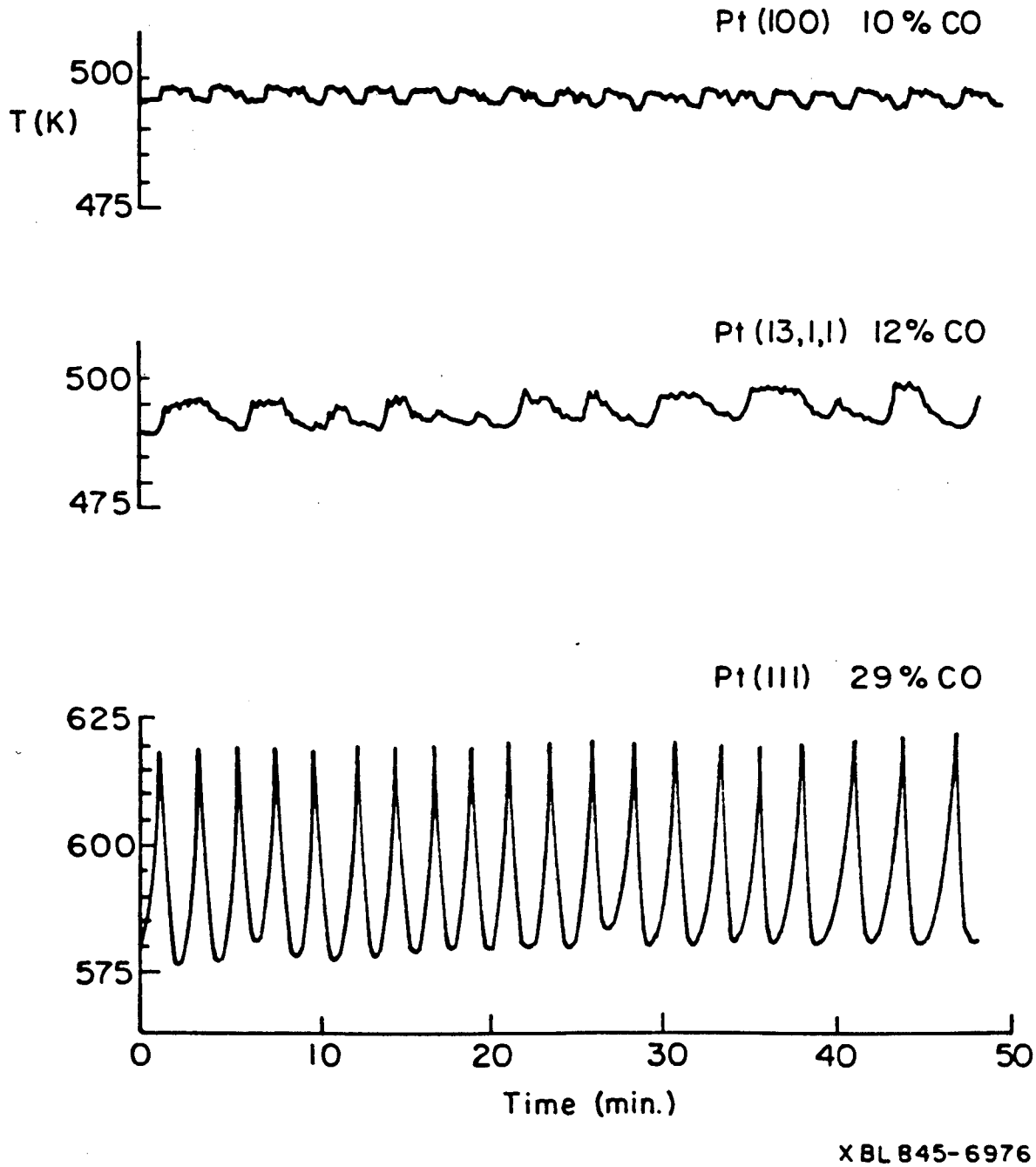
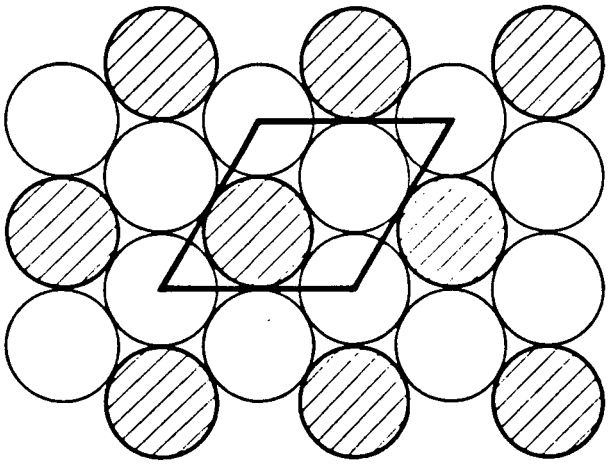
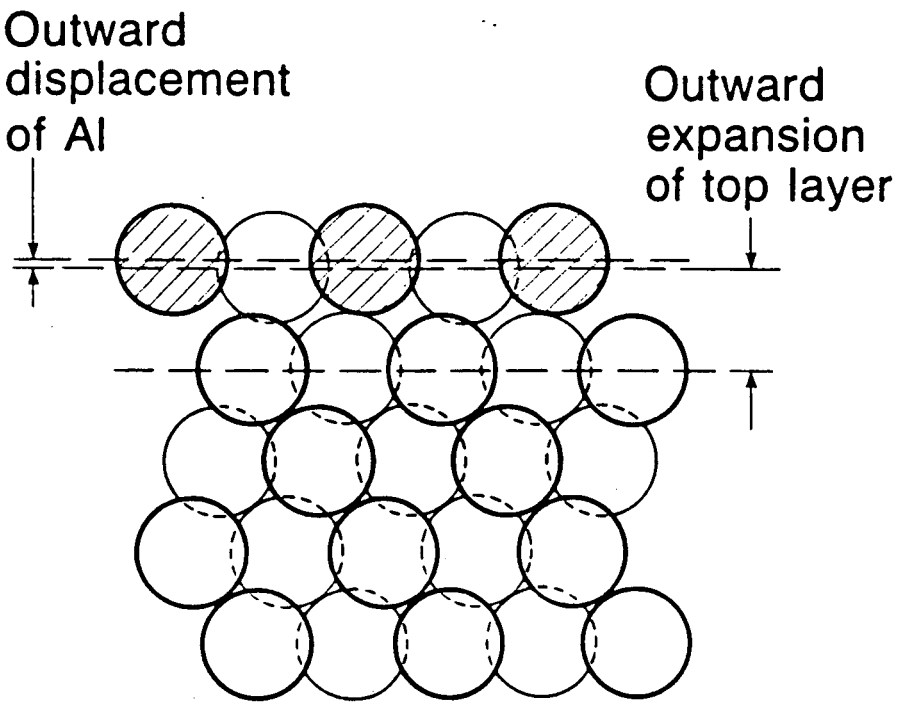

Pt (100) 10 % CO
500
T (K)
475
Pt (13,1,1) 12% CO
500
475
Pt (111) 29 % CO
625
600
575
0
10
20
30
40
50
Time (min.)
XBL 845-6976

Fig. 9

α - Cu Al (III) - ($\sqrt{3}$ x $\sqrt{3}$) R30°
Substitutional Al Model Parameters
Al Atom Shaded



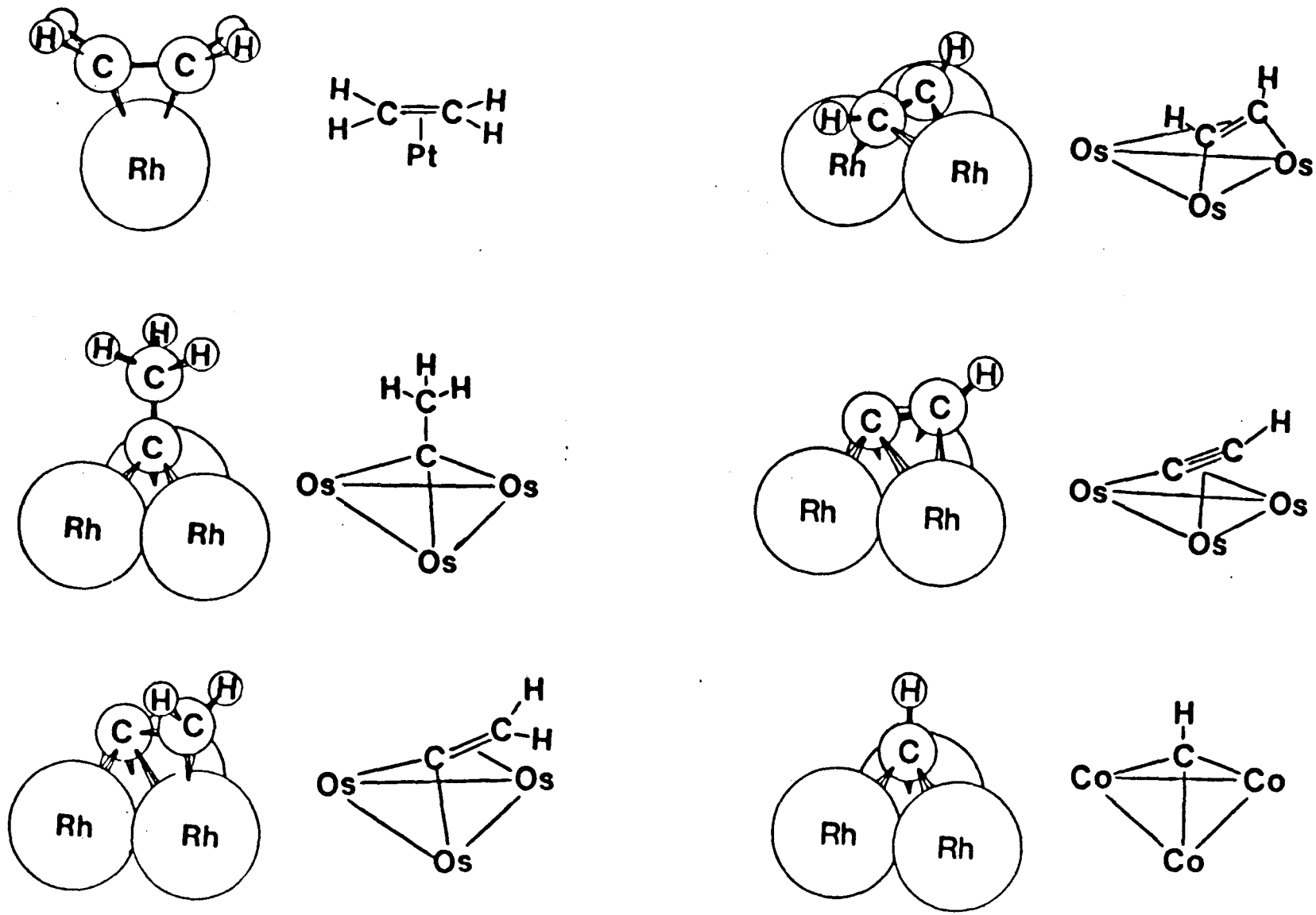
Top view



Side view

XBL 855-9971

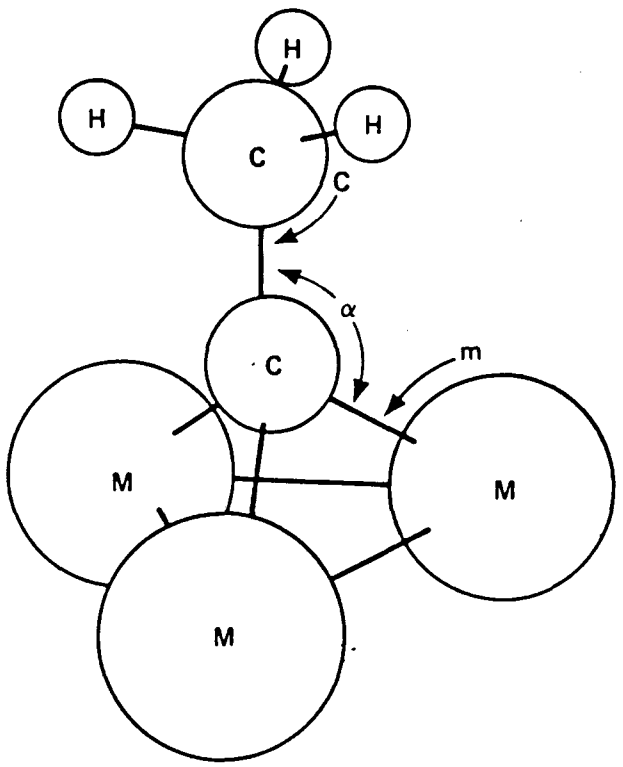
Fig. 10



XBL 886-2259

Fig. 11

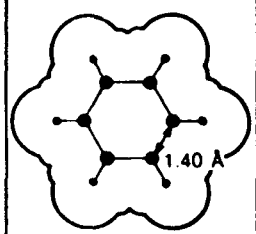
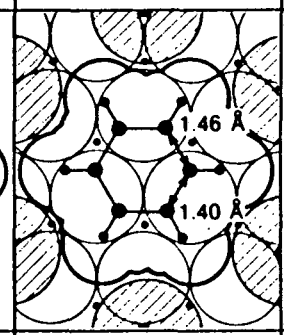
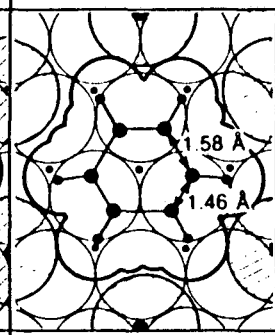
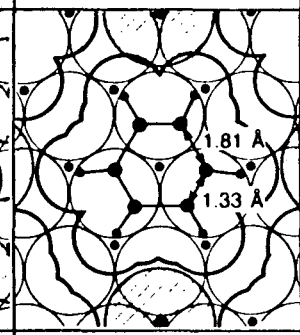
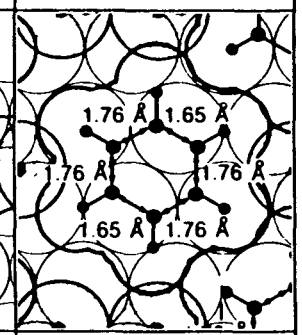
Different ethylidyne species: bond distances and angles
(r_C = carbon covalent radius; r_M = bulk metal atomic radius)



	C [Å]	m	r_M	r_C	α [°]
$Co_3(CO)_9CCH_3$	1.53 (3)	1.90 (2)	1.25	0.65	131.3
$H_3Ru_3(CO)_9CCH_3$	1.51 (2)	2.08 (1)	1.34	0.74	128.1
$H_3Os_3(CO)_9CCH_3$	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
$H_3C - CH_3$	1.54			0.77	109.5
$H_2C = CH_2$	1.33			0.68	122.3
$HC \equiv CH$	1.20			0.60	180.0

XBL 818-11196

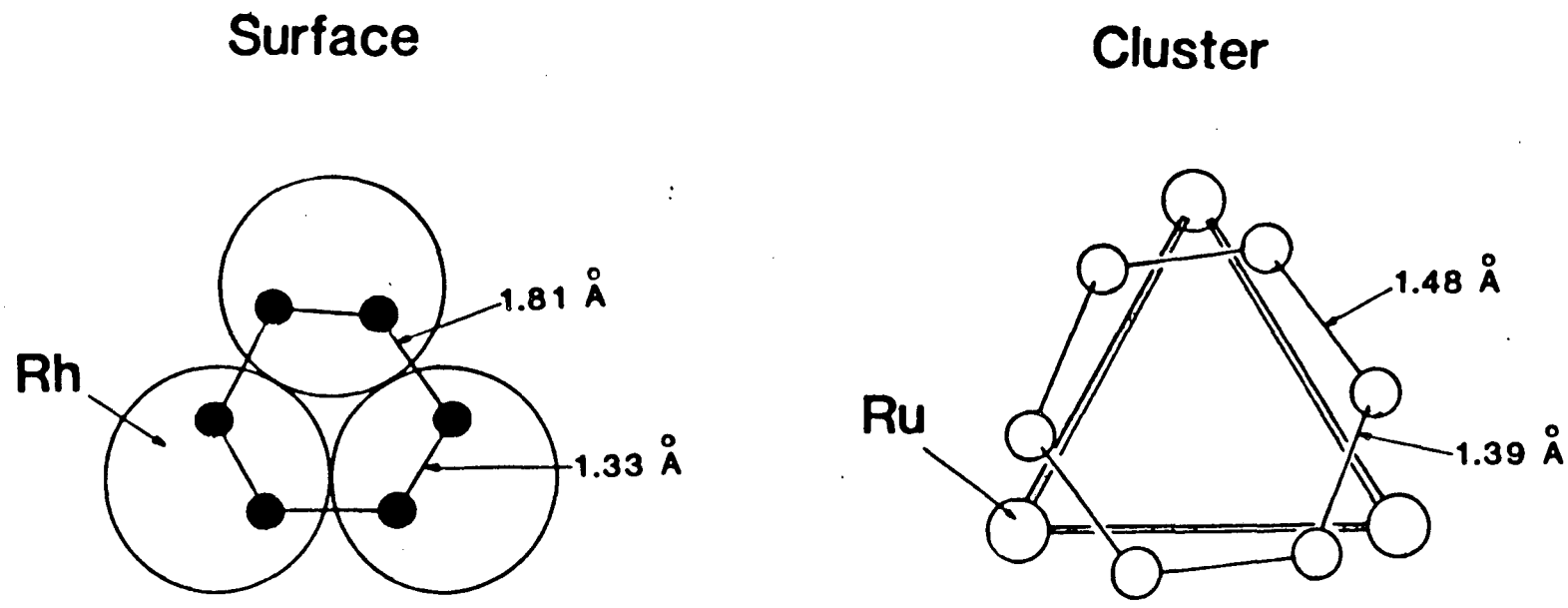
Fig. 12

Substrate	(Gas Phase)	Pd(111)	Rh(111)		Pt(111)
Surface Structure		(3x3)-C_6H_6 + 2CO	(3x3)-C_6H_6 + 2CO	c($2\sqrt{3}$x4)rect-C_6H_6 + CO	($2\sqrt{3}$x4)rect-2C_6H_6 +4CO
The Structure of Benzene					
C_6 Ring Radius (Å)	1.40	1.43±0.10	1.51±0.15	1.65±0.15	1.72±0.15
d_{M-C}(Å)	-	2.39±0.05	2.30±0.05	2.35±0.05	2.25±0.05
γ_{CH}(cm^{-1})*	670	720-770	780-810		830-850

XBL 878-3565

Fig. 13

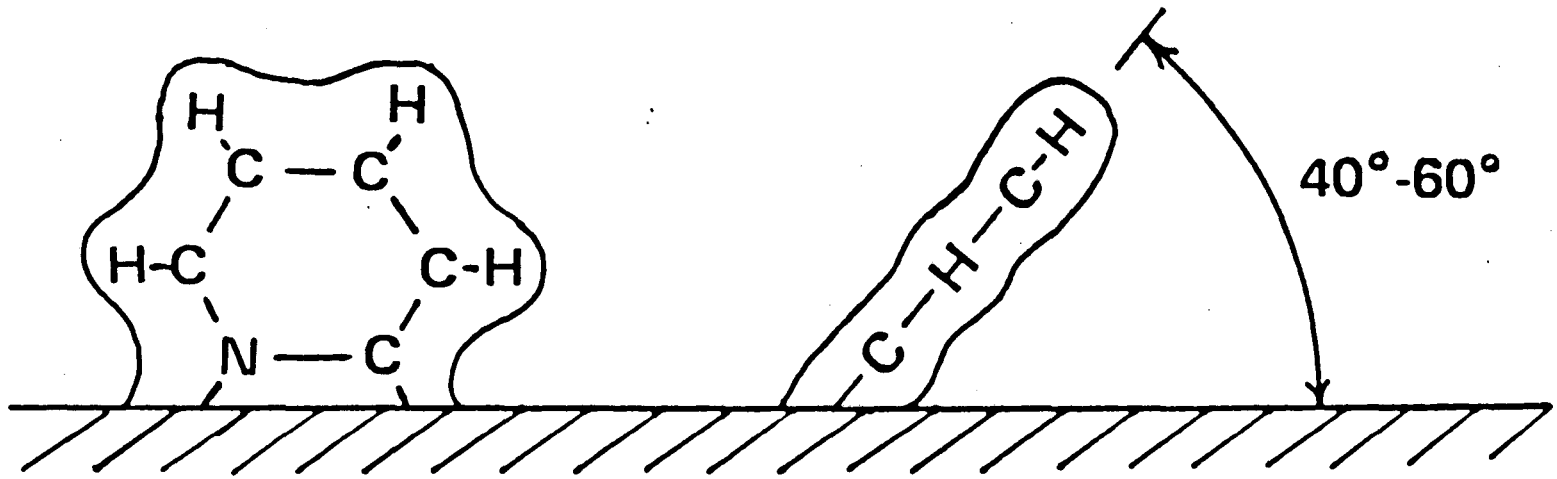
Benzene Bonding Geometries



XBL 886-2260

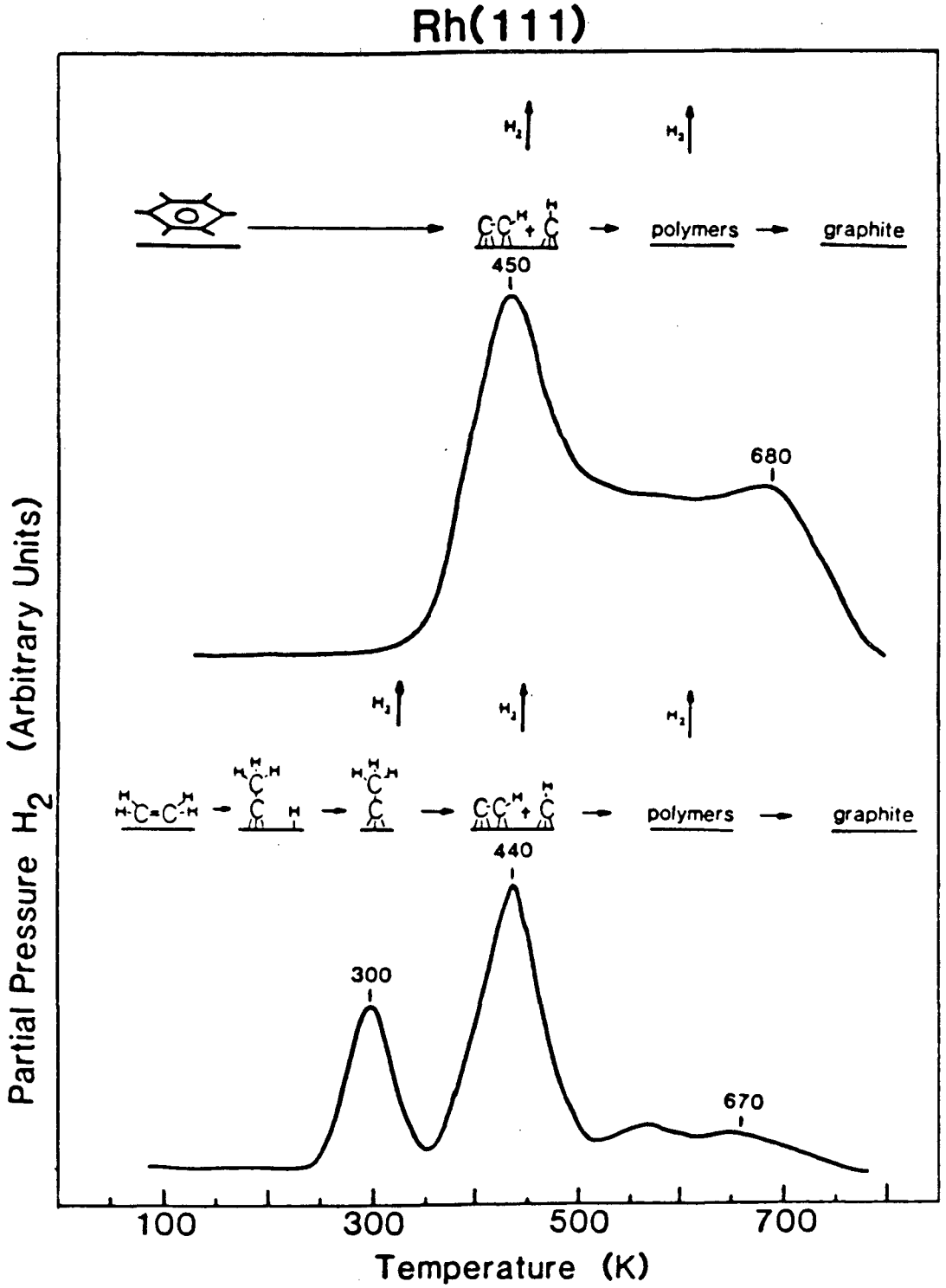
Fig. 14

α- pyridyl on Rh(111)



XBL 886-2257

Fig. 15

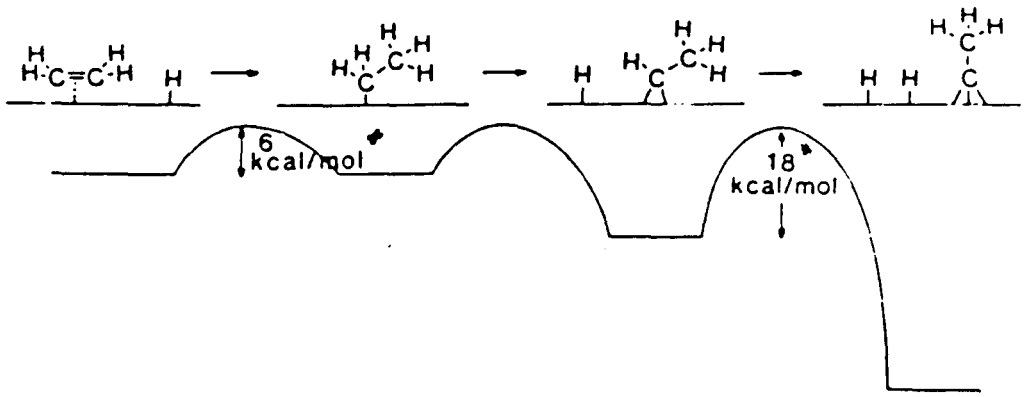


XBL 886-2254

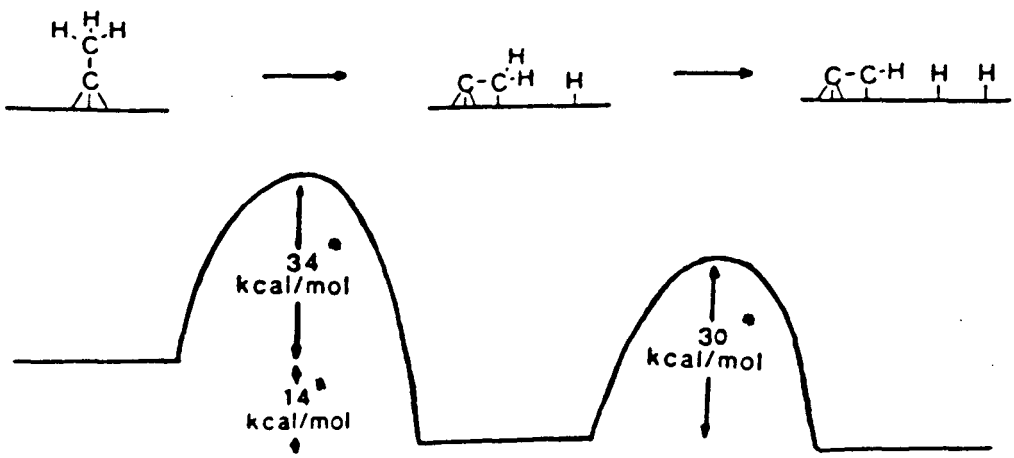
Fig. 16

Proposed Surface Reaction Mechanisms

Conversion of Ethylene to Ethylidyne (CCH_3)

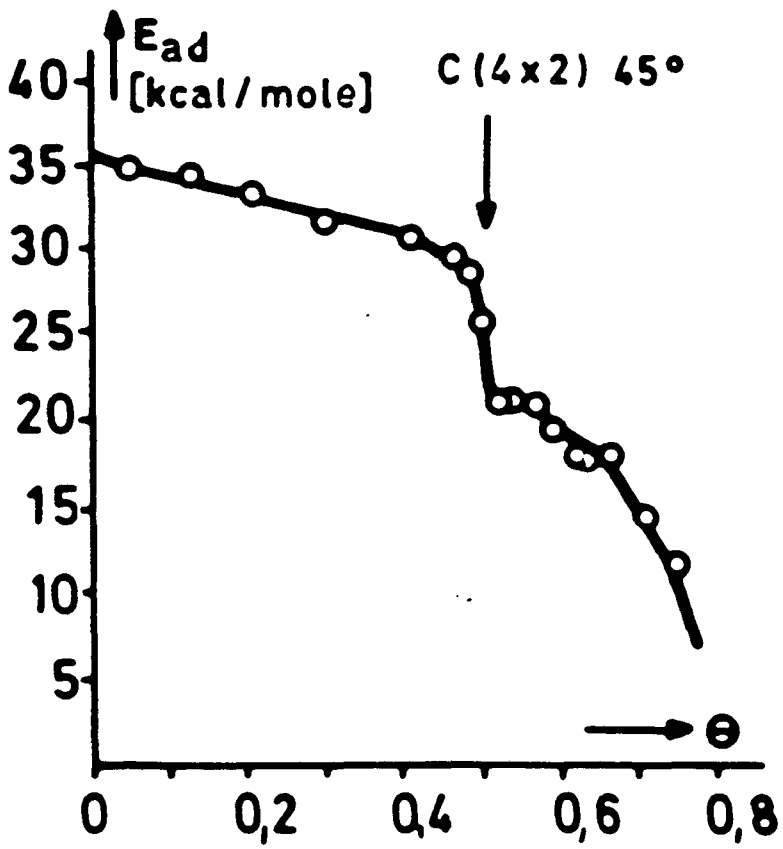


Fragmentation of Ethylidyne to Vinylidene (CCH_2) and Acetylide (CCH)



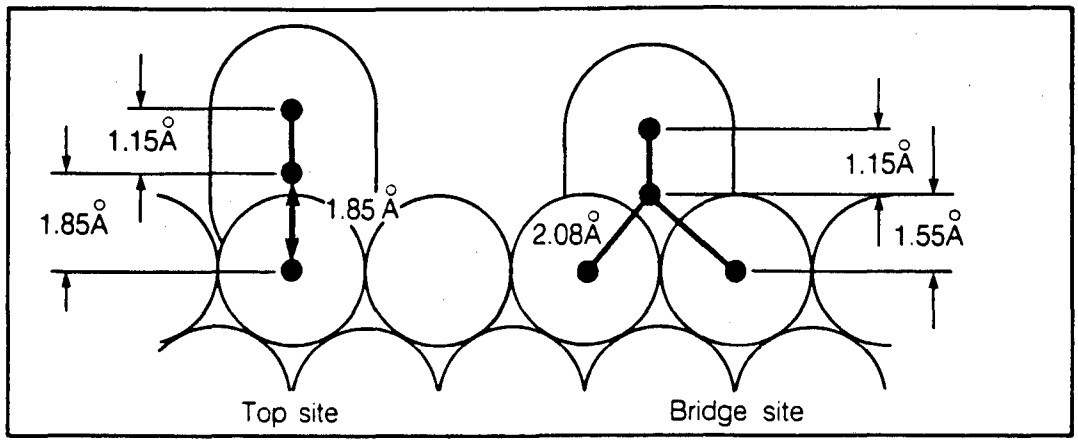
XBL 886-2250

Fig. 17

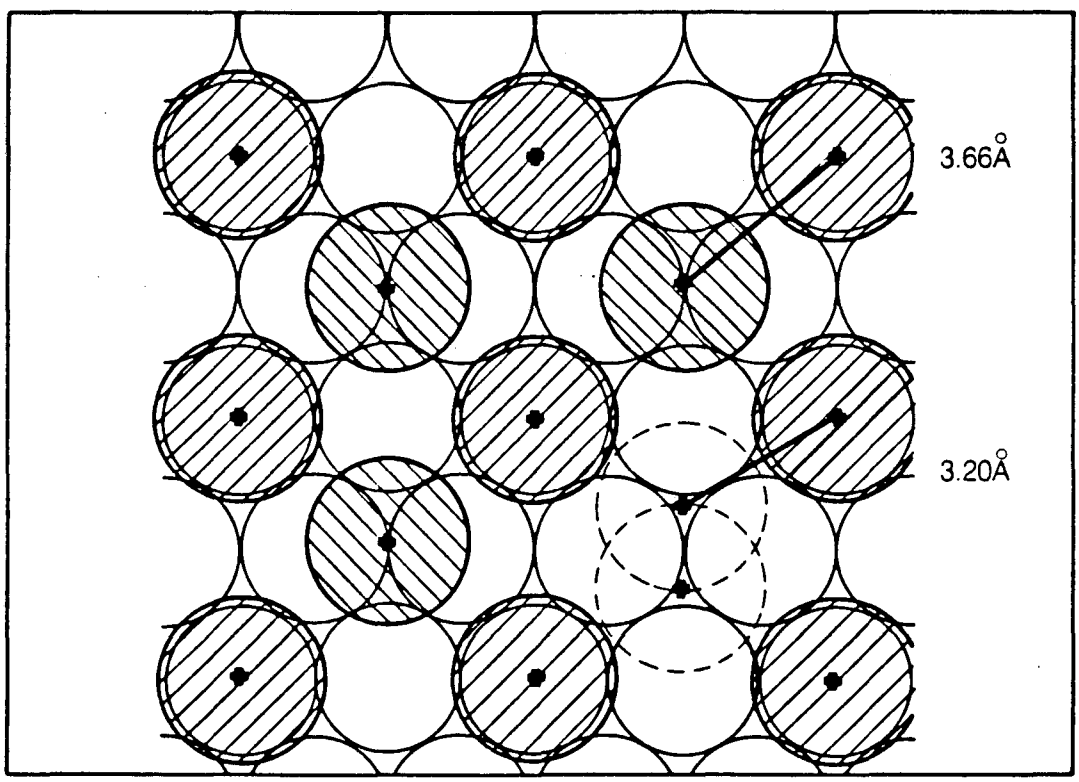


XBL 7911-12823

Fig. 18



Side view



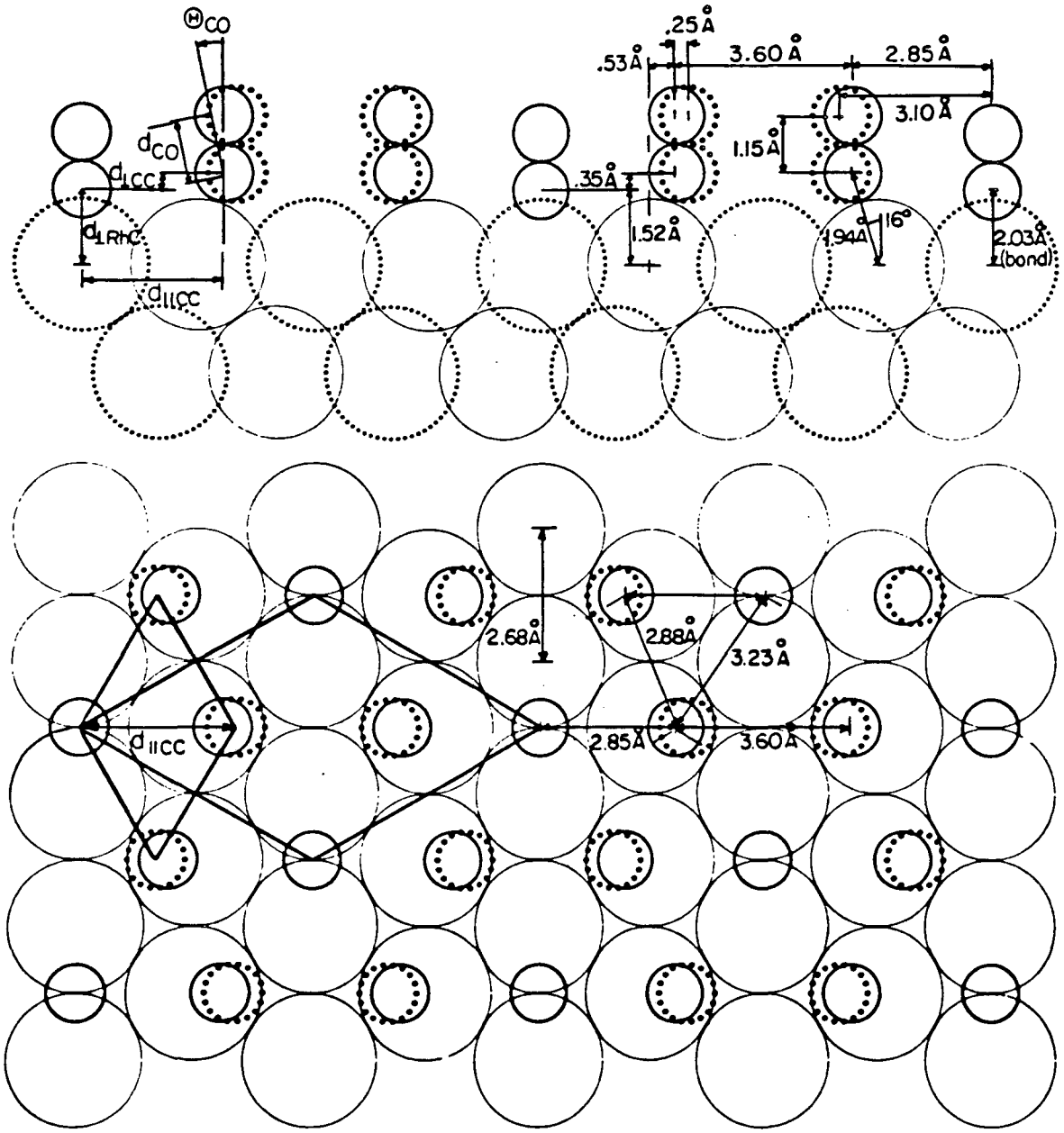
Top view

Pt (111)– c (4×2) – 2 CO
LEED Structure
at T = 150 K

XBL 857-3135

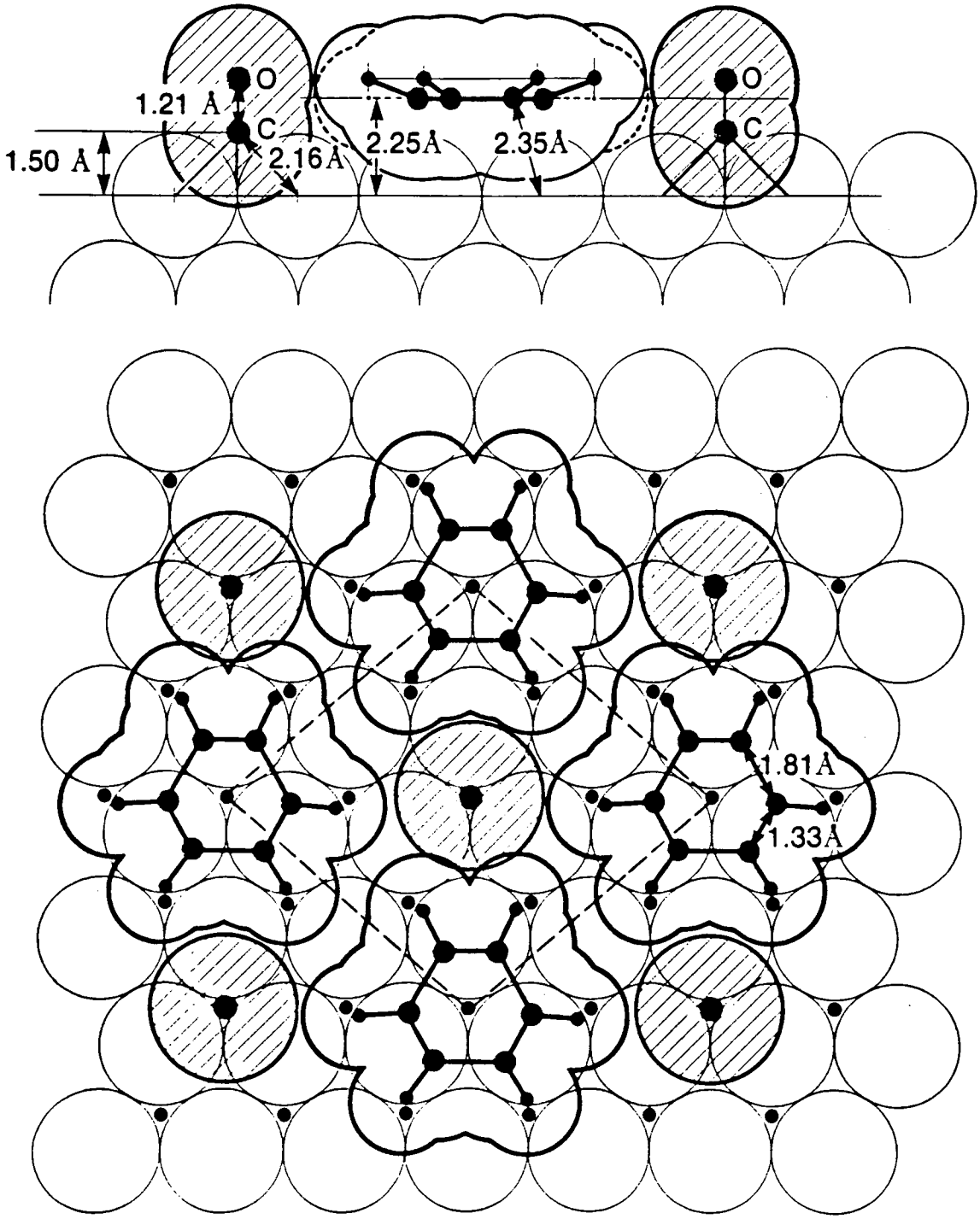
Fig. 19a

Rh(111) (2×2) - 3 CO



XBL 828-6270

Fig. 19b



$Rh(111)-(^{31}_{13})-C_6H_6 + CO$

XBL 851-9917

Fig. 20

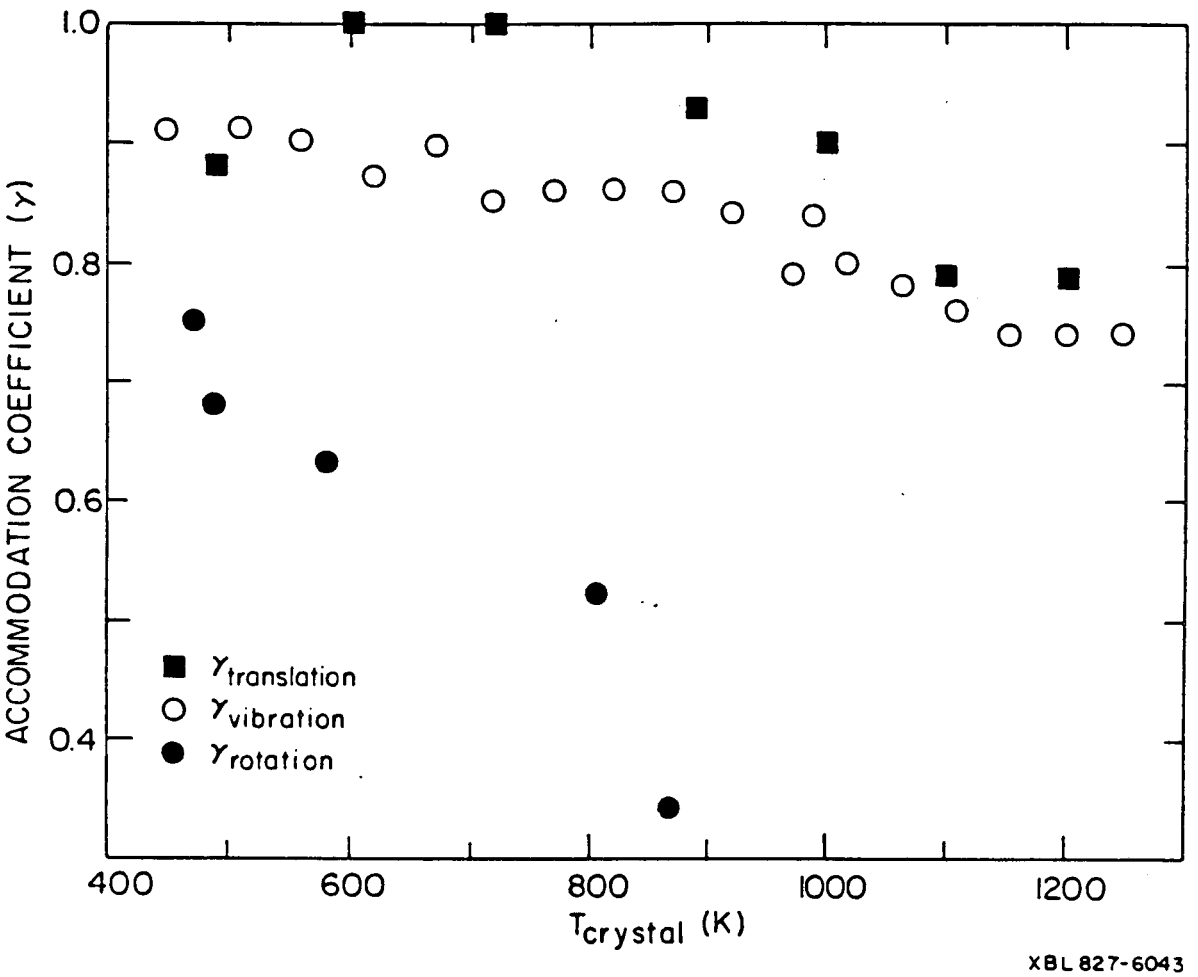
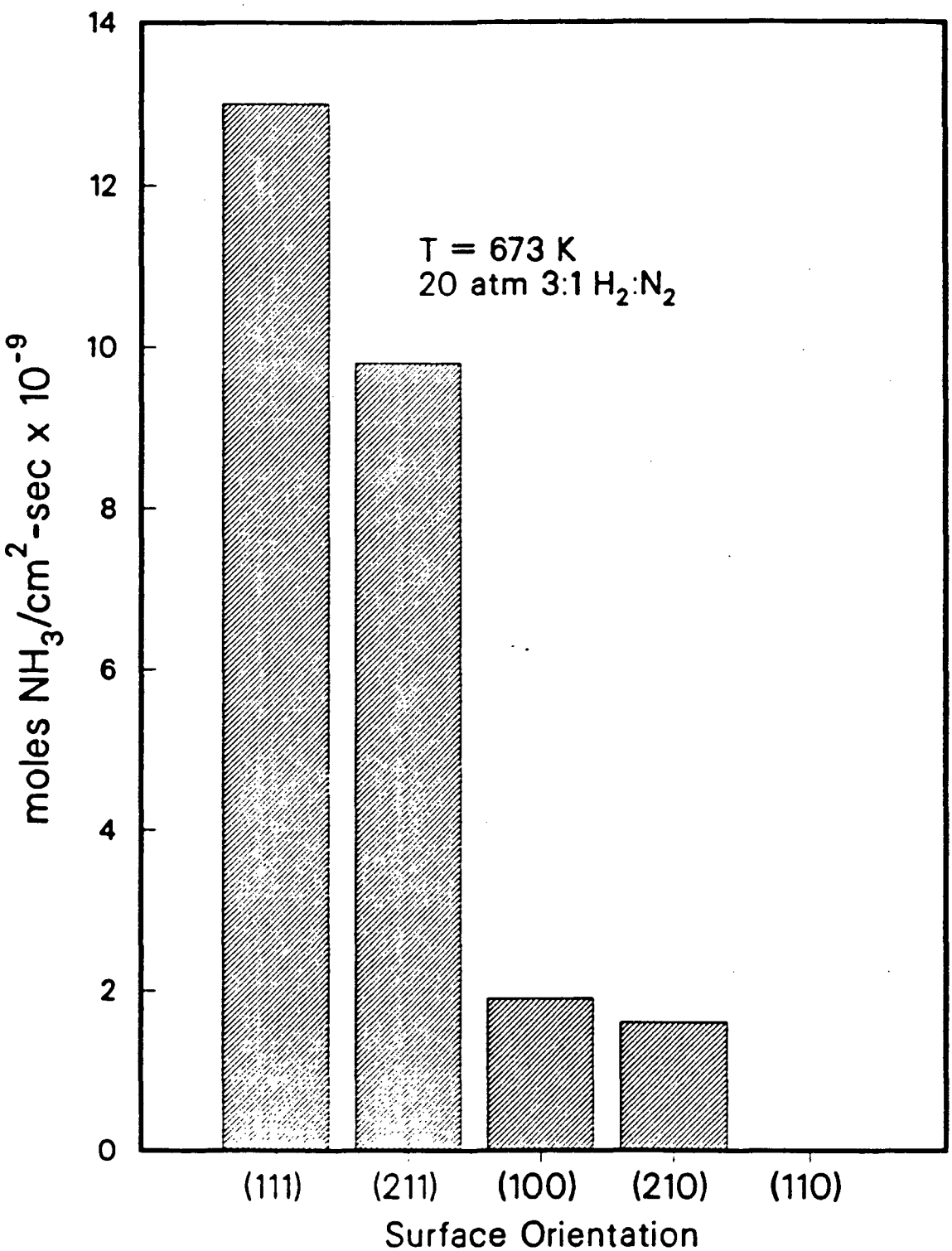
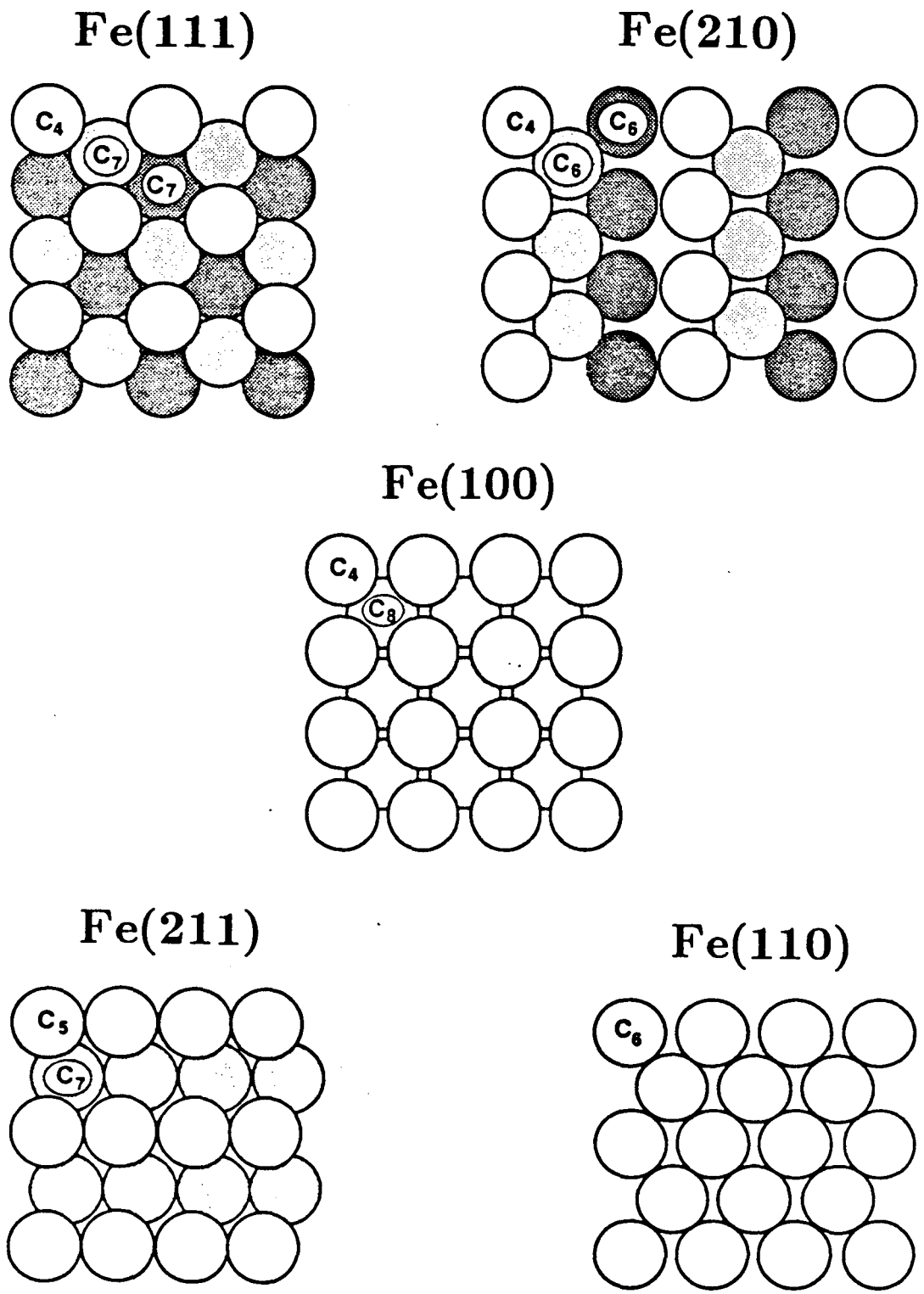

1.0
0.8
0.6
0.4
ACCOMMODATION COEFFICIENT (γ)
γtranslation
γvibration
γrotation
400
600
800
1000
1200
Tcrystal (K)
XBL 827-6043

Fig. 21



XBL 864-1663

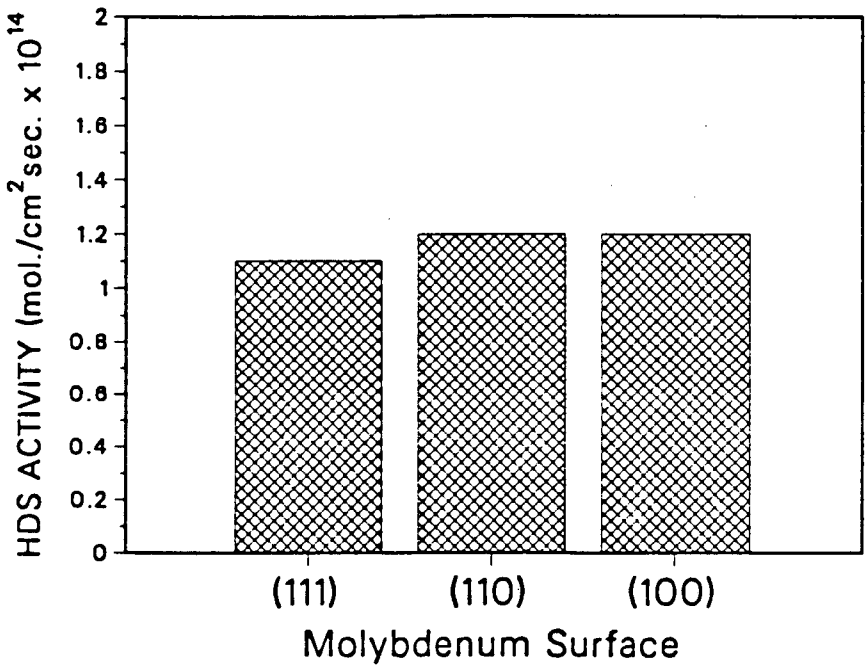
Fig. 22



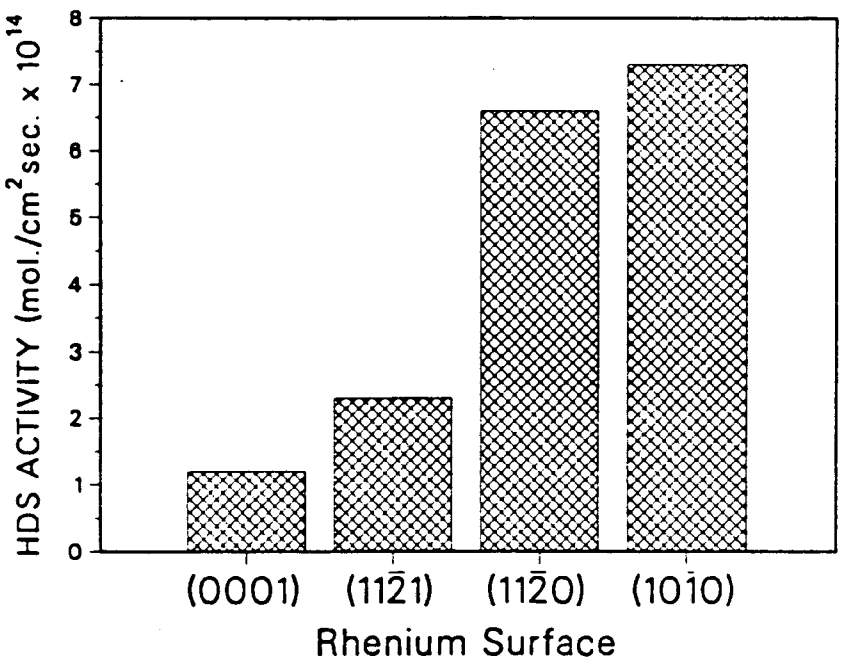
XBL 864-1664

Fig. 23

a)



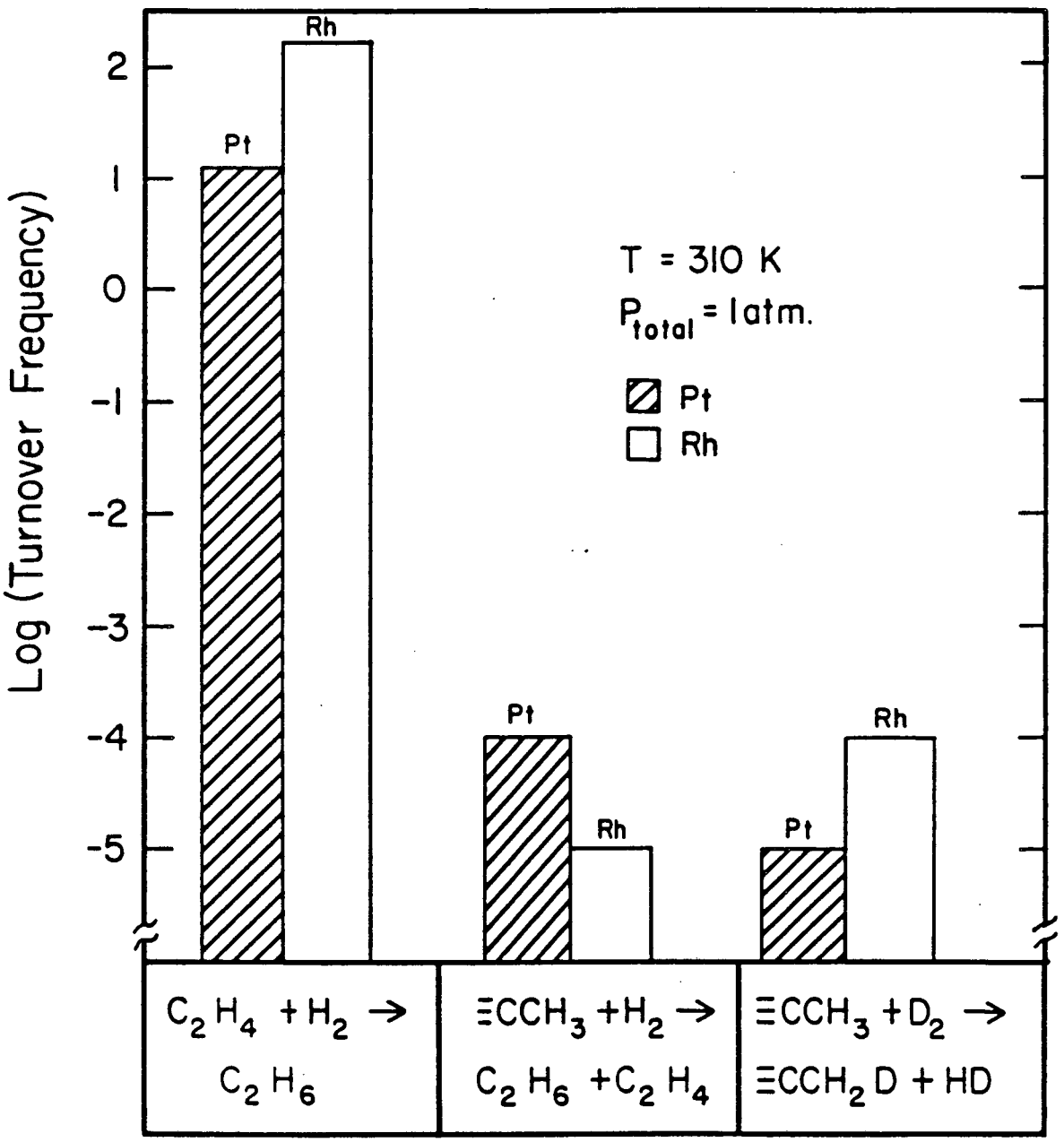
b)



XBL 878-3473

Fig. 24

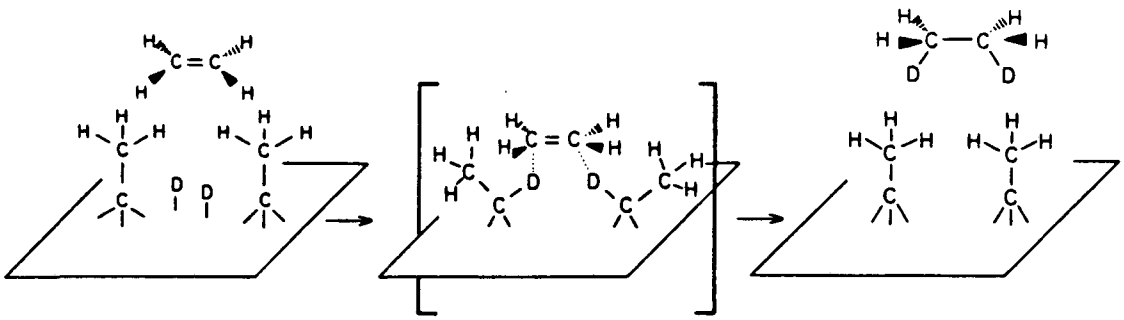
Comparison of Hydrogenation Rates
over Pt(111) and Rh(111) Single-Crystal Surfaces



XBL 846-2487

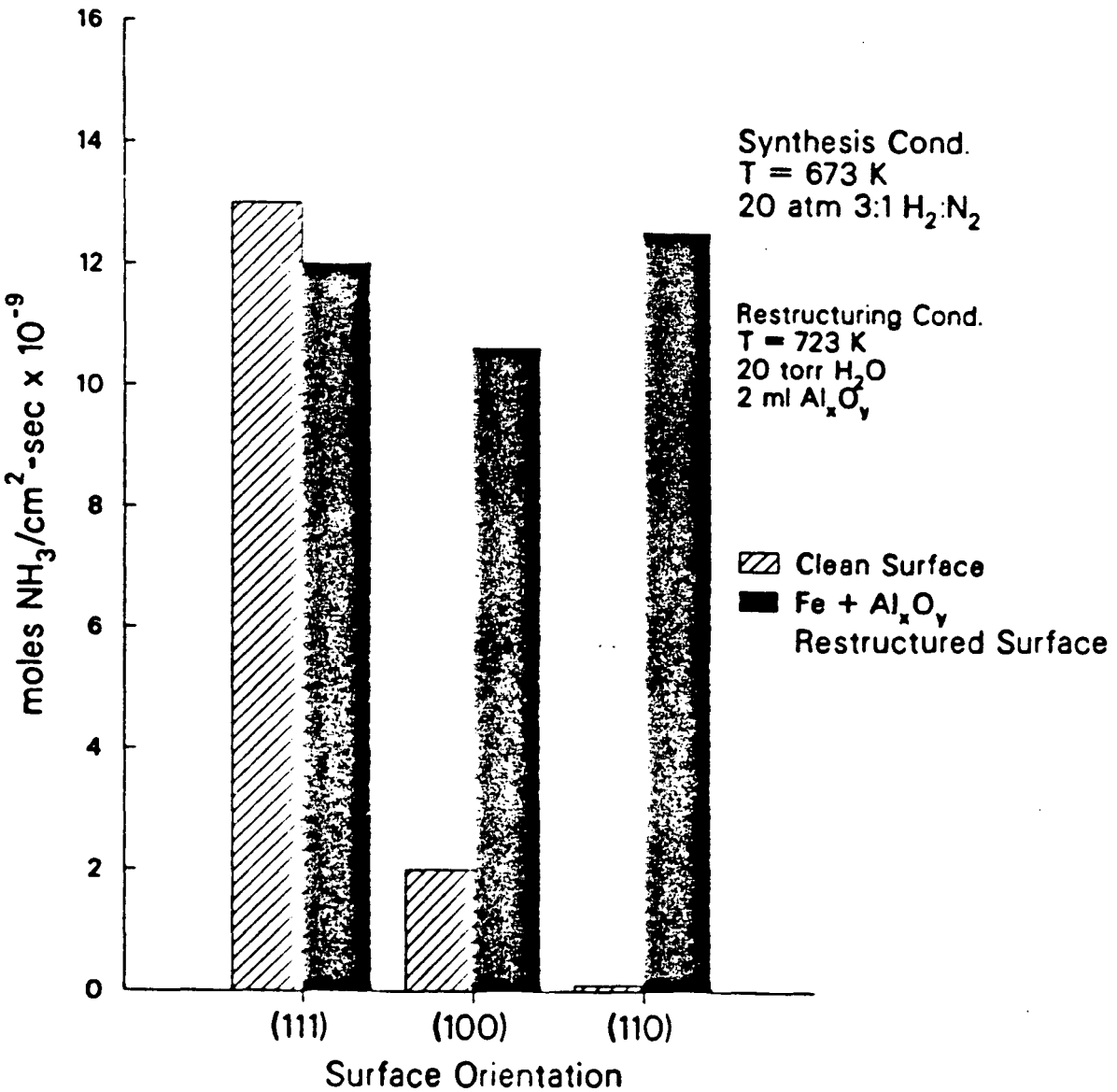
Fig. 25

PROPOSED MECHANISM FOR ETHYLENE HYDROGENATION



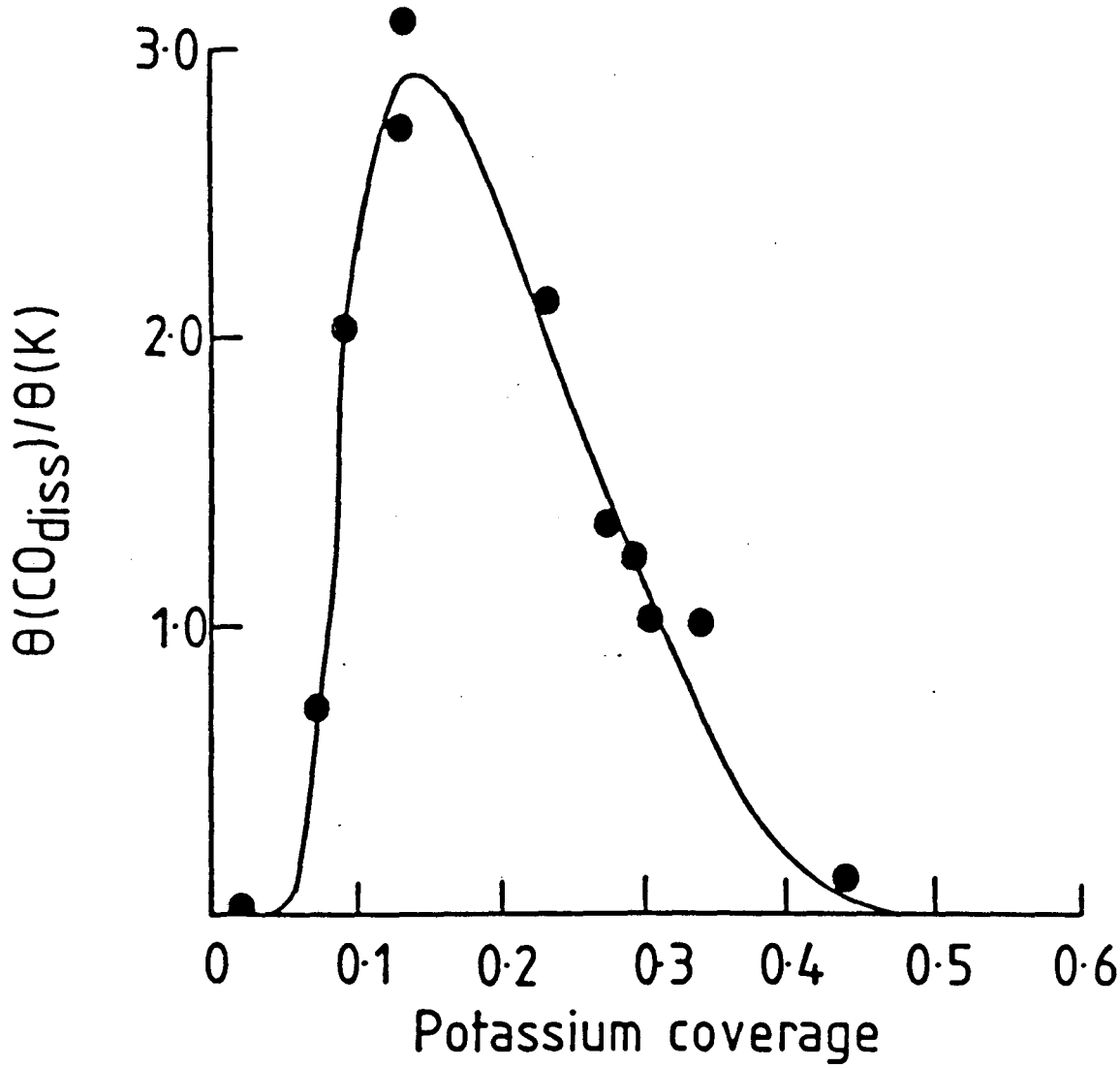
XBL 846-2494

Fig. 26



XBL 886-2258

Fig. 27



XBL 886-2251

Fig. 28

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