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MOLECULAR INGREDIENTS OF HETEROGENEOUS CATALYSIS

G.A. Somorjai and R.C. Yeates

July 1983

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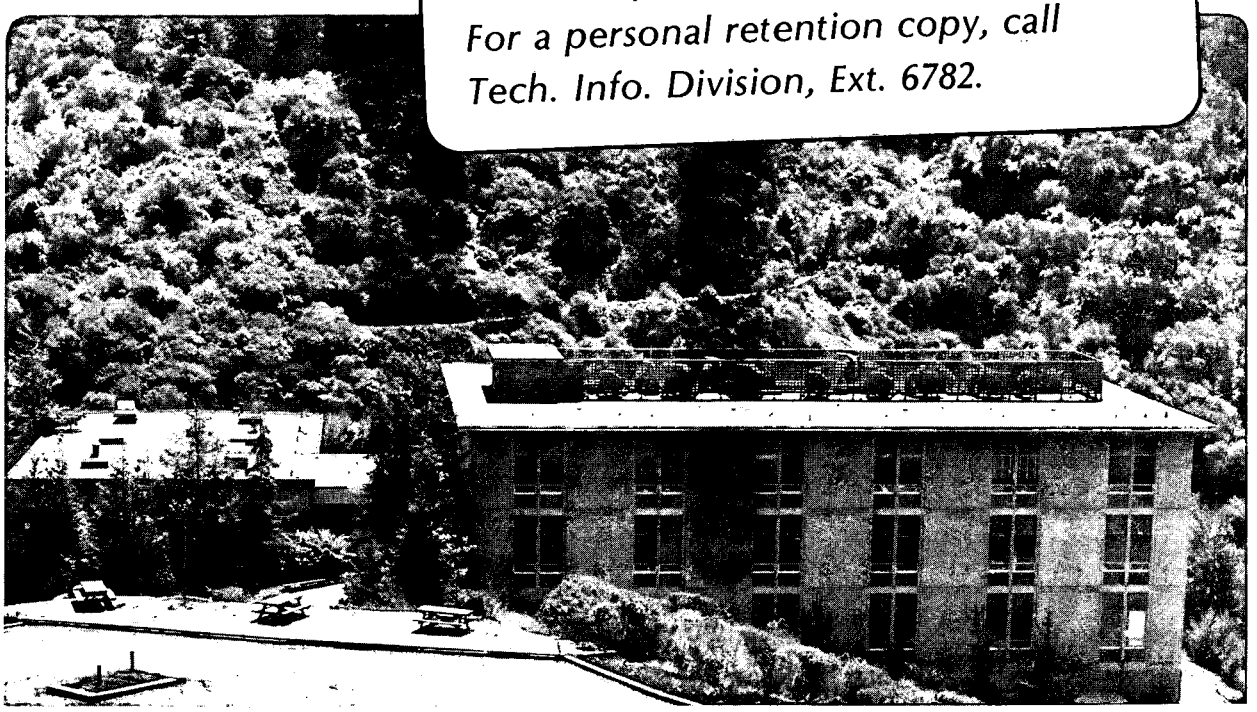

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MOLECULAR INGREDIENTS OF HETEROGENEOUS CATALYSIS

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ABSTRACT

The purpose of this paper is to present a review and status report of the rapidly developing surface science of heterogeneous catalysis. We describe the experimental results that identified three molecular ingredients of catalysis: a) structure; b) carbonaceous deposit; and c) the oxidation state of surface atoms. The hydrogenation of ethylene at both the gas-solid and liquid-solid interfaces is described.

1. INTRODUCTION

The explosively rapid development in surface science over the past 15 years was concentrated on studies of the solid-gas and solid-vacuum interfaces. Electron, atom, and ion scattering techniques revealed the atomic structure and composition at the surface (1). Many of these techniques that are frequently used in surface studies are listed in Table 1. The same techniques could not be used to probe the solid-liquid interface. The high elastic and inelastic scattering cross sections that make these probes surface sensitive render them ineffective in studies of interfaces between two phases of high atomic densities. As a result, studies of solid-liquid interfaces were pursued by the use of an ultra-high vacuum-liquid cell that permitted in situ investigations of electrochemical reactions and then the direct transfer of the electrode surface into ultra-high vacuum for analysis of the surface structure and composition (2). These cells are similar in design to the low pressure-high pressure cells developed in our laboratory (3) for combined low pressure surface science and high pressure catalysis studies and have been most valuable in studies of platinum electrodes and electrocatalysis. More recently, high intensity electromagnetic

radiation emanating from lasers (4) or from the synchrotron (5) has been employed increasingly for studies of the solid-liquid interface. Laser Raman spectroscopy, infrared ellipsometry, grazing angle X-ray scattering, and Fourier transform infrared techniques are among those that hold great promise for in situ, molecular level analysis of the solid-liquid interface.

In this paper we shall review what has been learned about the atomic structure and composition of clean surfaces from surface science studies of the solid-vacuum interface. We shall show the surface structures of a few organic molecules that have been determined by combined LEED and HREELS studies. We shall then describe the model of the working metal catalyst surface as revealed by single crystal studies primarily using platinum surfaces. We shall correlate what is known about the hydrogenation of ethylene, C_2H_4, that was studied over the Pt(111) crystal face, both at the solid-liquid and solid-gas interfaces. Finally, we shall review what needs to be done, in our estimation, to accelerate the development of solid-liquid interface studies which are clearly at the frontier of surface science.

A.1 The Atomic Structure of Clean Low-Miller-Index Surfaces

Low energy electron diffraction studies have revealed two important features of atomic surface structure: 1) relaxation; 2) reconstruction. It has been found that for most solid surfaces, the spacing between the first and second layers is shortened as compared to the spacing between the second and third, which in turn is shortened as compared to the third and fourth, and so on. This contraction is larger for more open surfaces, that is, for surfaces having lower atomic density. For

example, the contraction for the (110) surface of face-centered cubic metals is greater than that of the higher density (111) surface. In the surface plane (xy plane) the atoms maintain the structure of the projection of the bulk unit cell onto the surface. The contraction occurs in the z direction, perpendicular to the surface. This phenomenon may be understood by considering the surface as an intermediate between a diatomic molecule and bulk crystal. The interatomic distance in diatomic molecules is much shorter than the interatomic distance in the solid crystal. The surface atoms, having fewer nearest neighbors than atoms in the crystal, exhibit a lattice parameter somewhere between these two extremes in order to compensate for the anisotropy of the forces (i.e. having atoms on one side and vacuum or atoms of another type on the other side).

Reconstruction is also a consequence of surface atom relaxation. When atoms are placed in an anisotropic environment, such as the surface, there are many dangling bonds that would like to pair up in order to maximize the binding energy between surface atoms. As a result, the atoms at the surface seek a new equilibrium position, not only in the z direction, but also in the surface (xy) plane. This massive dislocation of surface atoms leads to reconstruction, the appearance of a new surface unit cell. Most semiconductors and many metal surfaces undergo these reconstructions (Fig. 1). Many of these structures have been analyzed by surface crystallography and the precise location of surface atoms has been determined (6).

A.2 The Structure of High-Miller-Index Surfaces

Studies of high-Miller-index surfaces by low energy electron diffraction have revealed that they are composed of low-Miller-index surfaces in stepped and kinked configurations. Typical high-Miller-index surfaces with various combinations of terraces and kinks are displaced in Figures 2 and 3. By cutting crystals along a high-Miller-index direction and suitable cleaning afterwards, one can obtain diffraction patterns from which the structure of these high-Miller-index surfaces can be determined. Because of the periodicity of the steps and/or kinks, structure determination by diffraction is possible. Steps of monatomic height provide minimum surface free energies for these surfaces and therefore are prevalent on clean high-Miller-index surfaces.

B. The Composition of Clean Surfaces

Because of differences in bonding at the surface and in the bulk, there is a considerable driving force for many impurities to segregate to the surface (7). Sulfur, carbon, boron, and silicon are often found to segregate to the surface upon heating. Although surface segregation of impurities is rather inconvenient when one would like to study the properties of clean surfaces, subsequent removal of the segregated impurity atoms provides a cleaning mechanism for many solids. For multicomponent systems, the surface free energy is minimized by placing that component which has the lowest free energy on the surface. As a result, surface compositions are almost always different from the bulk composition for multicomponent systems (Fig. 4). This is particularly important for alloys, because metals, having high surface energy in the range of thousands of ergs per square centimeter, provide a large

thermodynamic driving force to segregate the component with the lowest surface energy to the surface, thus minimizing the total surface energy. Several thermodynamic models predict surface segregation in alloy surfaces (8).

It should be noted that the adsorption of gas atoms or molecules that form bonds of different strengths with a different alloy constituent can change the surface composition markedly. For example, copper is segregated to the surface of clean copper/nickel alloys (9). Upon adsorption of carbon monoxide, which forms a much stronger bond with nickel than with copper, nickel diffuses to the surface, altering the surface composition (10). When carbon monoxide is desorbed, the copper moves back onto the surface and provides a copper rich alloy phase.

It should be noted that, in order to observe the surface segregation predicted by thermodynamic models, one needs to provide large enough diffusion rates to facilitate equilibration between the surface and bulk. At sufficiently low temperatures, one may freeze in metastable surface compositions. The surface segregation is minimized when the bulk lattice forces are strong enough to overcome any change due to the introduction of a surface. As a general rule, if the heat of mixing or the heat of compound formation is much greater than the surface energy differences of the components, surface segregation may be unimportant.

C. Structure of Alkenes and Benzene on Metal Surfaces

Our low energy electron diffraction and high resolution energy loss spectroscopy studies have been directed towards the determination of the molecular structure and bonding of hydrocarbons on platinum and rhodium

surfaces. Figure 5 shows the stable structures of ethylene, propylene, and butene adsorbed on platinum and rhodium surfaces in our laboratory (11) and on palladium and nickel surfaces in other laboratories. The carbon-carbon bond closest to the metal surface is perpendicular to the surface plane, and is elongated to a single bond, 1.5A. The carbon closest to the metal sits in a three-fold hollow site with a carbon-metal distance of 2.0A, considerable shorter than the 2.2A covalent bond length expected. This indicates a very strong multiple carbon-metal bond of carbene- or carbye-like character. The methyl group or ethyl groups are away from the surface and are rotating rather freely. Only at high coverages will these side groups order to from new surface structures. These structures are called alkylidyne because of their similarity to several organometalic cluster compounds. Benzene lies flat on the (111) crystal face of these transition metals with the center of the benzene ring above the three-fold hollow site (Fig. 6). The surface structure is highly symmetrical, as determined by both LEED and HREELS studies. As the temperature is increased, selective C-H and C-C bond breaking occurs and organic fragments, C_2, C_2H, and CH, form on the surface. These fragments are very stable and seem to be present in the temperature range of 140 to 400 degrees centigrade (12), perhaps the most important temperatures for catalytic reactions. The hydrogen-deuterium exchange in these organic fragments is very facile. The carbon atoms are strongly bound to the surface and stay on the surface for periods much longer than the turnover times of most catalytic reactions. The function of these fragments in a catalytic reaction appears to be one of hydrogen storage. They readily supply their hydrogen to incoming organic reactants and intermediates. Above 400 degrees centigrade, all

the hydrogen desorbs and a graphitic overlayer forms. This layer poisons the transition metal surface for heterogeneous catalysis.

D. The Model of the Working Metal Catalyst During Hydrocarbon Conversion

Over the last ten years, studies of hydrocarbon conversion reactions using single crystal surfaces have revealed the dominant molecular ingredients of hydrocarbon conversion catalysis. These are the atomic structure of the metal surface, its composition, and the oxidation state of the surface atoms. How does the reaction rate depend on the atomic structure of the catalyst surface? To answer this question, reaction rate studies using various flat, stepped and kinked single crystal surfaces have been very useful indeed. For the important aromatization reaction of n-hexane to benzene and n-heptane to toluene, we discovered that the hexagonal platinum surface, where each surface atom is surrounded by six nearest neighbors, is three to seven times more active than the platinum surface with a square unit cell (13). Aromatization reaction rates increase further for stepped and kinked platinum surfaces (14). Reaction rate studies on more than ten different crystal surfaces with various terrace orientations and step and kink concentrations indicate that maximum aromatization activity is achieved on stepped surfaces with terraces of hexagonal orientation, about five atoms wide (Fig. 7).

The reactivity pattern of platinum crystal surfaces for alkane isomerization reactions is completely different than that for aromatization (15). Our studies revealed that that maximum rates and selectivity (the rate of the desired reaction divided by the total rate) for butane isomerization reactions are obtained on the flat crystal face with the

square unit cell. Isomerization rates for this surface are four to seven times higher than those for the hexagonal surface and are only increased slightly by surface irregularities (steps and kinks) on the platinum surface (Fig. 8). For the undesirable hydrogenolysis reactions that require C-C bond scission, we found that the two flat surfaces with the highest atomic density exhibit very similar reaction rates (15). However, the distribution of hydrogenolysis products varies sharply over these two surfaces. The hexagonal surface displays high selectivity for scission of the terminal C-C bond, whereas the surface with the square unit cell always prefers cleavage of C-C bonds located in the center of the reactant molecule. The hydrogenolysis rate increases markedly, three to five-fold, when kinks are present in high concentrations on the platinum surfaces.

Since different reaction are sensitive to different structural features of the catalyst surface, one must prepare the catalyst with an appropriate structure to obtain maximum activity and selectivity. As indicated, H-H and C-H bond breaking processes are more facile on stepped surfaces than on the flat crystal faces, while C-C bond scission is aided by kink sites.

What is the composition of the working metal catalyst surface? When the surface of platinum was examined after carrying out any one of the hydrocarbon conversion reactions, it was always covered by a near monolayer amount of carbonaceous deposit. Studies of carbon 14 labeled organic molecules and thermal desorption spectroscopy revealed that the turnover time of the carbon fragments was longer than the turnover times of the catalytic reactions (17). Deuterium exchange studies indicate

rapid exchange of the hydrogen atoms between the adsorbing reactant molecules and the active, but irreversibly adsorbed carbon fragment deposits. The carbon atoms in this layer do not exchange. One important property of the carbonaceous deposit is its ability to store and exchange hydrogen. 10 to 15% of the surface remains uncovered, while the rest of the metal surface is covered by the organic deposit. The fraction of uncovered metal sites decreases slowly with increasing temperature (17). The structure of these uncovered metal islands is not very different from the structure of the initially clean metal surface.

The result of our catalytic hydrocarbon conversion reaction studies on platinum crystal surfaces was to develop a model (18) for the working platinum and other transition metal catalysts and is shown in Figure 9. Between 80 and 95% of the catalyst surface is covered with an irreversibly adsorbed carbonaceous deposit that stays on the surface from times much longer than the reaction turnover time. The structure of these carbonaceous deposits vary continuously from two dimensional to three dimensional with increasing reaction temperature, and there are platinum patches that are not covered by this deposit. These metal sites can accept the reacting molecules and are responsible for the observed structure sensitivity and turnover rates. While there is evidence that the carbonaceous deposit participates in some of the reactions by hydrogen transfer and by providing sites for rearrangement and desorption while remaining inactive in other reactions, its chemical role requires further exploration.

In other catalytic reactions, such as the hydrogenation of carbon monoxide, the oxidation state of the transition metal ions at the sur-

face plays an important role in reaction selectivity. It was found that, using rhodium metal, carbon monoxide and hydrogen proceed to form methane (19) and nothing else (Fig. 10). When rhodium was used in the 3+ formal oxidation state as lanthanum rhodate (20) or rhodium oxide (21), oxygenated molecules such as acetic acid, ethanol, acetaldehyde, and methanol were produced. Changing the nature of adsorbed molecules by changing the oxidation state of the transition metal can drastically alter the reaction selectivity. In the case of the hydrogenation of carbon monoxide, the insertion of a carbon monoxide molecule into the growing organic chain can only occur in the presence of higher oxidation state transition metal ions. In the presence of the metallic state, hydrogenation and CO dissociation predominate to produce mostly methane.

E. Ethylene Hydrogenation at the Solid-Liquid and Solid-Gas Interfaces of Pt(111)

One of the few reactions that has been studies at both the solid-liquid and solid-gas interfaces using combined low-pressure surface science techniques and high-pressure catalytic techniques is the hydrogenation of ethylene. The research at the solid-liquid interface is being carried out by Hubbard (22) and his co-workers and the hydrogenation of ethylene at the solid-gas interface was carried out in our laboratory (23). In both cases the reaction exhibited an insensitivity to the surface structure and only depended on the number of surface platinum atoms.

When a clean platinum single crystal surface was exposed to ethylene in the gas phase, a saturation coverage of ethylidyne formed with the structure shown in Fig. 5. The rate of hydrogenation of the

ethylidyne molecules was much slower than the observed hydrogenation rate, indicating that the ethylidyne molecule is not a direct intermediate. Since the ethylidyne molecules block the metal atoms and prevent the direct adsorption of ethylene on the metal surface, the ethylene molecules adsorp on top of the ethylidyne layer and are hydrogenated by hydrogen transfer from the ethylidyne. This mechanism explains the structure insensitivity of this reaction. The hydrogenation reaction has an activation barrier of 10.8 Kcal/mole (Fig. 11) with a reaction order of 1.3 for hydrogen and -0.60 for ethylene (Fig. 12).

When a clean platinum single crystal surface was exposed to an aqueous ethylene solution, a strongly adsorbed ethylene layer formed. The structure of this adsorbed ethylene has not yet been determined. Two mechanisms appear to be important in the hydrogenation of ethylene at the solid-liquid interface. The adsorbed ethylene molecule can accept two electrons from the platinum electrode and subsequently react with two hydrogen ions in solution. Also, hydrogen ions can be reduced at the platinum surface. These adsorbed hydrogen atoms can then react with reversibly adsorbed ethylene to form ethane. The dependence of the reaction on temperature has not yet been determined.

F. Needs for Accelerated Development of Atomic Scale Studies at the Solid-Liquid Interface

There is no doubt, the chemistry that occurs at the solid-liquid interface is at the frontier of modern surface science. Our challenge is to determine the atomic structure at the solid-liquid interface and the surface composition under adsorption and various reaction conditions. A molecular level understanding of many phenomena in

electrochemistry and in biology depends on closer scrutiny of the solid-liquid interface. There are many new techniques that promise to open up this interface to closer scrutiny. The new high intensity photon scattering techniques are certainly among those that are likely to be used in these studies. Techniques that use high intensity, tunable synchrotron radiation and laser techniques are at the forefront of the promising technologies. It is our hope that the intensive use of these techniques and the development of new techniques will accelerate the understanding of solid-liquid interfaces at the atomic level.

We should emphasize the need for studies of chemisorption of the same atoms and molecules on the same surface at both the solid-liquid and solid-gas interfaces. By detailed studies of both interfaces, one should be able to correlate the different phenomenon and perhaps use the tremendous amount of data available about solid-gas interfaces to aid in the understanding of the solid-liquid interface on the molecular scale.

It is equally important to study catalytic reactions at the solid-liquid and solid-gas interfaces on the same crystal face. Candidates, in addition to ethylene hydrogenation, are the oxidation of hydrogen and partial oxidation reactions of small molecules. It should be noted, that while temperature dependence studies reveal kinetic parameters readily, temperature dependence measurements are rarely made in solid-liquid interface studies.

Acknowledgments

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FIGURE CAPTIONS

Fig. 1. Arrangement of atoms on the reconstructed (100) surface of platinum, gold, and iridium.

Fig. 2. Structure of several high-Miller-index stepped surfaces with different terrace widths and orientation.

Fig. 3. Structure of several high-Miller-index surfaces with different kink concentrations.

Fig. 4. Surface concentration of Au-Ag alloy plotted versus the bulk concentration.

Fig. 5. Atomic surface structure of alkylidyne species adsorbed on Pt(111).

Fig. 6. Atomic surface structure of benzene adsorbed on Rh(111).

Fig. 7. The dependence of dehydrocyclization selectivities as a function of surface structure ($P_{n\text{-heptane}}$ = 15 torr, P_{H_2} = 480 torr, and T = 573K).

Fig. 8. The dependence of isomerization rate of various alkanes as a function of surface structure.

Fig. 9. Model for the working surface composition of a platinum reforming catalyst.

Fig. 10. The product distributions of the hydrogenation of carbon monoxide over rhodium and various rhodates.

Fig. 11. Arrhenius plots for ethylene hydrogenation with H_2 and D_2 over Pt(111). $P_{C_2H_4}$ = 10 torr P_{H_2} or D_2 = 20 torr, P_{N_2} = 80 torr.

Fig. 12. Product accumulation curve as a function of time for ethylene hydrogenation over Pt(111). T = 333K. The product was measured by mass spectrometry (0) and gas chromatography (●).

TABLE 1.

Table of some of the frequently utilized surface characterization techniques to determine the structure and composition of solid surfaces. Adsorbed species present at concentrations of 1% of a monolayer can be readily detected.

SURFACE ANALYSIS METHOD	ACRONYM	PHYSICAL BASIS	TYPE OF INFORMATION OBTAINED
Low energy electron diffraction	LEED	Elastic backscattering of low energy electrons	atomic surface structure of surfaces and of adsorbed gases
Auger electron spectroscopy	AES	Electron emission from surface atoms excited by electron x-ray of ion bombardment	surface composition
High resolution electron energy loss spectroscopy	HREELS	Vibrational excitation of surface atoms by inelastic reflection of low energy electrons	Structure and bonding of surface atoms and adsorbed species
Infrared spectroscopy	IRS	Vibrational excitation of surface atoms by absorption of infrared radiation	Structure and bonding of adsorbed gases
X-ray and ultraviolet photoelectron spectroscopy	XPS UPS	Electron emission from atoms	Electronic structure and oxidation state of surface atoms and adsorbed species
Ion scattering spectroscopy	ISS	Inelastic reflection of inert gas ions	Atomic structure and composition of solid surfaces
Secondary ion mass spectroscopy	SIMS	Ion beam induced ejection of surface atoms as positive & negative ions	surface composition
Extended X-ray absorption fine structure analysis	EXAFS	Interference effects during x-ray emission	atomic structure of surfaces and adsorbed gases
Thermal desorption spectroscopy	TDS	Thermally induced desorption or decomposition of adsorbed species	Adsorption energetics composition of adsorbed species

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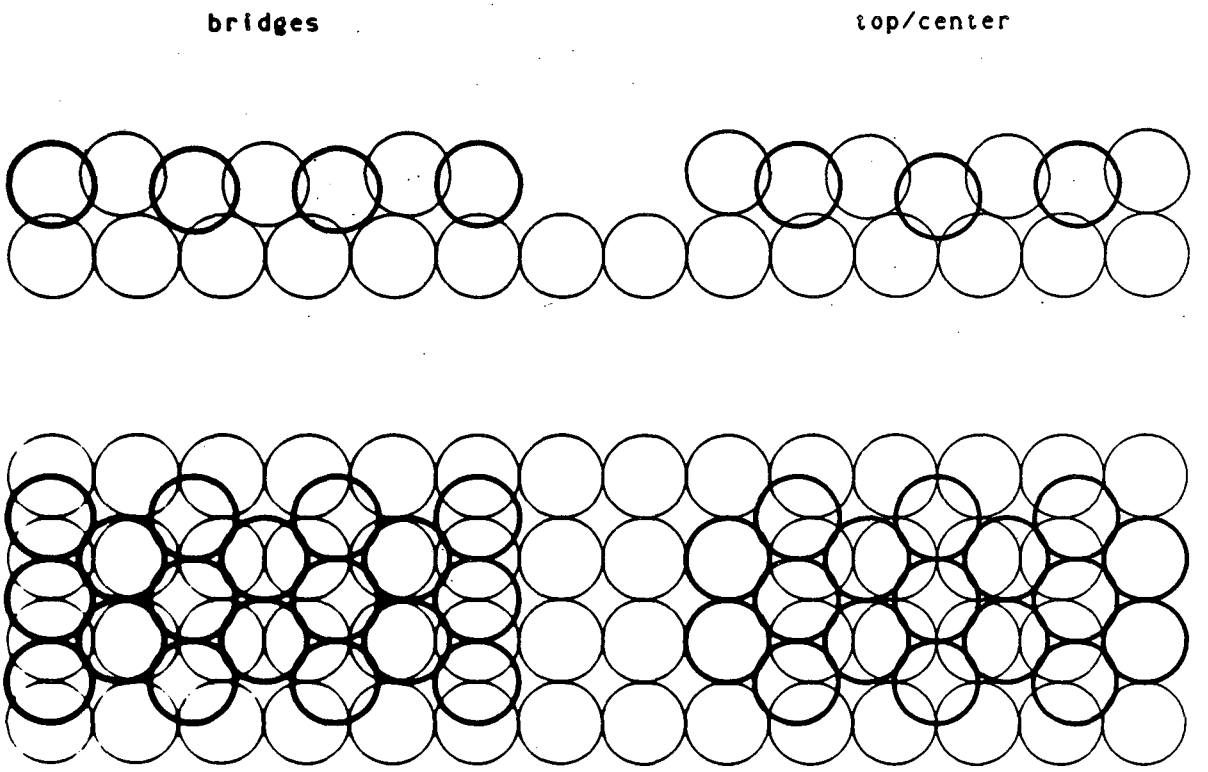
Auger electron spectroscopy	AES	Electron emission from surface atoms excited by electron x-ray of ion bombardment	surface composition
High resolution electron energy loss spectroscopy	HREELS	Vibrational excitation of surface atoms by inelastic reflection of low energy electrons	Structure and bonding of surface atoms and adsorbed species
Infrared spectroscopy	IRS	Vibrational excitation of surface atoms by absorption of infrared radiation	Structure and bonding of adsorbed gases
X-ray and ultraviolet photoelectron spectroscopy	XPS UPS	Electron emission from atoms	Electronic structure and oxidation state of surface atoms and adsorbed species
Ion scattering spectroscopy	ISS	Inelastic reflection of inert gas ions	Atomic structure and composition of solid surfaces
Secondary ion mass spectroscopy	SIMS	Ion beam induced ejection of surface atoms as positive & negative ions	surface composition
Extended X-ray absorption fine structure analysis	EXAFS	Interference effects during x-ray emission	atomic structure of surfaces and adsorbed gases
Thermal desorption spectroscopy	TDS	Thermally induced desorption or decomposition of adsorbed species	Adsorption energetics composition of adsorbed species

fcc (100) : buckled hexagonal top layer



XBL 837-10781

Fig. 1

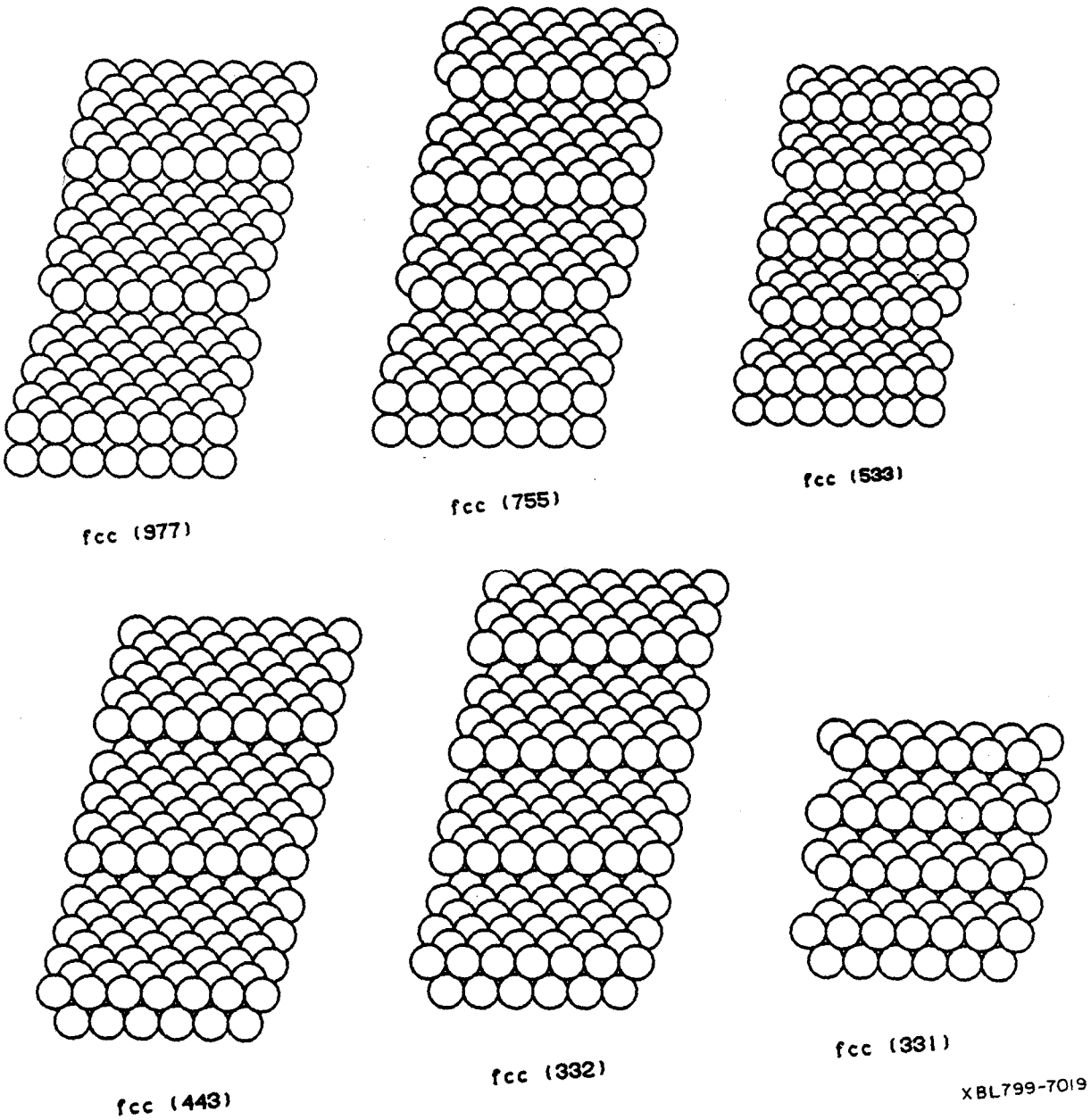


Fig. 2

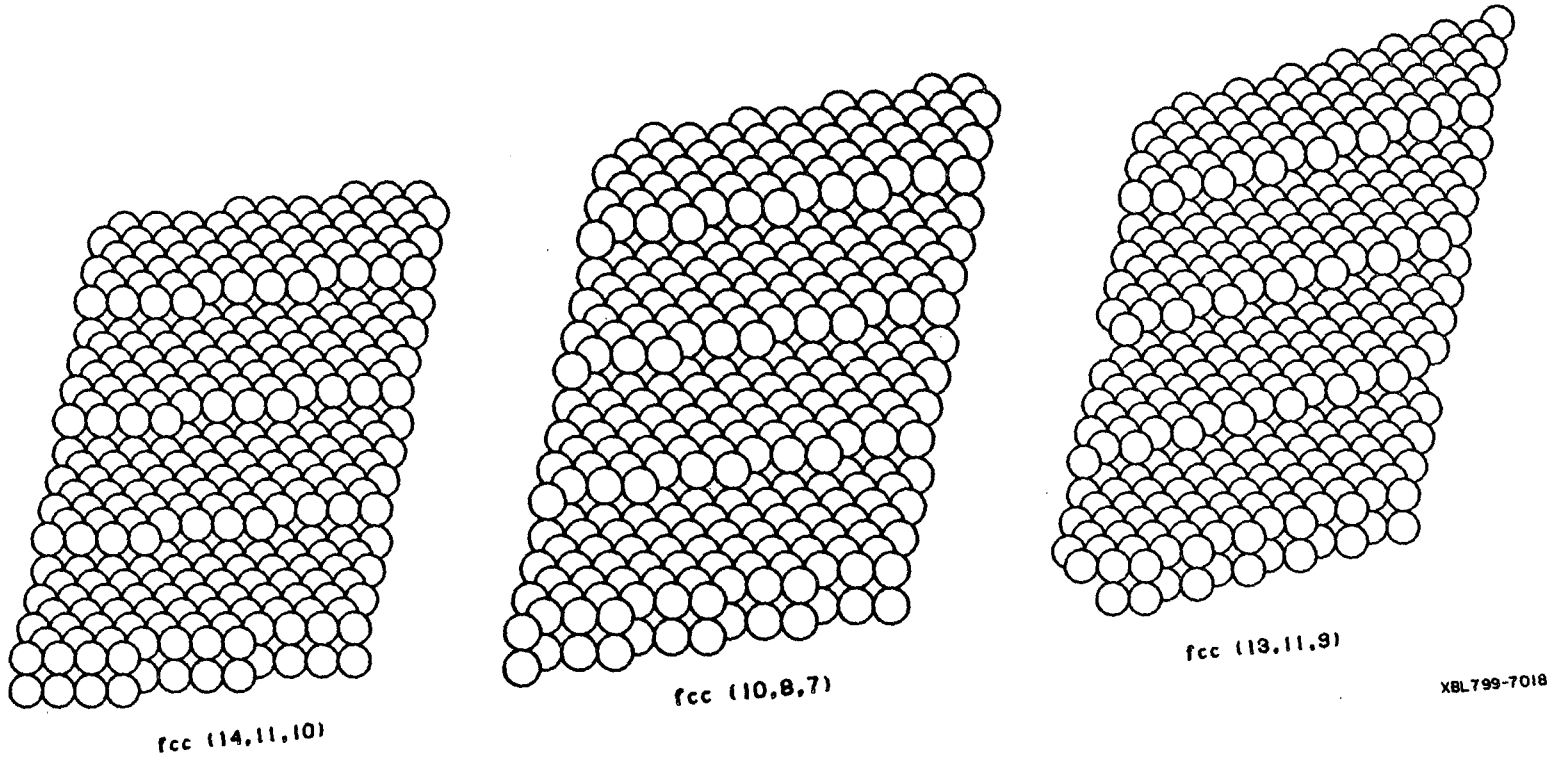
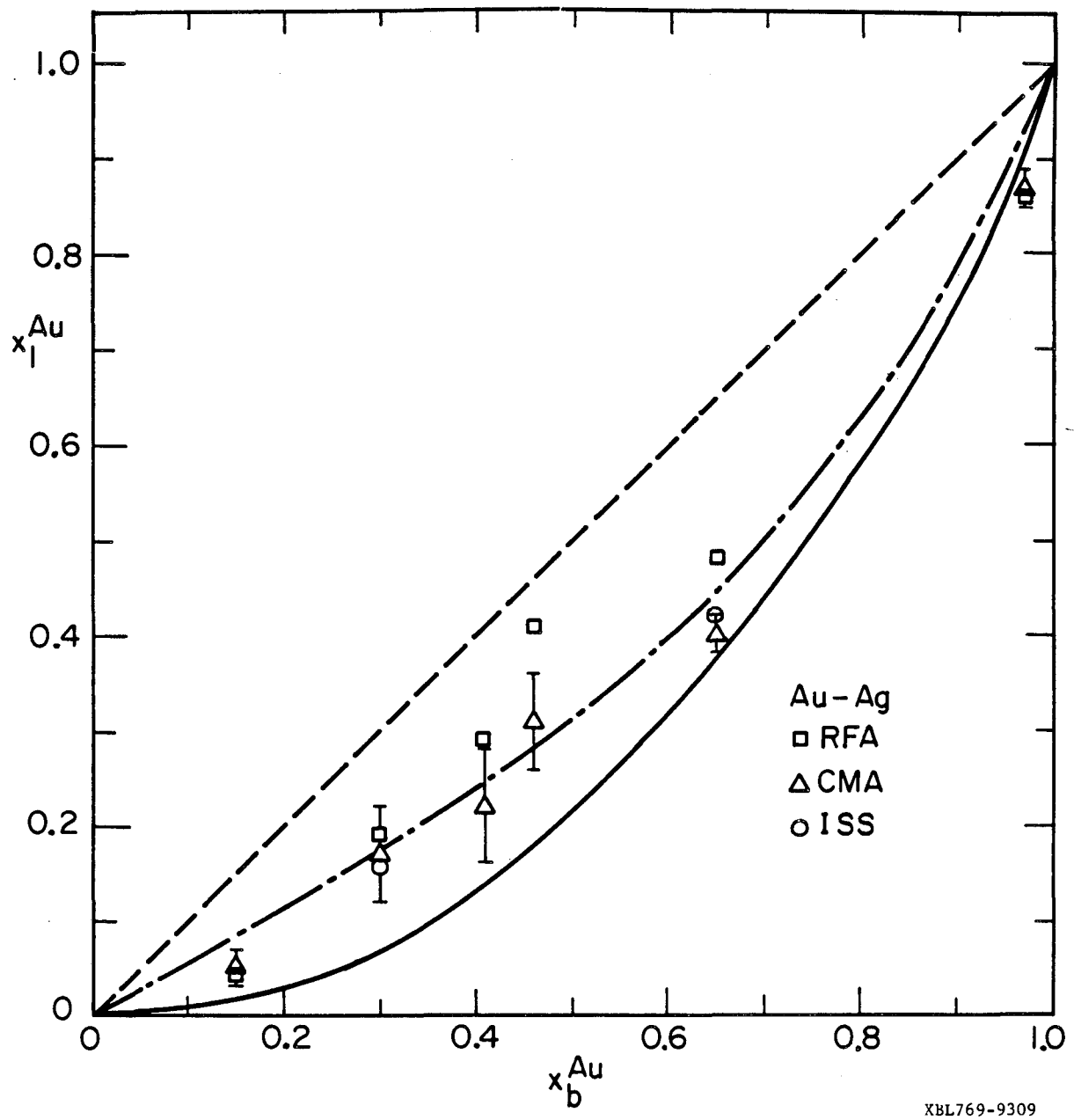


Fig. 3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0.8
0.6
0.4
0.2
0
x_l^{Au}
0
0.2
0.4
0.6
0.8
1.0
x_b^{Au}
Au-Ag
RFA
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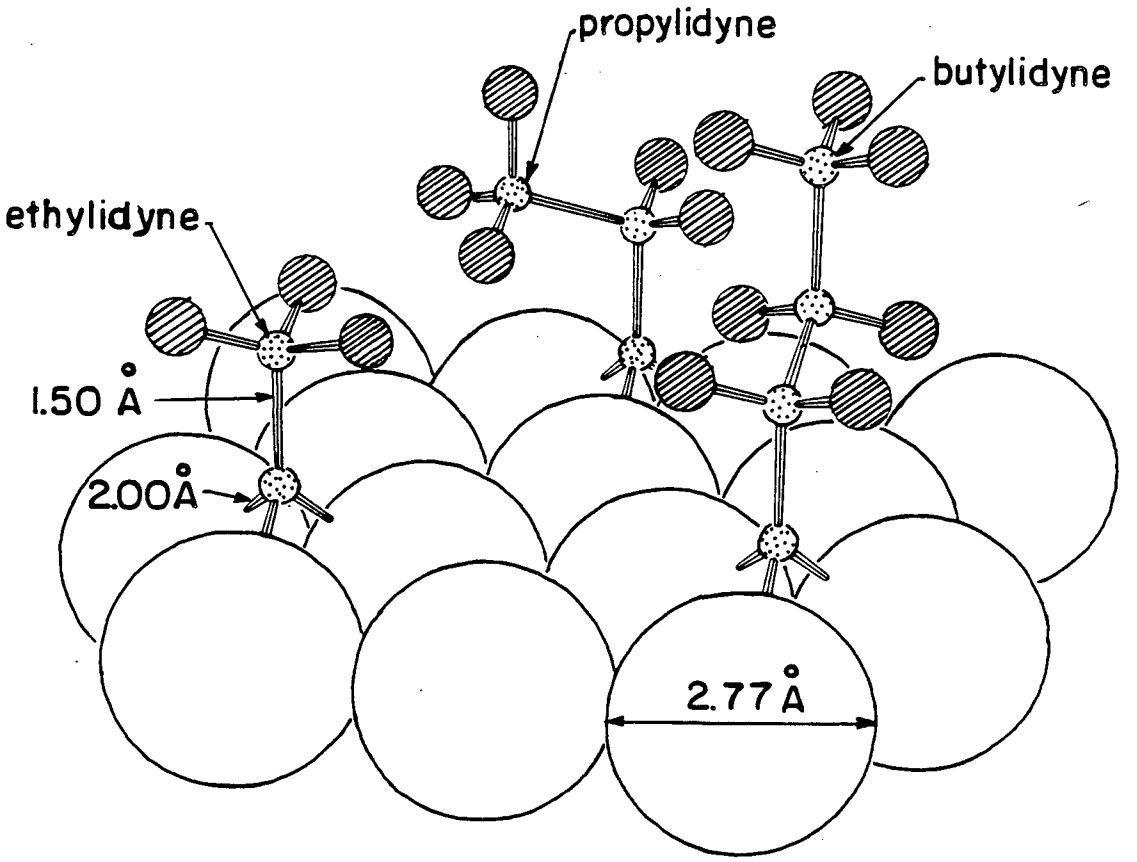
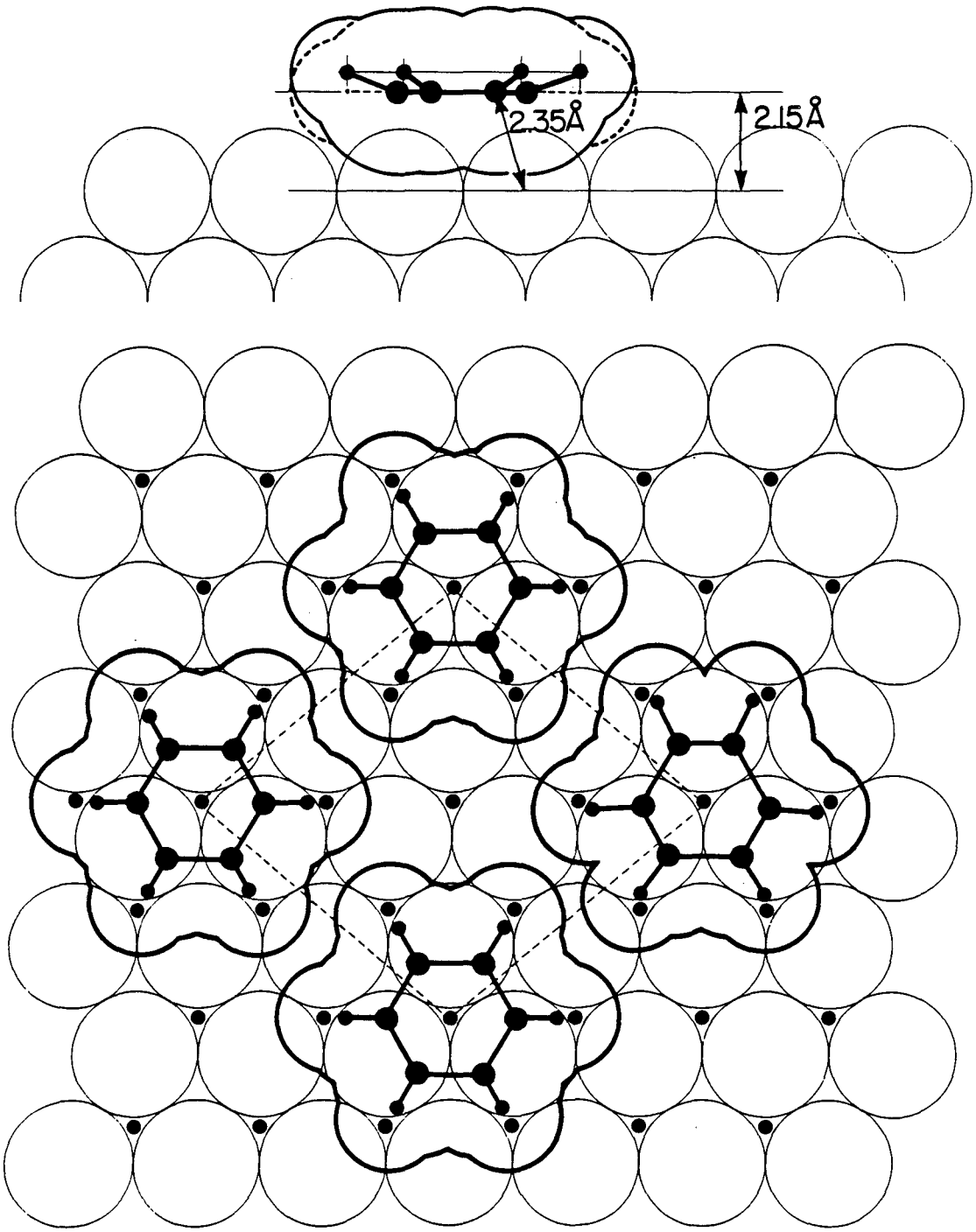
Fig. 4



Pt (111) + ethylidyne, propylidyne and butylidyne

XBL 8110-6882

Fig. 5



Rh(III)-$\begin{pmatrix} 3 & 1 \\ 1 & 3 \end{pmatrix}$ C_6H_6

XBL 835-198

Fig. 6

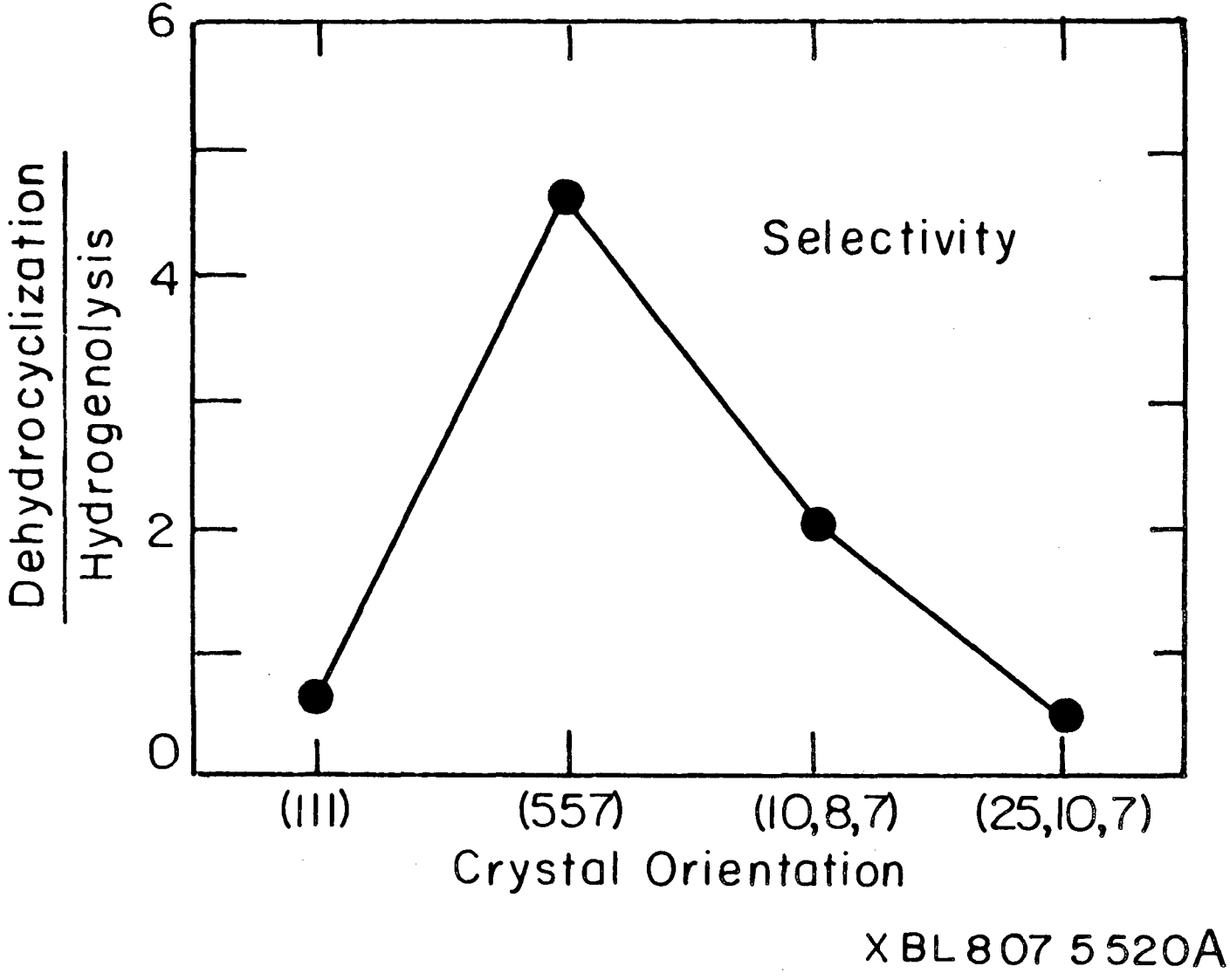
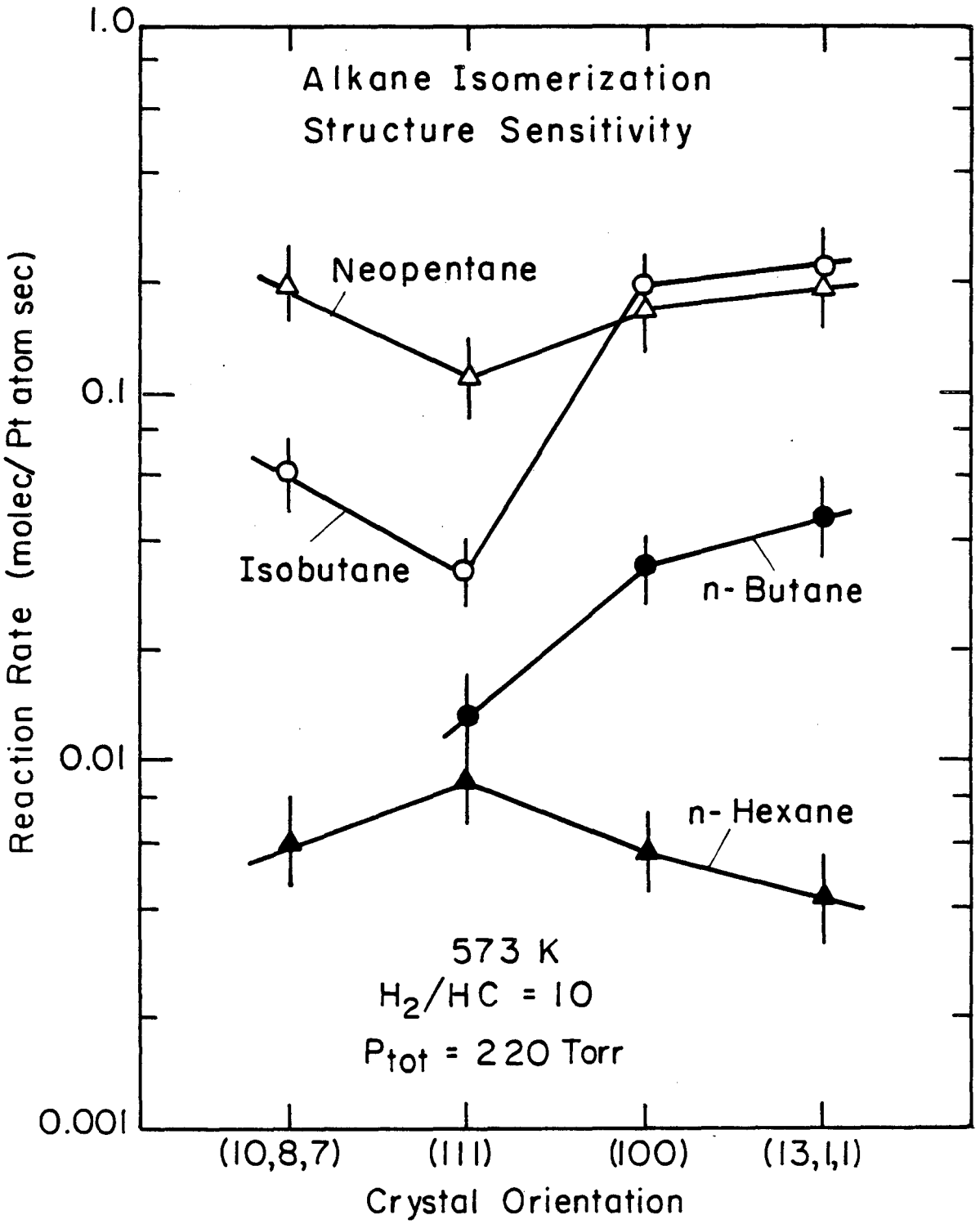

6
4
2
0
Dehydrocyclization / Hydrogenolysis
Selectivity
(111)
(557)
(10,8,7)
(25,10,7)
Crystal Orientation
XBL 807 5520A

Fig. 7



XBL816-5915

Fig. 8

MODEL FOR THE WORKING PLATINUM CATALYST

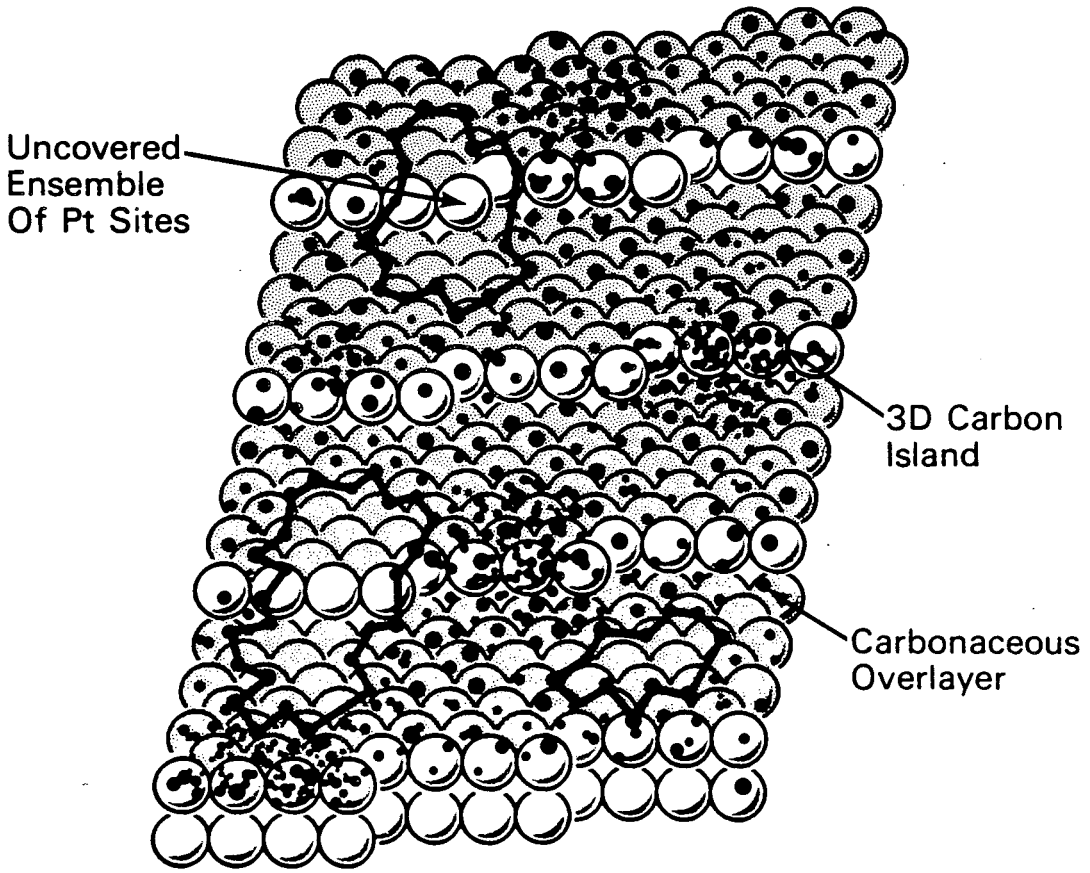
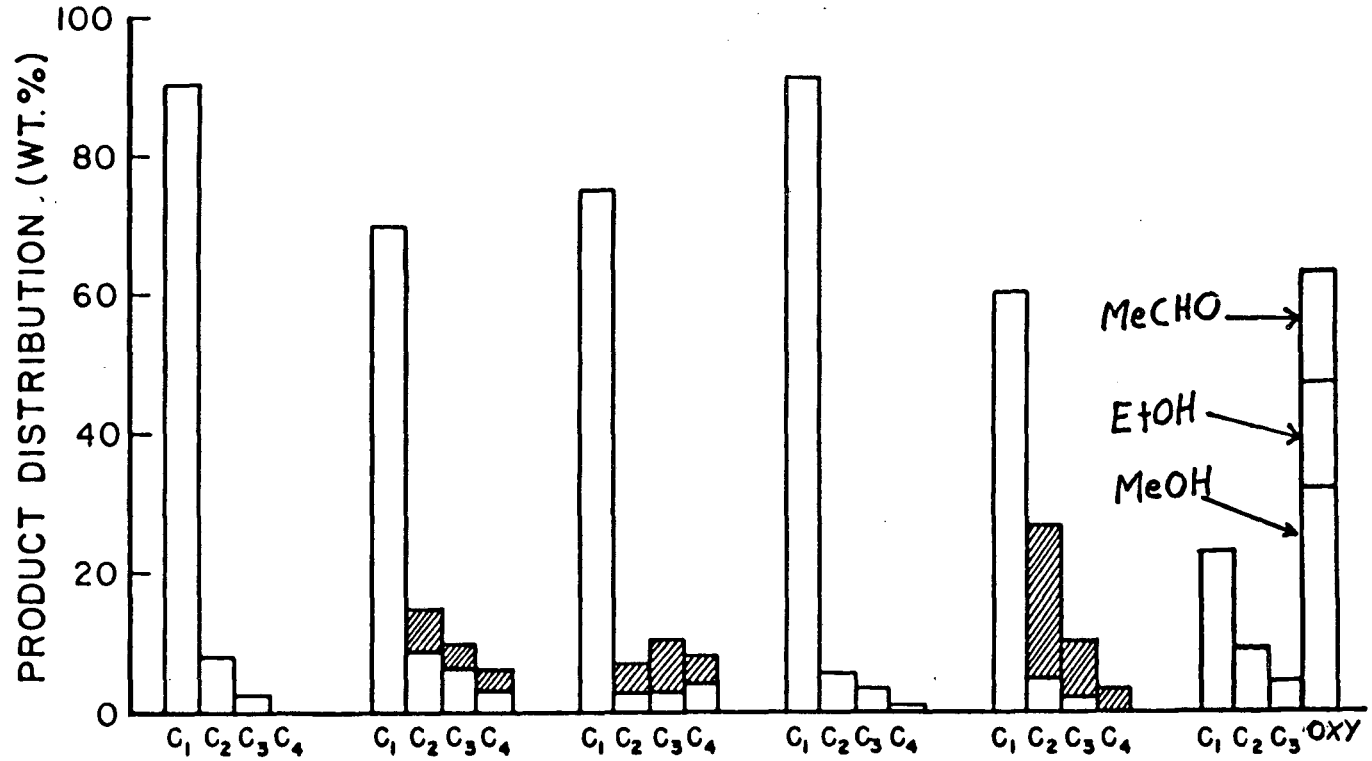


Fig. 9

Compound	Rh_{foil}	Na_2RhO_3	$TiRhO_3$	$CuRh_2O_4$	$FeRhO_3$	$LaRhO_3$
CH_4 Turnover Frequency	0.37	0.08	0.07	~0.001	0.03	0.06



XBL 832-8320

Fig. 10

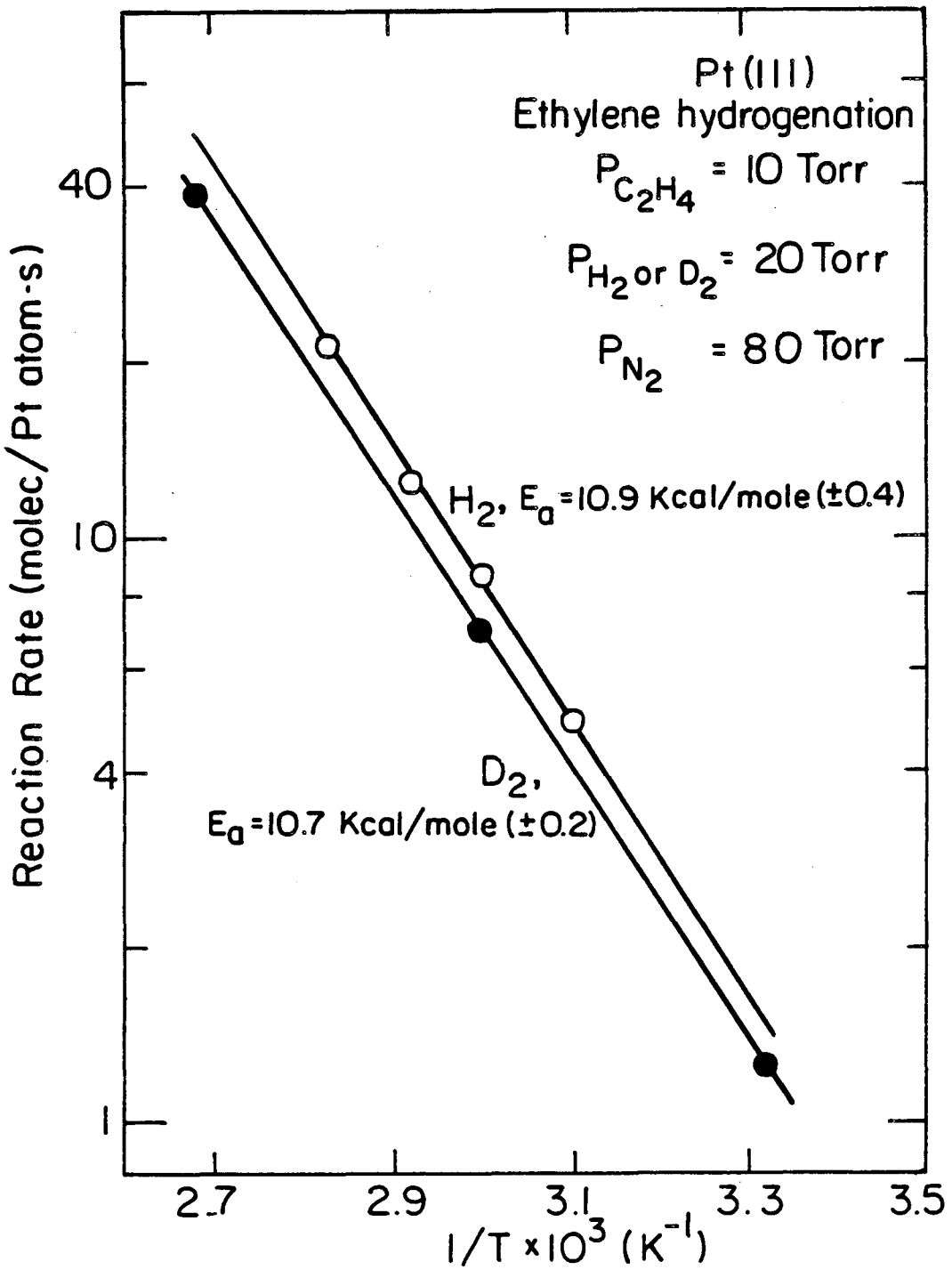
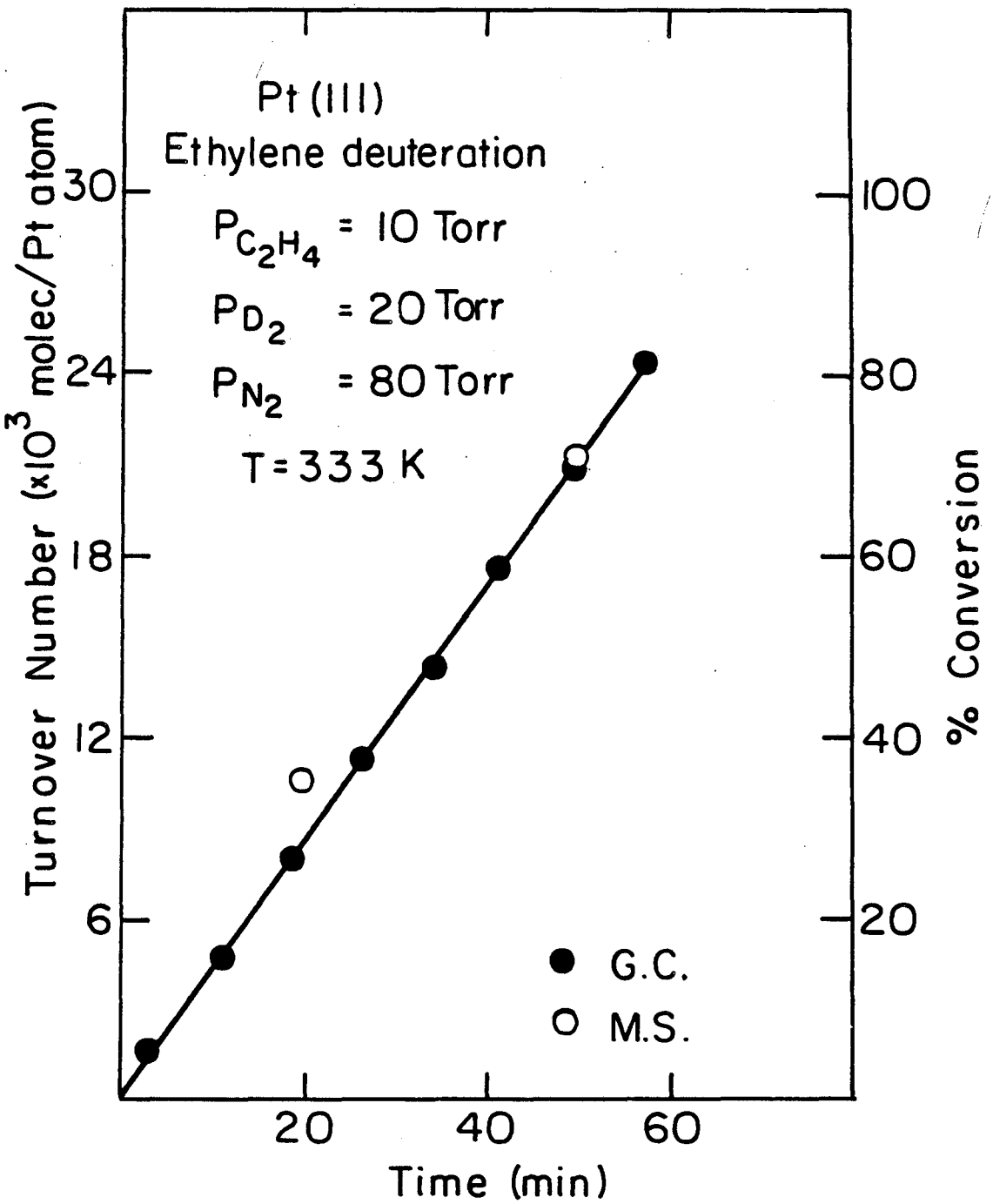

Pt(111)
Ethylene hydrogenation
$P_{C_2H_4}$ = 10 Torr
$P_{H_2 \text{ or } D_2}$ = 20 Torr
P_{N_2} = 80 Torr
H_2, E_a=10.9 Kcal/mole (±0.4)
D_2,
E_a=10.7 Kcal/mole (±0.2)
Reaction Rate (molec/Pt atom-s)
40
10
4
1
2.7
2.9
3.1
3.3
3.5
$1/T \times 10^3$ (K^{-1})
XBL 835-5637

Fig. 11



XBL 835-5636

Fig. 12

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