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Building of Complex Catalysts on Single Crystal Surfaces

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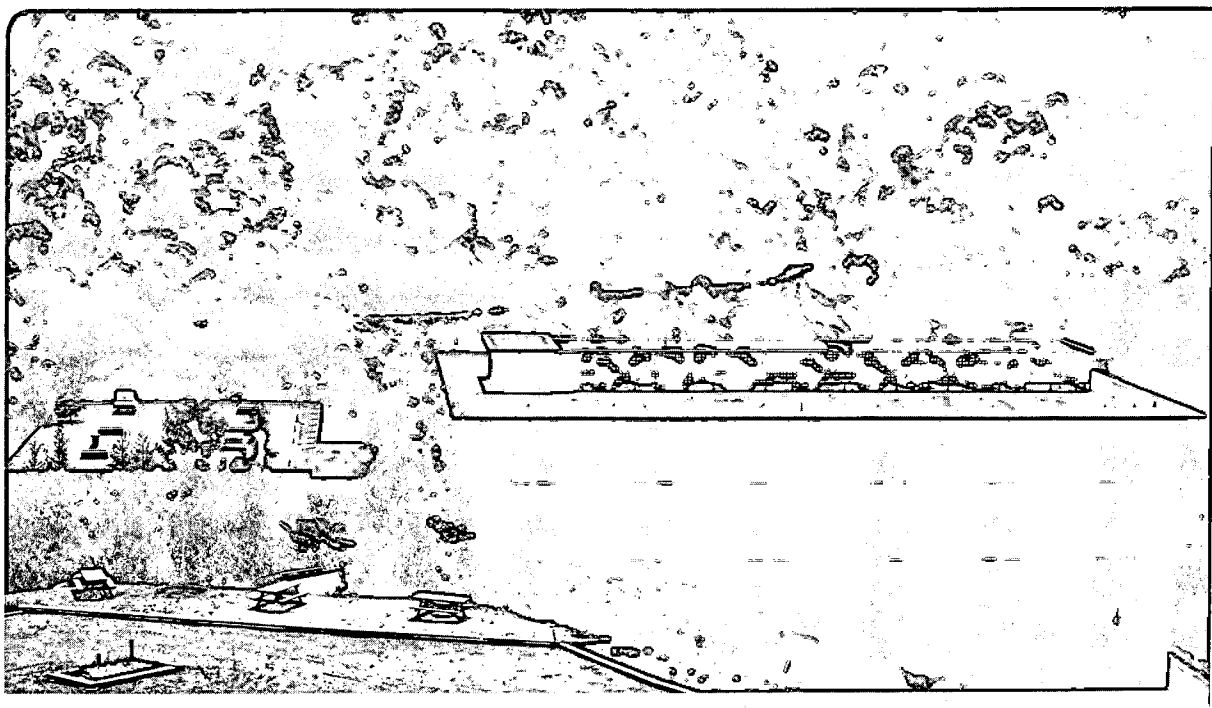
April 1991



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Building of Complex Catalysts on Single Crystal Surfaces

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Combined catalytic reaction and surface science studies using small area metal single crystal surfaces have shown these systems to be excellent model catalysts. In order to investigate more complex, multicomponent catalysts, other metals, oxides, chlorine, and sulfur were deposited from the vapor phase in controlled concentrations on the metal single crystals or polycrystalline foils to investigate their functions as structure or bonding modifiers. From studies of several of the complex catalyst systems (Pt/Au, Pt/Al_2O_3, Pt/Al_2O_3/Cl, Fe/Al_2O_3, Fe/Al_2O_3/K, Pt/Re, Pt/Re/S, Mo/S, Mo/Co/S), the molecular ingredients of their catalytic performance have been identified. These are the a) need for surface roughness; b) structural stabilization of rough surfaces; c) the presence of a strongly chemisorbed overlayer that causes surface restructuring; d) bonding modifier cooadsorbates; 3) active oxide-metal interfaces and f) active bimetallic interfaces.

Early studies in our laboratory indicated that single crystal surfaces of transition metals of about $1cm^2$ surface area have detectable turnover rates for several catalytic reactions to be considered as model catalyst systems [1]. A high pressure-low pressure apparatus was constructed [2] that permits surface characterization and preparation of single crystal surfaces in uhv and then their exposure to high pressure reaction conditions without contamination by ambient gases. Using this apparatus, catalytic reactions could be studied in batch or in flow modes in what amounts to a microreactor system as long as the turnover rates were greater than 10^{-4} molecule/surface site/second and the reactor walls remained inert to the reaction mixture. Studies of hydrocarbon conversion reactions on platinum single crystals revealed the importance of atomic steps and kinks at the surface to obtain higher rates and selectivity [3]. The ammonia synthesis was studied on iron crystal surfaces and orders of magnitude larger turnover rates were found for the (111) and (211) crystal faces (Fig. 1) than for the more close packed (110) and (100) surfaces [4]. Thus, the surface structure sensitivity of certain catalytic reactions was discovered or reproduced on these model single crystal catalyst surfaces.

However, catalysts that are used in the chemical technology are complex systems containing several additives. To explore the role of these "promoters", alumina was deposited on the iron crystal face from the vapor phase in well controlled concentrations and its role in ammonia synthesis has been explored [5].

Its structural promotion was due to its ability to facilitate the restructuring of iron to produce (111) crystal faces under ammonia synthesis conditions by forming an iron aluminate phase that acts as a substrate for the restructured iron (Fig. 2). Then the promoter role of potassium was explored by depositing known amounts of the metal on iron. Its major effect is to decrease the heat of adsorption of ammonia on the metal surface, thereby reducing its surface concentration during the reaction [6]. Since ammonia blocks some of the active sites for dinitrogen dissociation, the reduction of its surface concentration greatly increases the reaction rate of ammonia synthesis, especially close to equilibrium when there is a large concentration of ammonia present over the iron catalyst.

Potassium alters the pressure dependence of the reaction rate on ammonia and hydrogen and also aids the dissociation of dinitrogen on the less active iron surfaces. These investigations were extended to probe the combined effects of Al_2O_3 and K that were co-deposited in different sequences. It was discovered that the formation of KAl_2O_4 should be avoided; as it is unreactive and blocks the active iron surface [7].

Single Crystal or Small Area Surface Studies of Multicomponent Catalyst Systems

The studies mentioned above pointed the way to investigate other complex catalyst systems using model single crystal surfaces and then sequentially depositing on them the various promoters from the vapor phase in vacuum. This way the surface atomic structure of the transition metal catalyst, the concentration, and location of the various additives can all be controlled independently. This method of building complex catalyst systems is similar in concept to the method of building microelectronic circuitry on silicon single crystal or on other semiconductor single crystal surfaces. If the reaction is not so surface structure sensitive, transition metal foils or gold foils could be used as substrates as well.

Over the past ten years, we studied the following catalyst systems:

1) Hydrocarbon conversion over platinum catalyst systems [8]. (n-heptane, n-hexane, methyl-cyclopentane, cyclohexane, ethylene, benzene) (Figs. 3 and 4)

Substrate	Promoters
Platinum crystal faces	Rhenium Rhenium, Sulfur Potassium Gold Copper
Platinum foil	Alumina Alumina, Chlorine
Rhenium crystal face	Platinum Platinum, Sulfur

Alumina film deposited on gold foil	Platinum Platinum, Chlorine

2) Ammonia synthesis over iron catalyst systems [9]

Substrate	**Promoters**
Iron crystal faces	Alumina Potassium Alumina, Potassium

3) Hydrodesulfurization of tiophene over molybdenum catalyst systems [10] (Fig. 5)

Substrate	**Promoters**
Molybdenum crystal faces	Sulfur Cobalt Cobalt, Sulfur Carbon Cobalt, Carbon

4) CO, CO_2, Acetone hydrogenation over rhodium catalyst systems [11]

Substrate	**Promoters**
Rhodium foil	Titanium Oxide Vanadium Oxide

In addition, surface science studies have been completed on the Cu(110)/ZnO [12] (Fig. 6), Pt(111)/ZrO_2 [13], Pt(111/Fe_2O_3 [14] (Fig. 7) systems to lay the foundation for their future use in catalysis. Several reactions are also under study using small area single component model catalysts (NH_3 + NO, hydrogenation of propylnitrile, CO + O_2, H_2 + O_2) in preparation for their investigations on more complex catalyst systems.

What have we learned from the combined surface science and catalytic studies using these model catalyst systems? By investigating the roles of each component of the system, many of the molecular ingredients of heterogeneous catalysis could be identified. In the following, we will discuss these in some detail.

Ingredients of Complex Catalyst Systems

Rough surfaces are more active for catalysis. Stepped surfaces of platinum were more active for H_2/D_2 exchange (Table 1) and for most hydrocarbon conversion reactions than flat low Miller index close packed surfaces [15]. Stepped Ni surfaces dehydrogenate C_2H_4 at much lower temperatures (< 150 K) than the (111) face of Ni (≈ 230 K) [16] (Fig. 8). The more open (111) and (211) crystal faces of Fe are orders of magnitude more active for NH_3 synthesis than the close packed Fe(110) crystal face which showed no detectable reaction rate.

Surface science studies show that clean metal surfaces exhibit relaxation [17]; that is, the surface atoms move inward, closer to the second layer of atoms. The rougher, more open the surface is, the larger the relaxation [18]. Thus, surface atoms with less nearest neighbors relocate readily to optimize surface bonding depending on the changing chemical environment. If we assume that the magnitude of relaxation indicates flexible surface structural behavior, the more flexible is the surface to restructure according to the demands of the surface chemical

environment, the more reactive it will be. This may be the reason for using small clusters as catalysts as these systems have many low coordination surface atoms and, therefore, should restructure readily as the chemical environment changes.

The catalytically active surface is covered with a strongly chemisorbed overlayer. During hydrocarbon conversion reactions, the platinum or other transition metal surfaces are covered with a carbonaceous overlayer of average composition of CH [19]. During ammonia synthesis, the iron crystal faces are covered by chemisorbed N. The Mo surface is covered with a mixture of S and C during hydrodesulfurization [20]. Nevertheless, the reactions proceed at a steady state rate in the presence of these overlayers. ^{14}C and ^{35}S labeling studies indicate that these overlayers are stagnant; they exchange with the gas phase reactants at rates that are orders of magnitude slower than the turnover rates of the catalytic reactions. Thus, they do not seem to impede the reaction turnover while they do not participate as reaction intermediates.

There are two ways of rationalizing the role of these strongly chemisorbed species in catalysis. Chemisorption leads to restructuring of the substrate metal surface. Adsorbate induced restructuring has been observed for every system that has been studied by surface crystallography including C/Ni [21], S/Fe [22], H/Rh [23], O/Cu [24], C_2H_3/Rh [25] (Figs. 9a,b,c,d,e). During chemisorption, the metal atom relocates to optimize bonding with the chemisorbed species at the expense of the strength of the metal-metal bond. The more open the surface, the more marked is the restructuring. I would like to propose that the chemisorption induced restructuring creates the catalytically active sites as the strongly chemisorbed overlayer is formed. Thus the strongly chemisorbed overlayer is an important part of the catalyst system.

The other possible explanation is that the strongly chemisorbed overlayer passivates the metal surface and the reaction occurs at a few uncovered sites of very high activity. Both of these proposals lack experimental verifications. One should monitor the structure of the surface and the bonding of the adsorbates in a time resolved mode that is shorter than the turnover time for the catalytic reaction. This way the catalytic site concentration and its dynamical restructuring behavior could be monitored. Hopefully these types of studies will be carried out in the future in

There is experimental evidence that the catalyst surface restructuring occurs not only on the timescale of chemisorption but also on the timescale of catalytic reactions [26]. This is observed during CO oxidation that exhibits oscillatory reaction rates in certain regimes of partial pressures of the reactants and in certain temperature ranges. The oscillation is due to two branches of this reaction, one for the oxygen rich surface, the other for the CO rich surface. Surface restructuring either induced by surface phase transformations or periodic partial oxidation and reduction of the metal surface has been detected.

High reactivity of oxide-metal interfaces. Depending on the oxide support, the high surface area transition metal catalyst can exhibit orders of magnitude variations of the reaction rates for the same reaction. This is shown for CH_4 formation [27] from CO and H_2 for Ni in Fig. 10. Recent studies indicate that TiO_2 is capable of increasing the activity of many transition metals for this reaction. Figure 11 shows the CH_4 formation rate from CO_2 and H_2 as a function of TiO_2 coverage [28]. The rate is at a maximum at about 50% oxide coverage and about 14 times greater than on the clean metal. TiO_x is unreactive and thus the oxide-metal interface must be responsible for the high reaction rates. There are several oxide-metal interfaces that exhibit similar large increases of activity as compared to the metal alone.

Recent surface science studies using scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) reveal that the oxide is somewhat reduced at the oxide-metal interface and Ti^{3+} ions have been detected for the TiO_2-metal systems. One possible explanation of the increased activity is the roughening of the metal at the interface that permits more facile adsorbate induced restructuring and thereby increased turnover rates. Again, time resolved studies of the dynamical changes of surface structure at the oxide-metal interface should help to verify the reasons for their uniquely high catalytic activities.

High reactivity of bimetallic systems. When gold was added to a Pd catalyst used for the H_2/O_2 reaction to produce water, the reaction rate increased 50-fold (Fig. 12) at a certain gold concentration [29]. Gold itself is a poor catalyst for this reaction. Enhancement of hydrocarbon conversion rates of platinum by the addition of gold were also reported from our laboratory (Fig. 13) using model single crystal systems [30]. There are many bimetallic catalyst systems Pt/Re, Os/Cu, that show much enhanced reactivity by the addition of a second inactive metal as compared to the turnover rate of the active metal component.

Again, we suggest roughening of the active metal at the bimetalic interfaces due to decreased coordination. This way its restructuring rate can be increased giving rise to higher catalytic turnover rates.

Coadsorbed bonding modifiers and structure modifiers. Increasing the coverage of a given chemisorbed atom or molecule usually leads to a decrease in its heat of adsorption [31]. This is due to repulsive interactions among the adsorbates (Fig. 14). When two different species are coadsorbed, one an electron donor and the other an electron acceptor to the transition metal substrate, the molecules order to form structures in which the molecules alternate [32]. One of these is shown for C_2H_3 and CO on Rh(111) (Fig. 15). Such a packing indicates an attractive interaction between the coadsorbates. Donor acceptor interaction appears attractive on transition metal surfaces, while the coadsorption of two donors or two acceptors leads to surface phase separation and island formation indicating repulsive interactions.

Alkali metal atoms are electron donors to transition metal surfaces. When coadsorbed with reactants that are electron acceptors, they interact to increase the heat of adsorption of the reactant. This is the case when K is used as a promoter in CO hydrogenation. K increases the heat of adsorption of CO thereby increasing it dissociation probability [33]. CO dissociation is one of the elementary steps for this catalytic reaction.

When K is used as a promoter during NH_3 synthesis, it reduces the heat of adsorption of ammonia, another electron donor on the Fe surface. Thus, this donor-donor repulsive interaction reduces the NH_3 reaction product surface concentration thereby reducing product poisoning in this catalytic reaction.

Chlorine is an electron acceptor and its promoter action may be associated with this property. However, surface science studies have not been used to investigate the effect of chlorine on other coadsorbed molecules as yet.

In all these descriptions of coadsorption, we neglect the possibility of the restructuring effects due to alkali-metals or to other promoter additives. There is evidence that such restructuring does occur on Fe_2O_3 (Fig. 16) and possibly for other catalyst surfaces as well [34]. Of course, Al_2O_3 on Fe exerts its promoter influence by restructuring the transition metal. Structure modifier and bonding modifier promoters may not be readily separated into two distinct classes.

There are adsorbate promoters that block sites, thereby deactivating it for a given undesirable or desirable reaction. In the first case, such a blocking adsorbate

is a promoter; in the second it is a poison. Sulfur is often used as an inhibitor of hydrogenolysis but it can also readily poison transition metal surfaces both by blocking active sites and by restructuring the surface.

Future Diresctions of Research Using Model Catalyst Systems

We identified several molecular ingredients of heterogeneous catalysis using model low surface area single crystal based complex catalyst systems. There are instrumentation limitations to explore in a time resolved way the dynamical changes that occur in the surface chemical bonds on both sides of the interface, the adsorbate and the substrate sides. There is increasing evidence of dynamical restructuring of surfaces during chemisorption, catalytic reactions, or longer timescales. We need time resolved techniques that can monitor these changes on a timescale that is short compared to the catalytic turnover times and can be utilized at high pressures.

We should explore the molecular ingredients of reactions that occur at solid-liquid interfaces and near room temperatures so that we can develop correlations between heterogeneous and biological catalysis.

Finally, new methods should be explored to develop model complex catalyst systems. There is evidence that ion sputtering deposition can produce thin films of chemically active alumina silicates [35]. It is hoped that many innovative approaches will be used to explore the molecular ingredients of important catalysts of increasing complexity.

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TABLE 1

Structure sensitivity of H_2/D_2 Exchange at Low Pressures ($\approx 10^{-6}$ torr).

	reaction probability
Stepped Pt(332)	0.9
Flat Pt(111)	$\approx 10^{-1}$
"Defect free" Pt(111)	$\leq 10^{-3}$

Figure 1. Rates of ammonia synthesis on various single crystal surfaces of iron.

Figure 2. A schematic diagram indicating the formation of iron aluminate on iron surfaces by the interaction of alumina islands with iron and the growth of iron(111) and (211) surfaces of iron during ammonia synthesis on these surfaces.

Figure 3. Preparation of Pt/Re/S model catalysts.

Figure 4. Preparation of model Pt-AlO_x-Cl catalysts.

Figure 5. Model Co-Mo-S surfaces for hydrodesulfurization.

Figure 6. Model Cu-ZnO_x surfaces for studies of methanol synthesis from carbon monoxide and hydrogen.

Figure 7. Preparation of ordered metal oxide thin films including iron oxide and zirconium oxide.

Figure 8. The composition of ethylene on the (111) (110) and the stepped single crystal surfaces of nickle.

Figure 9a. The carbon adsorption induced restructuring of the Ni(100) crystal face.

Figure 9b. The sulfur adsorption induced restructuring of the Fe(111) crystal face.

Figure 9c. The hydrogen adsorption induced restructuring of the Rh(110) crystal face.

Figure 9d. The oxygen chemisorption induced restructuring of the Cu(110) crystal face.

Figure 9e. The ethylene adsorption induced restructuring of the Rh(111) crystal face.

Figure 10. Effect of various supports on CO hydrogenation over Ni catalysts.

Figure 11. The rate of methane formation from carbon dioxide and hydrogen as a function of titania coverage over rhodium.

Figure 12. The rate of formation of water from hydrogen and oxygen over palladium as a function of addition of gold.

Figure 13a. The total conversion of n-hexane in the presence of hydrogen over platinum(111) and (100) single crystal surfaces as a function of the addition of gold coverage.

Figure 13b. The rate of cyclohexane dehydrogenation to benzene over platinum(111) crystal faces as a function of gold coverage.

Figure 14. The heat of adsorption of potassium on rhodium as a function of potassium coverage.

Figure 15. The coadsorbed surface structure of carbon monoxide and ethylidyne on the Rh(111) crystal face.

Figure 16. Model for alkali induced restructuring of one monolayer of FeO_x on Pt(111).

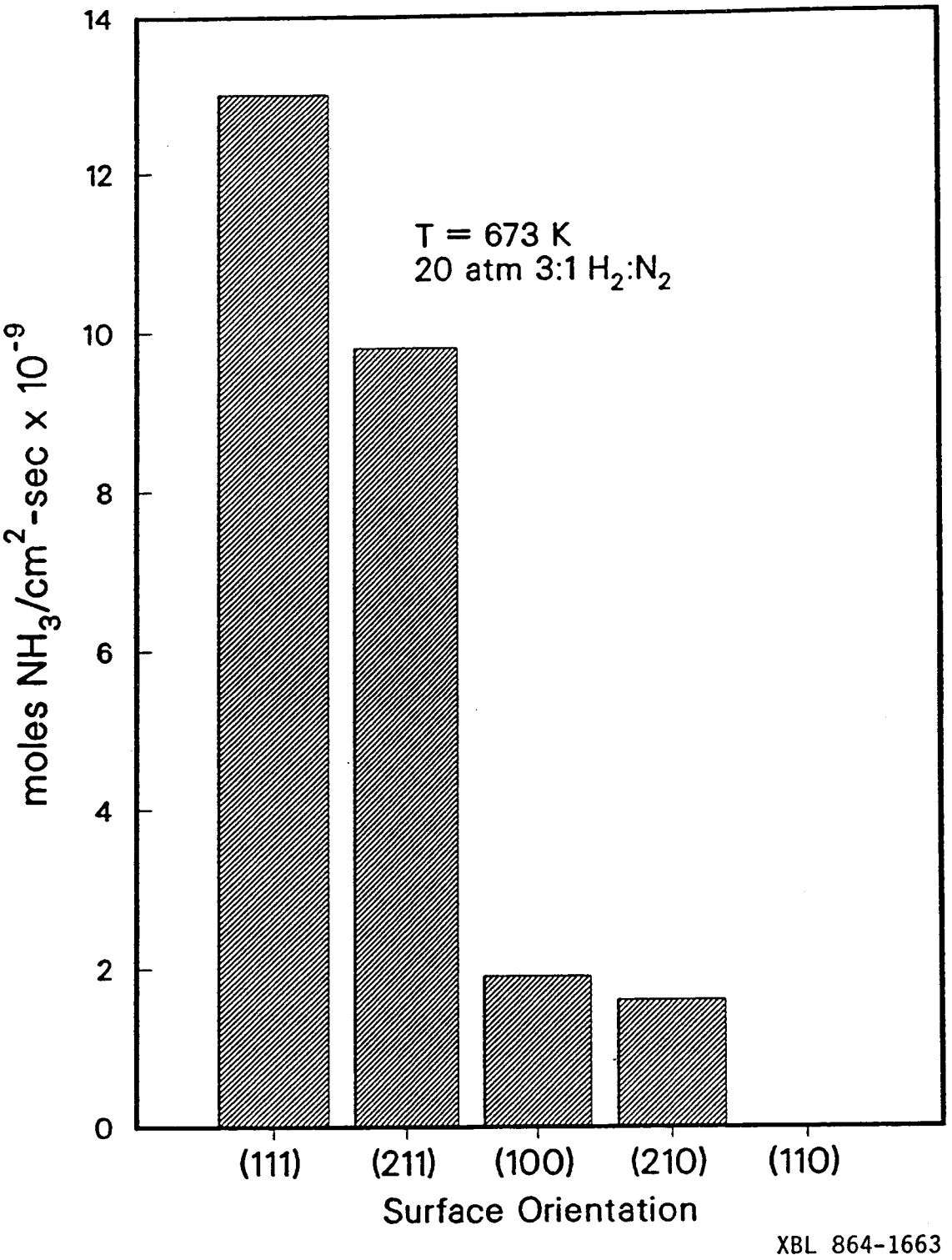
14
12
10
8
6
4
2
0
moles NH_3/cm^2-sec x 10^{-9}
T = 673 K
20 atm 3:1 H_2:N_2
(111)
(211)
(100)
(210)
(110)
Surface Orientation
XBL 864-1663

Fig. 1

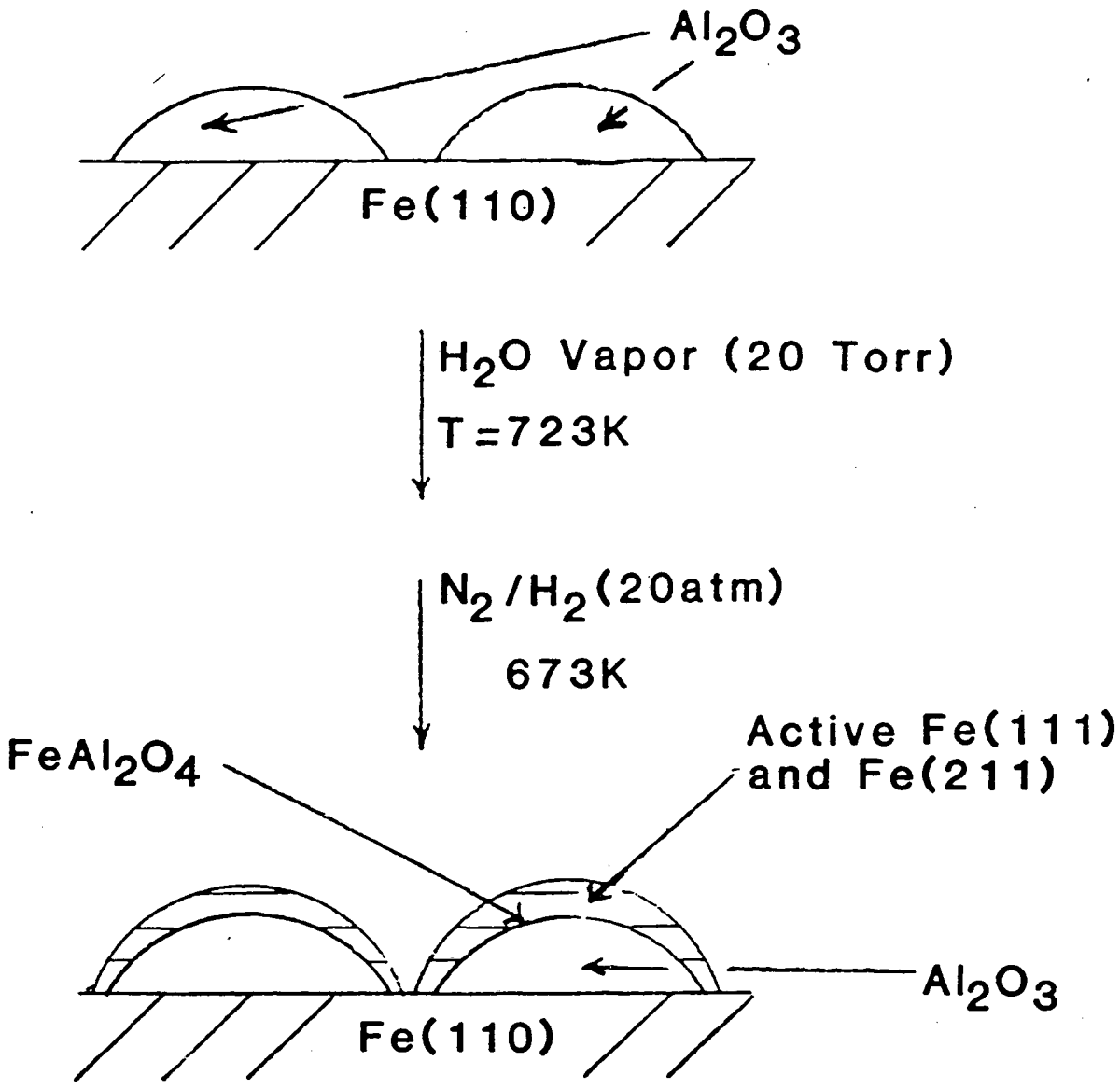

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Fig. 2

Preparation of Pt/Re/S Model Catalysts

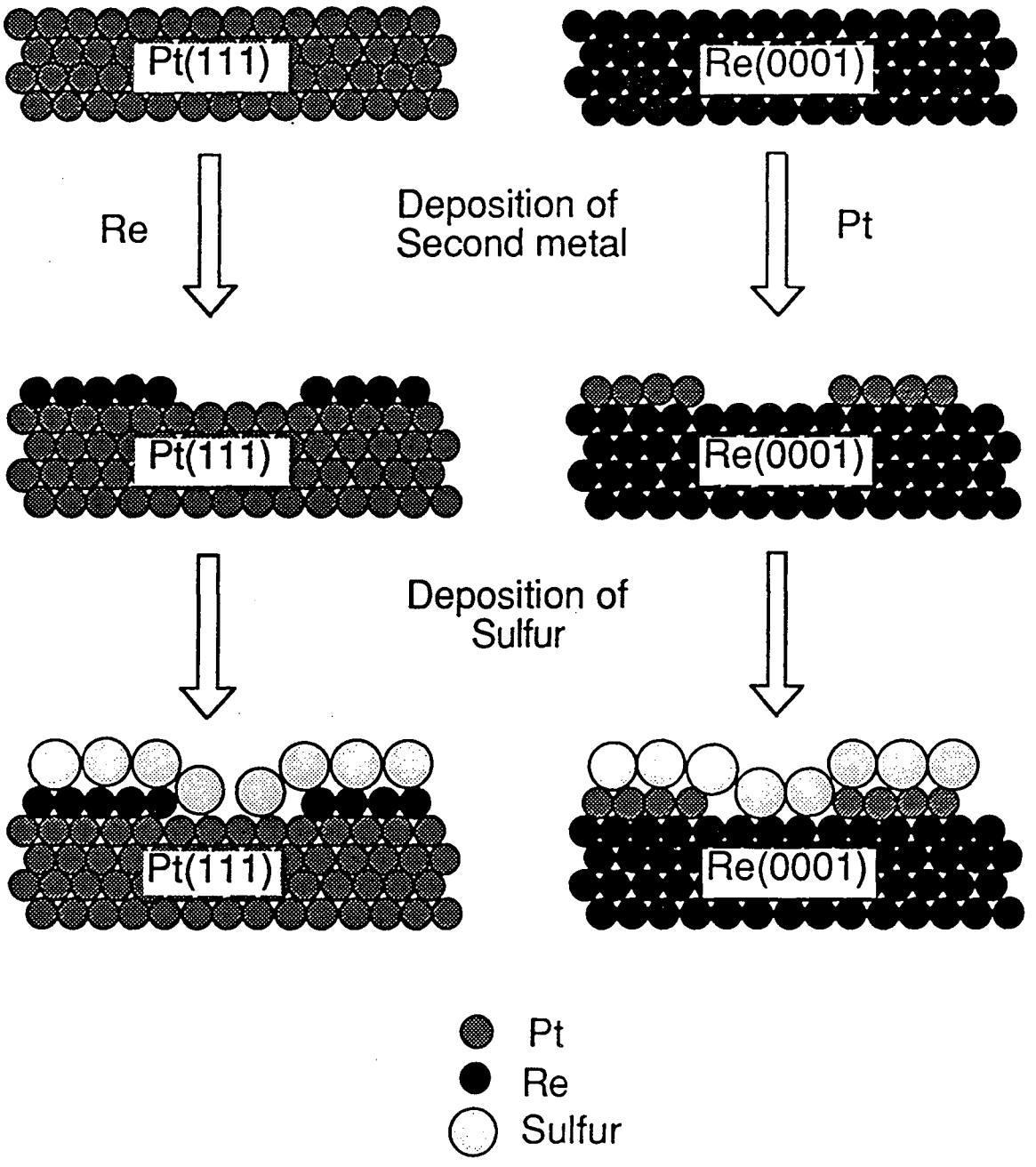

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Fig. 3

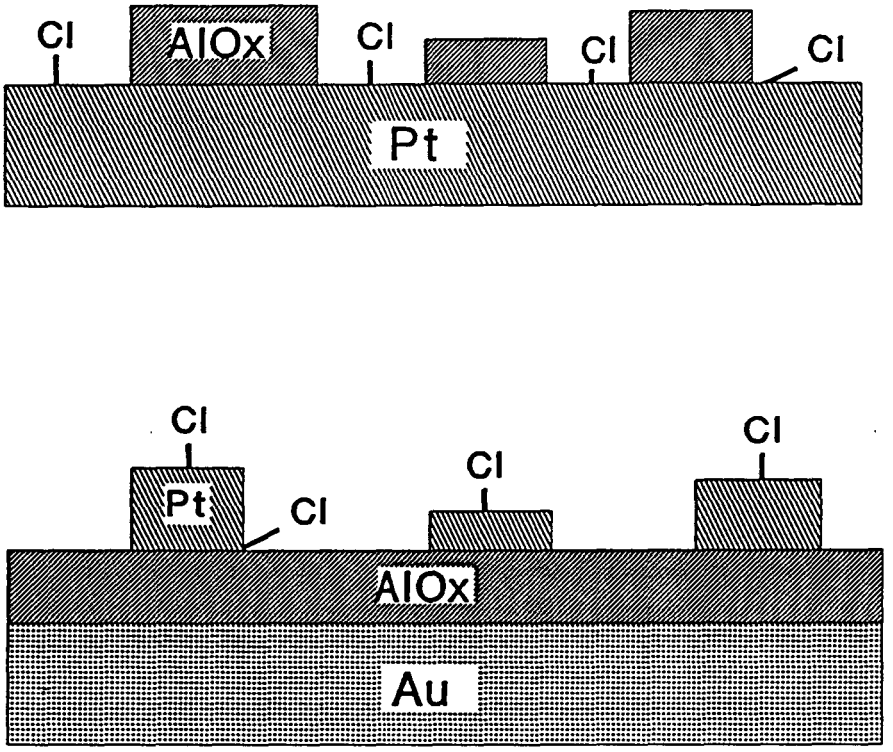

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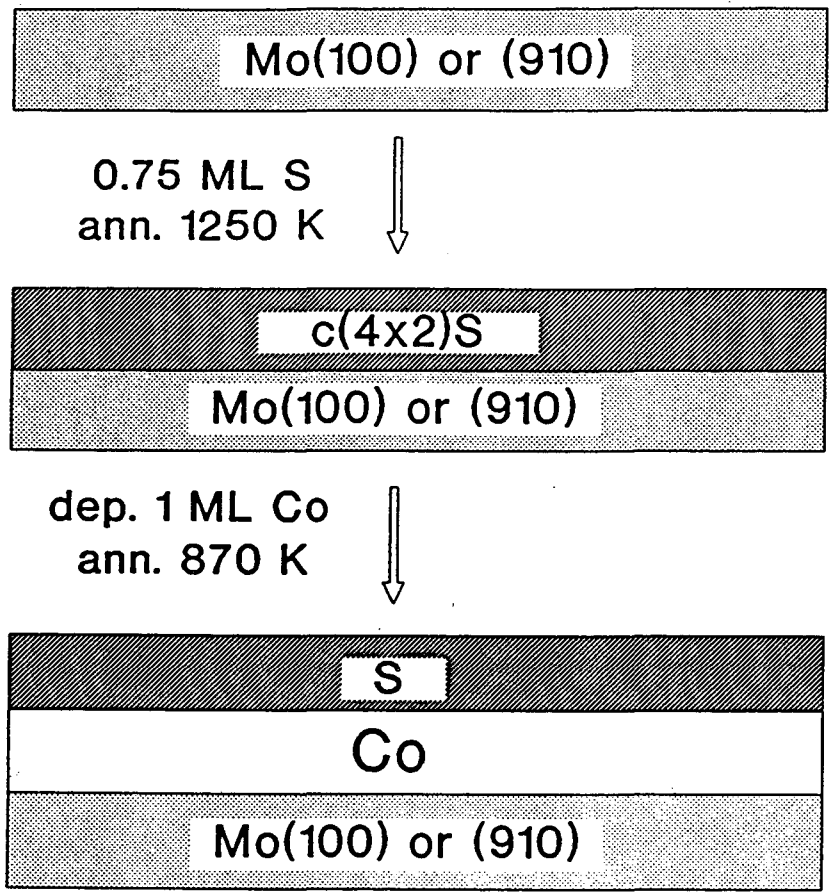
Fig. 4

Model Co-Mo-S Surfaces for HDS



(3x1) surface structure

S segregates on top of Co

$$C_4H_4S + H_2 \xrightarrow{613\ K} C_4H_y + H_2S$$

XBL 9010-3356

Fig. 5

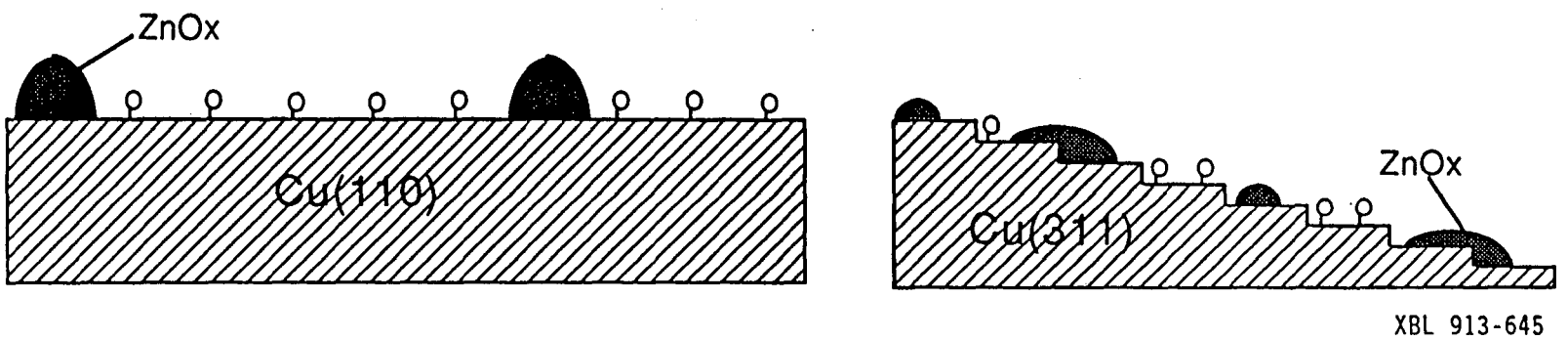
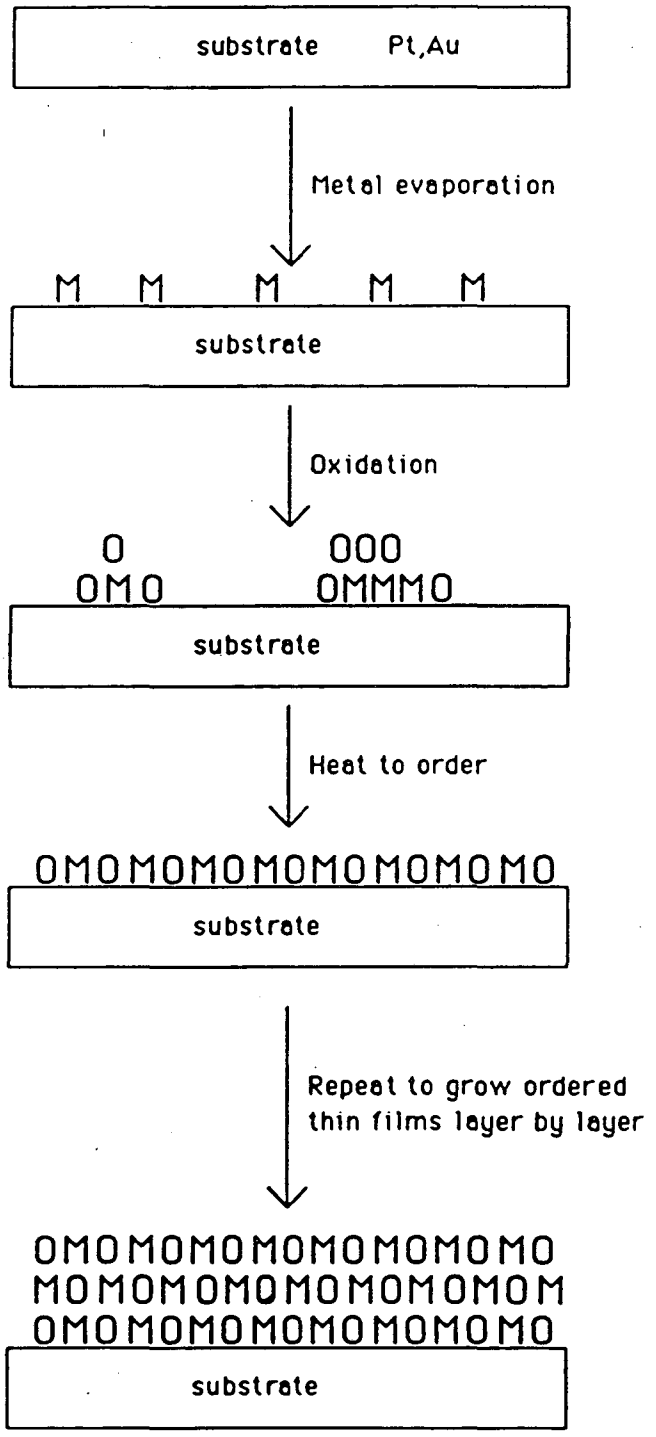


Fig. 6

Preparation of Ordered Metal Oxide Thin Films



XBL 918-1688

Fig. 7

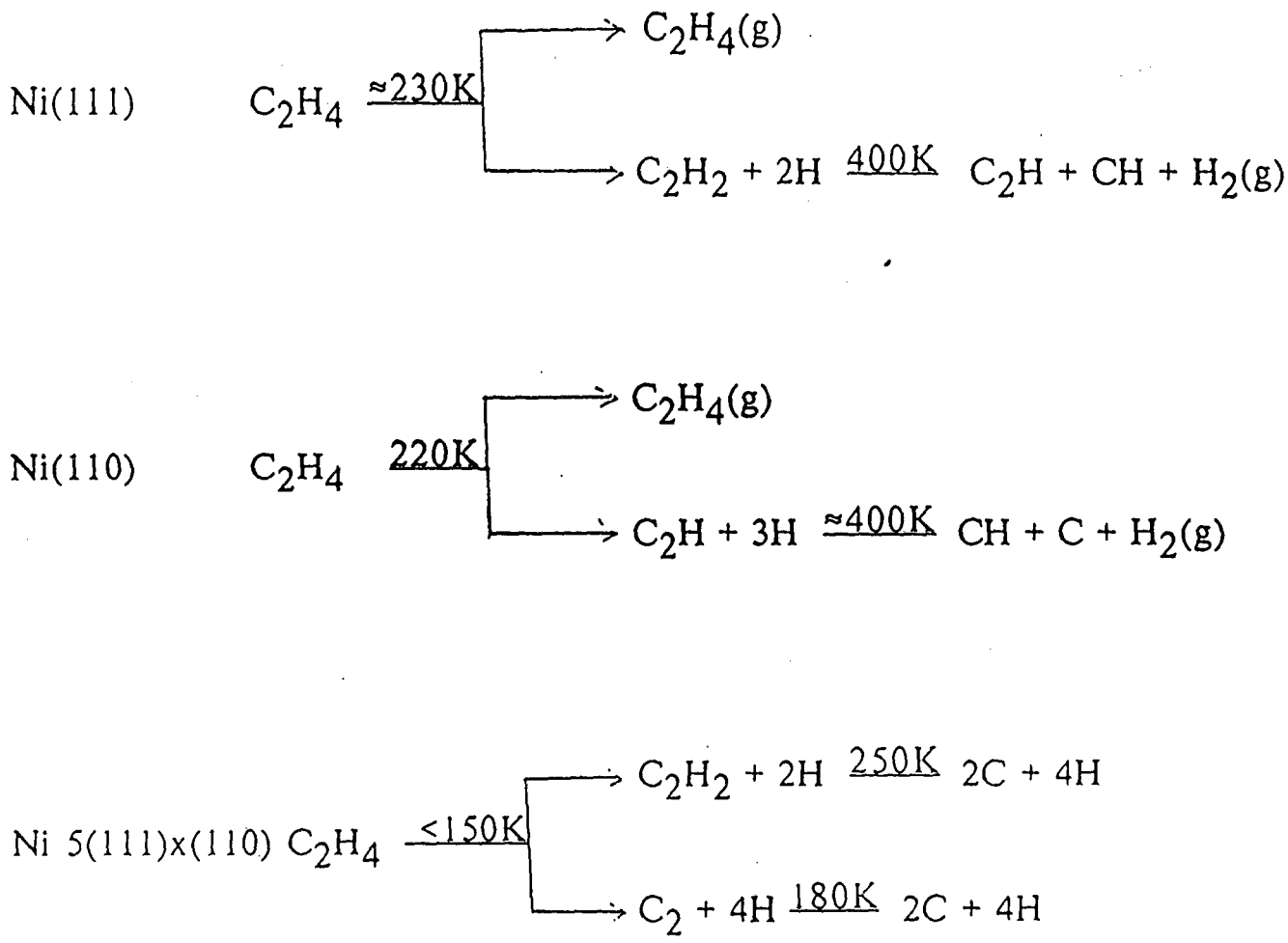

Ni(111)
C2H4
≈230K
C2H4(g)
C2H2 + 2H
400K
C2H + CH + H2(g)
Ni(110)
C2H4
220K
C2H4(g)
C2H + 3H
≈400K
CH + C + H2(g)
Ni 5(111)x(110) C2H4
<150K
C2H2 + 2H
250K
2C + 4H
C2 + 4H
180K
2C + 4H

Fig. 8

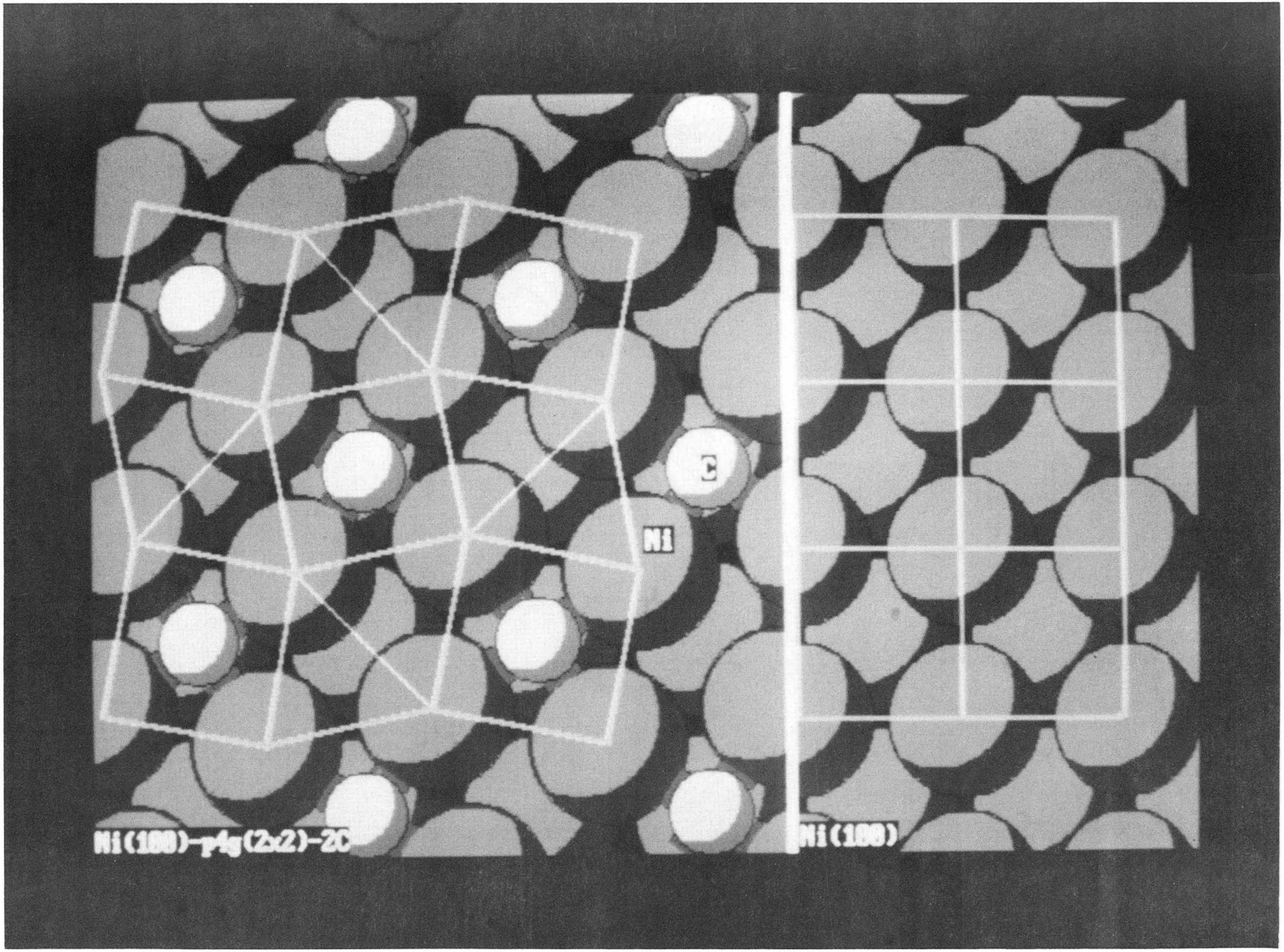


Fig. 9a

CBB 915-3852

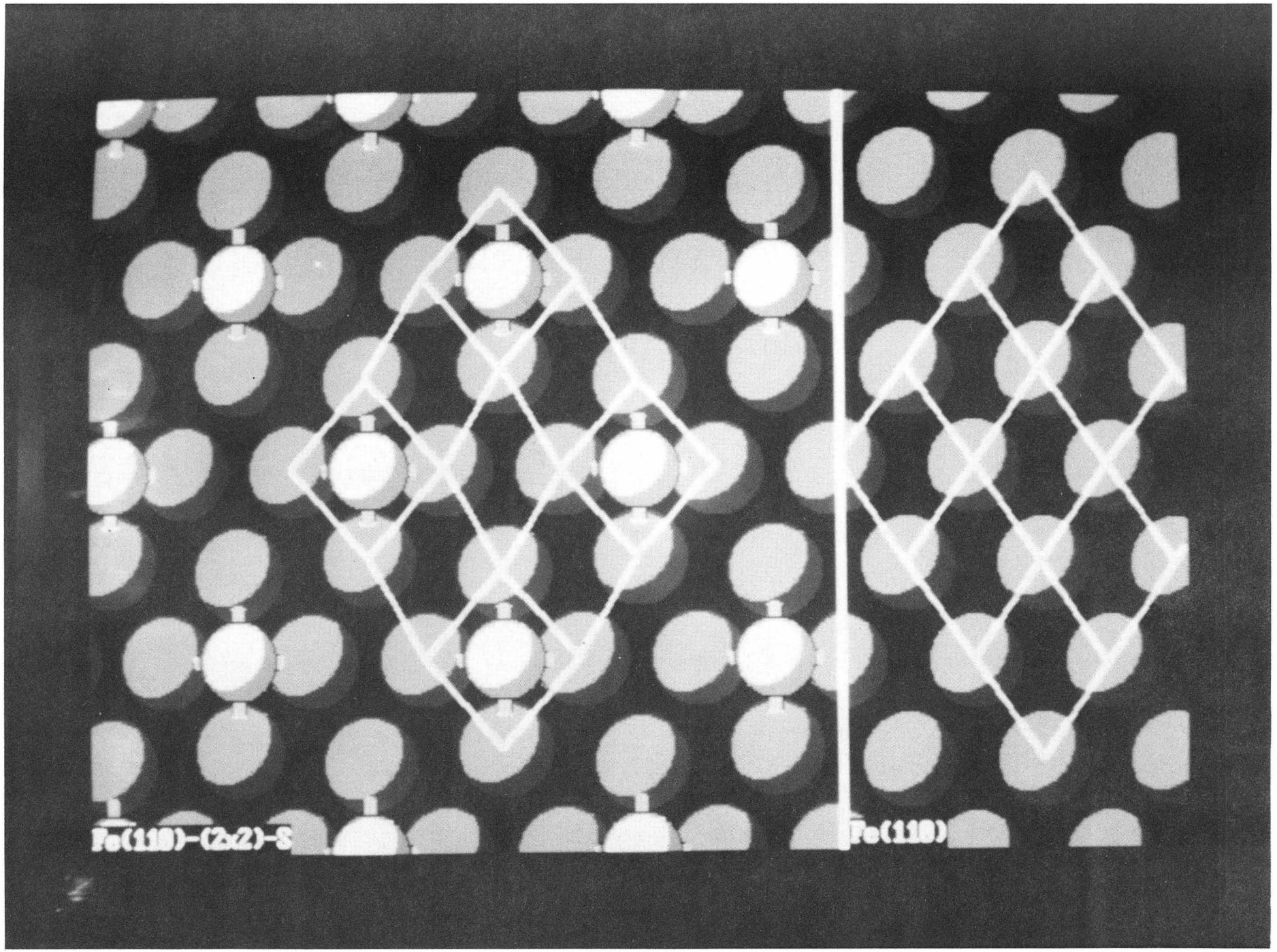
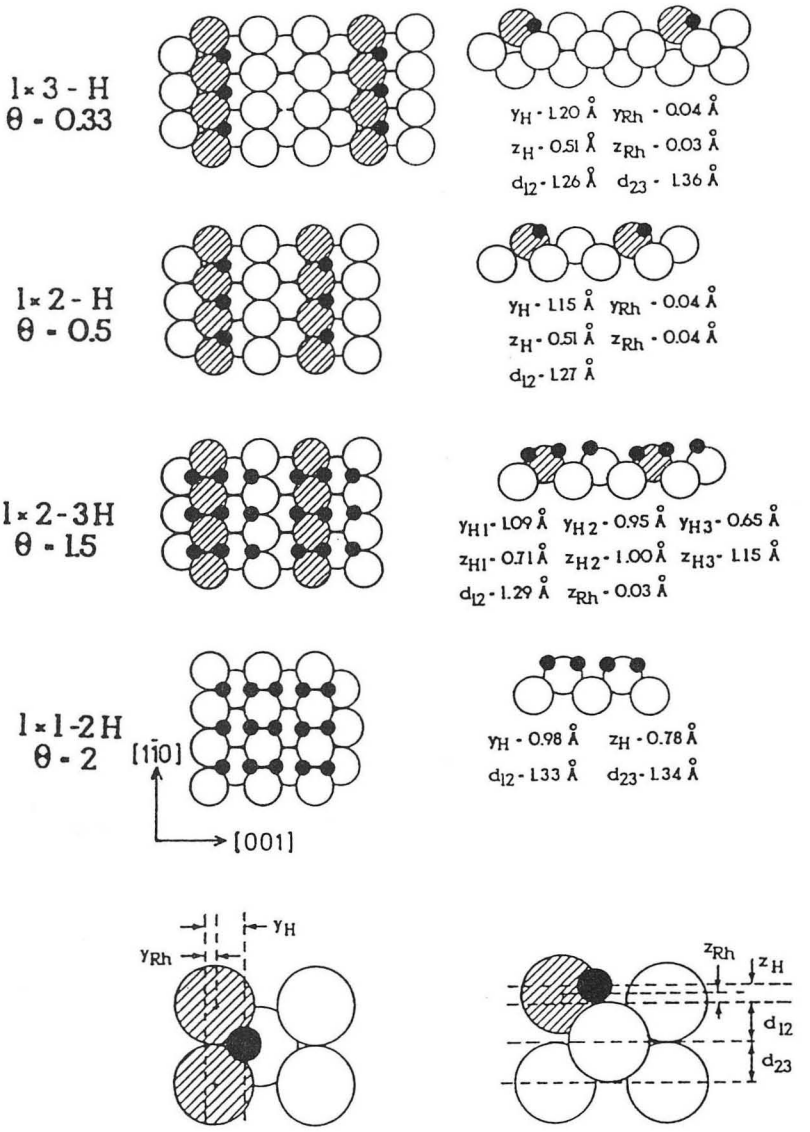


Fig. 9b

CBB 915-3850

H/Rh(110)

W.Nichtl-Pecher, W.Oed, H.Landskron, K.Heinz and K.Müller, Vacuum 41 (1990) 297



Real space configuration of the Rh(110) surface for different hydrogen coverages. Shaded Rh atoms represent the buckling in the first Rh layer.

XBL 915-1051

Fig. 9c

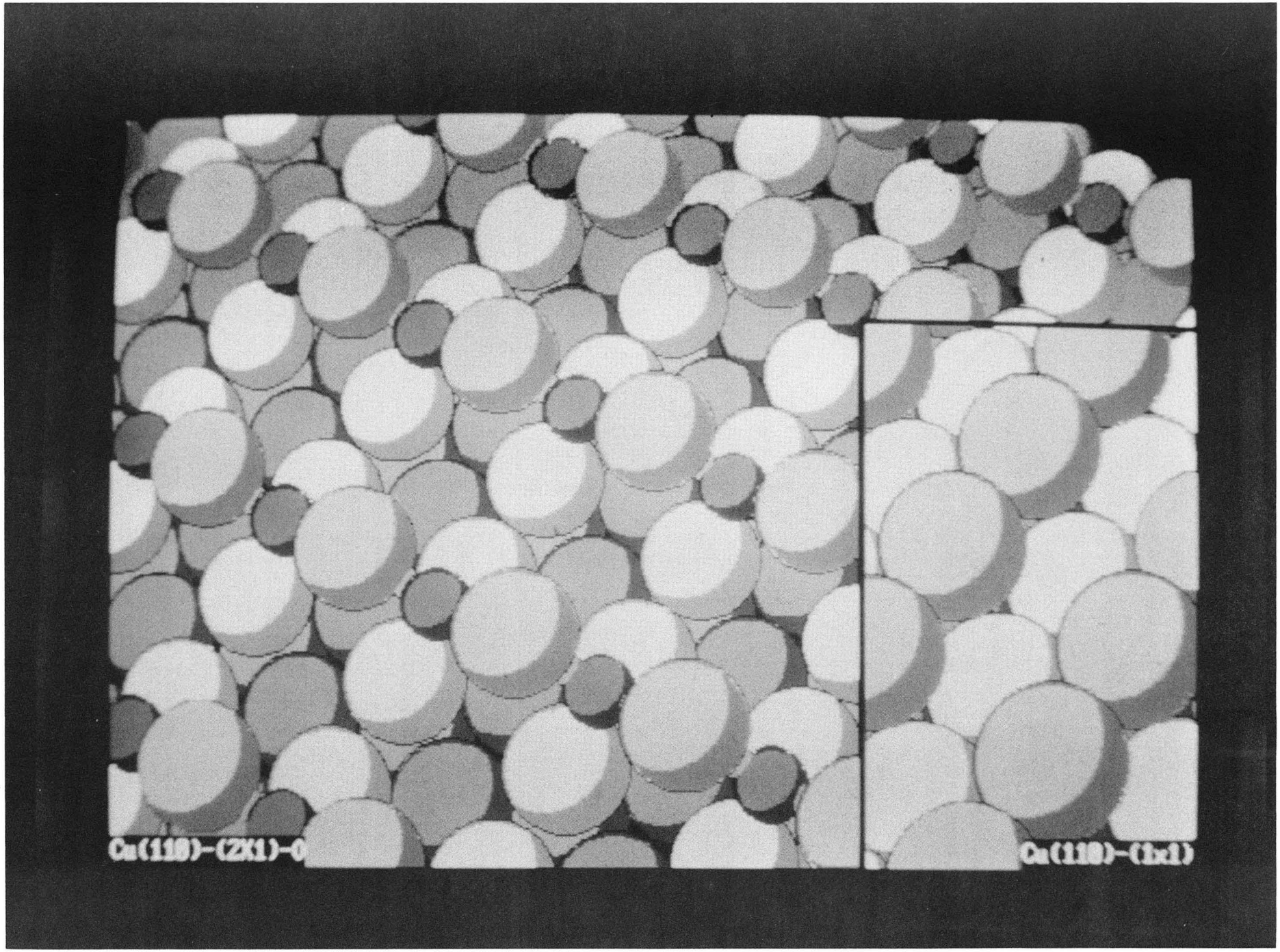


Fig. 9d

CBB 915-3854

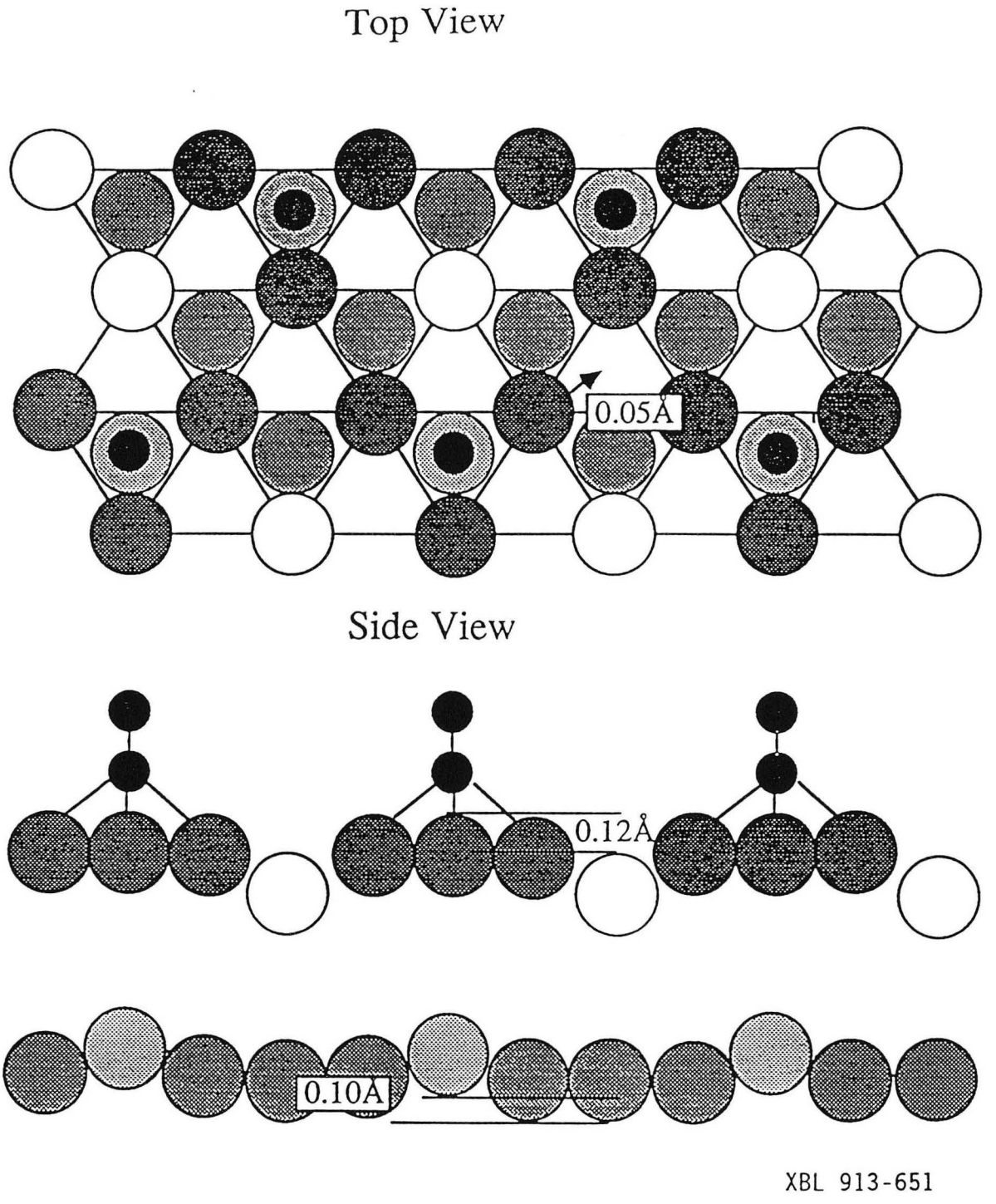


Fig. 9e

Effect of Support on CO Hydrogenation over Ni Catalysts

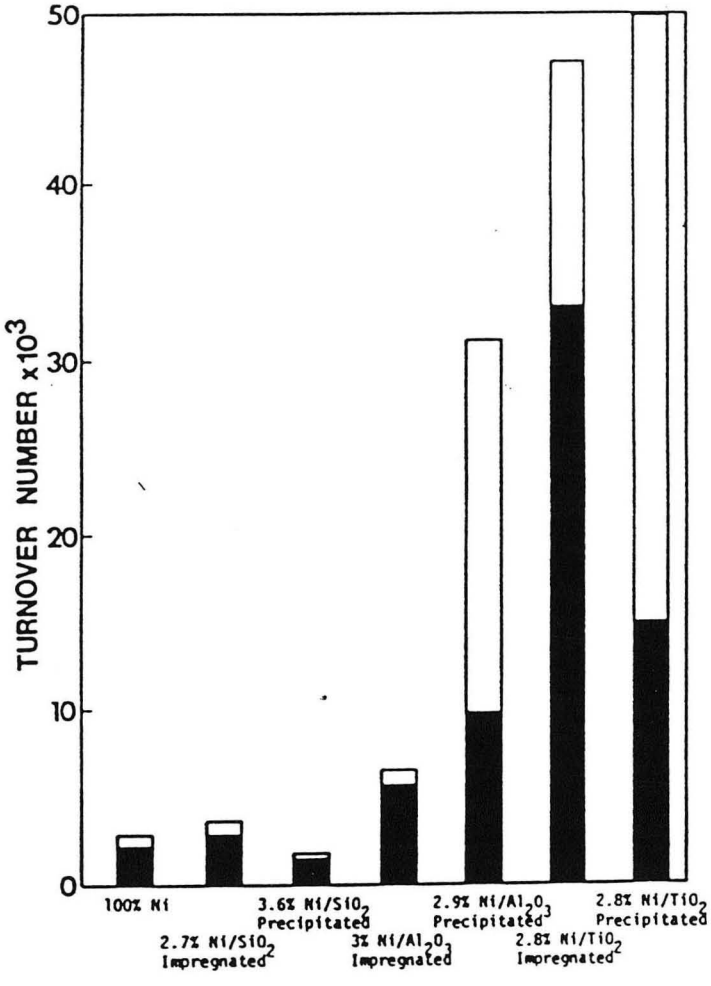


FIG. 4. Effects of support and preparation on methane turnover number at 525 K for Ni: ■ CH_4 turnover No.; □ C_{2+} hydrocarbon turnover No.; total bar length is CO turnover No.

Bartholomew, C.H., Pannell, R.B., and Butler, J.L., *J. Catal.*, **65**, 335, (1980).

XBL 918-1686

Fig. 10

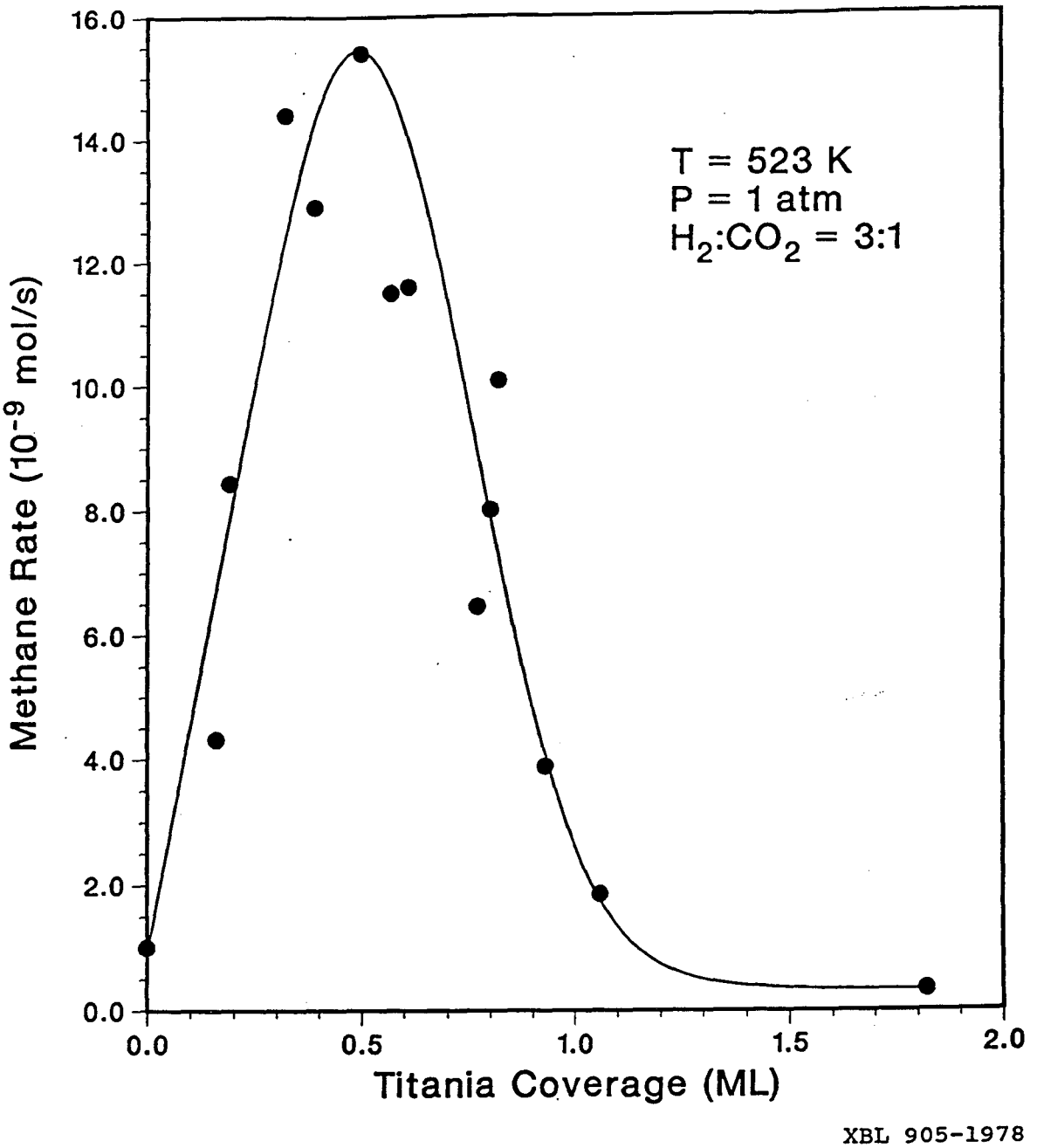
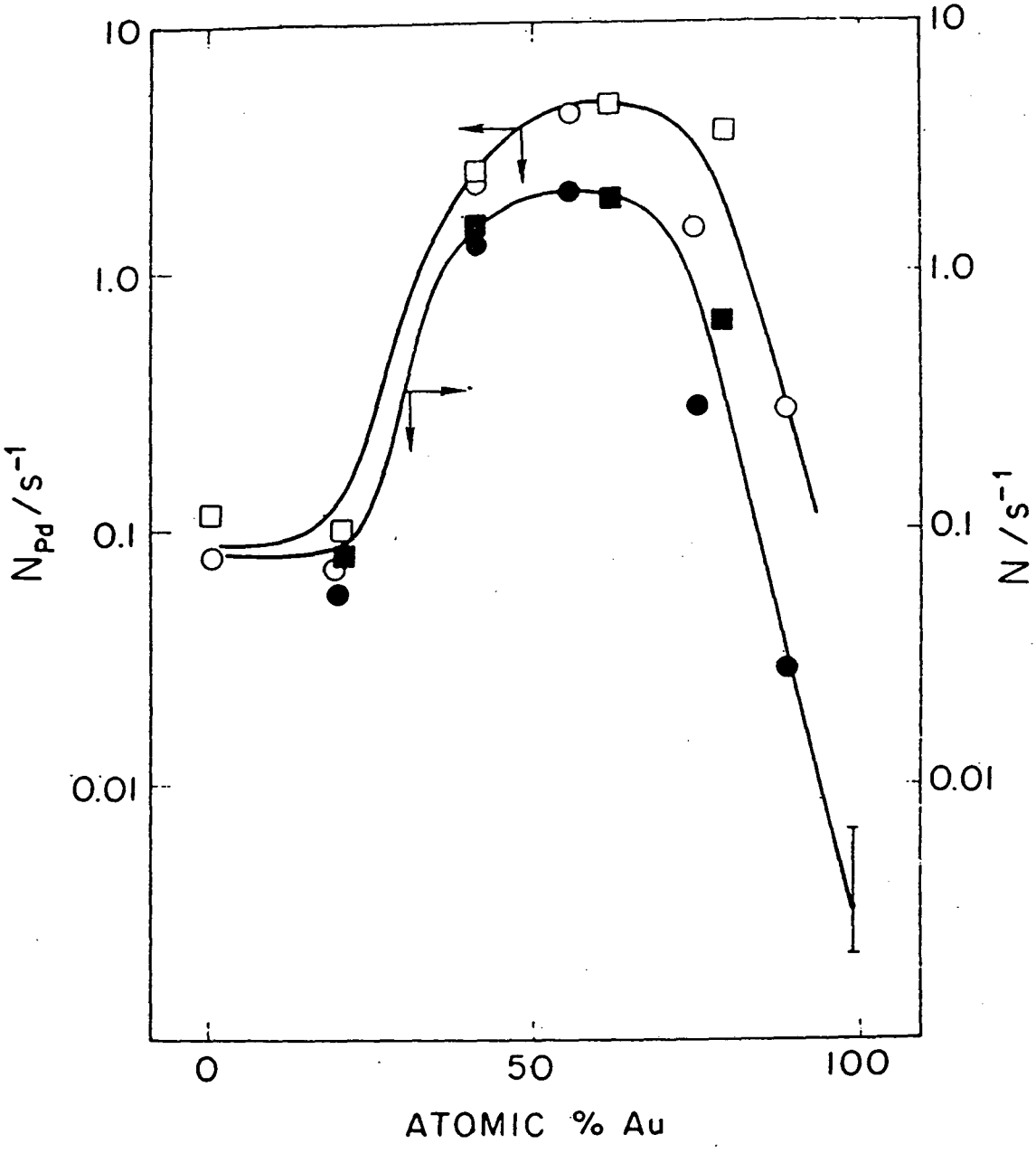
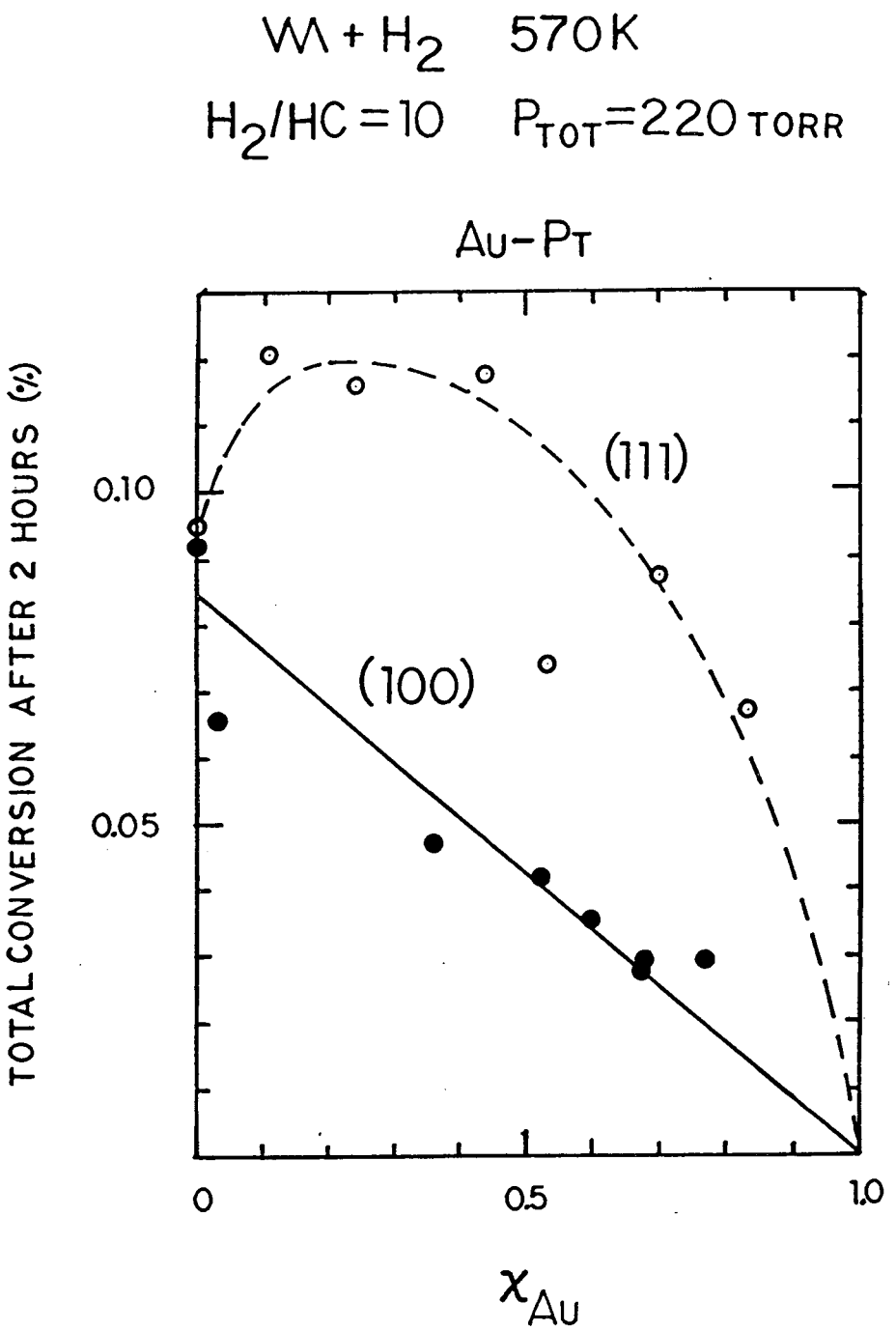

16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
Methane Rate (10^{-9} mol/s)
T = 523 K
P = 1 atm
H_2:CO_2 = 3:1
0.0
0.5
1.0
1.5
2.0
Titania Coverage (ML)
XBL 905-1978

Fig. 11



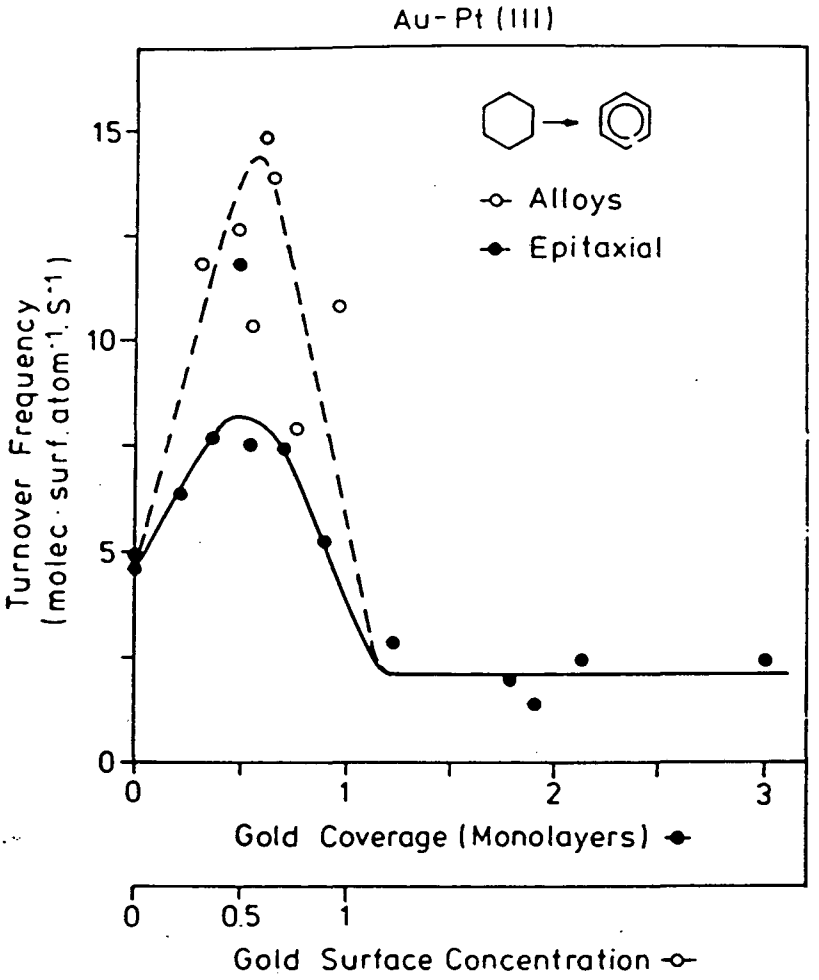
XBL 913-438

Fig. 12



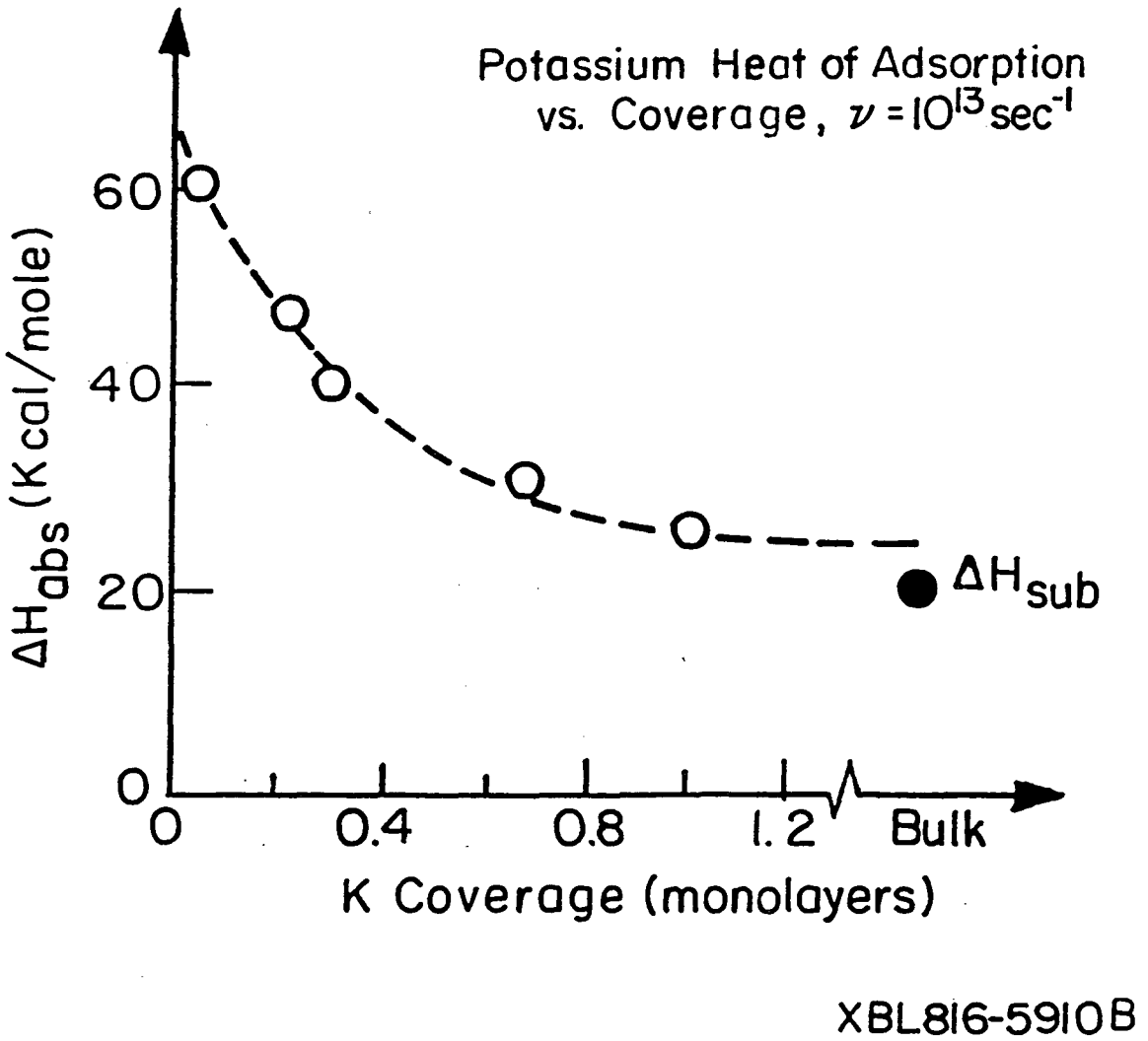
XBL 854-2031

Fig. 13a



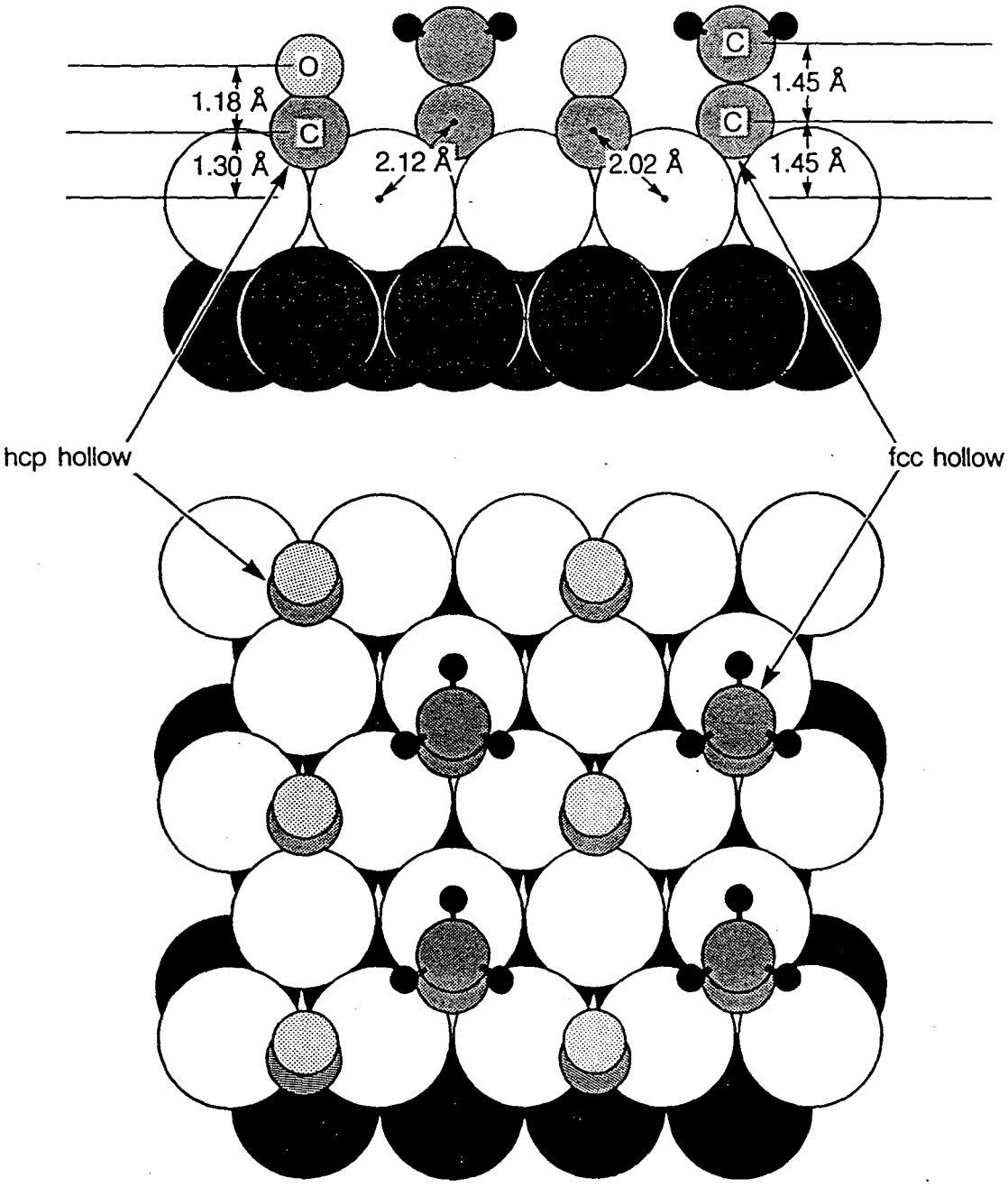
XBL 918-1687

Fig. 13b



XBL816-5910B

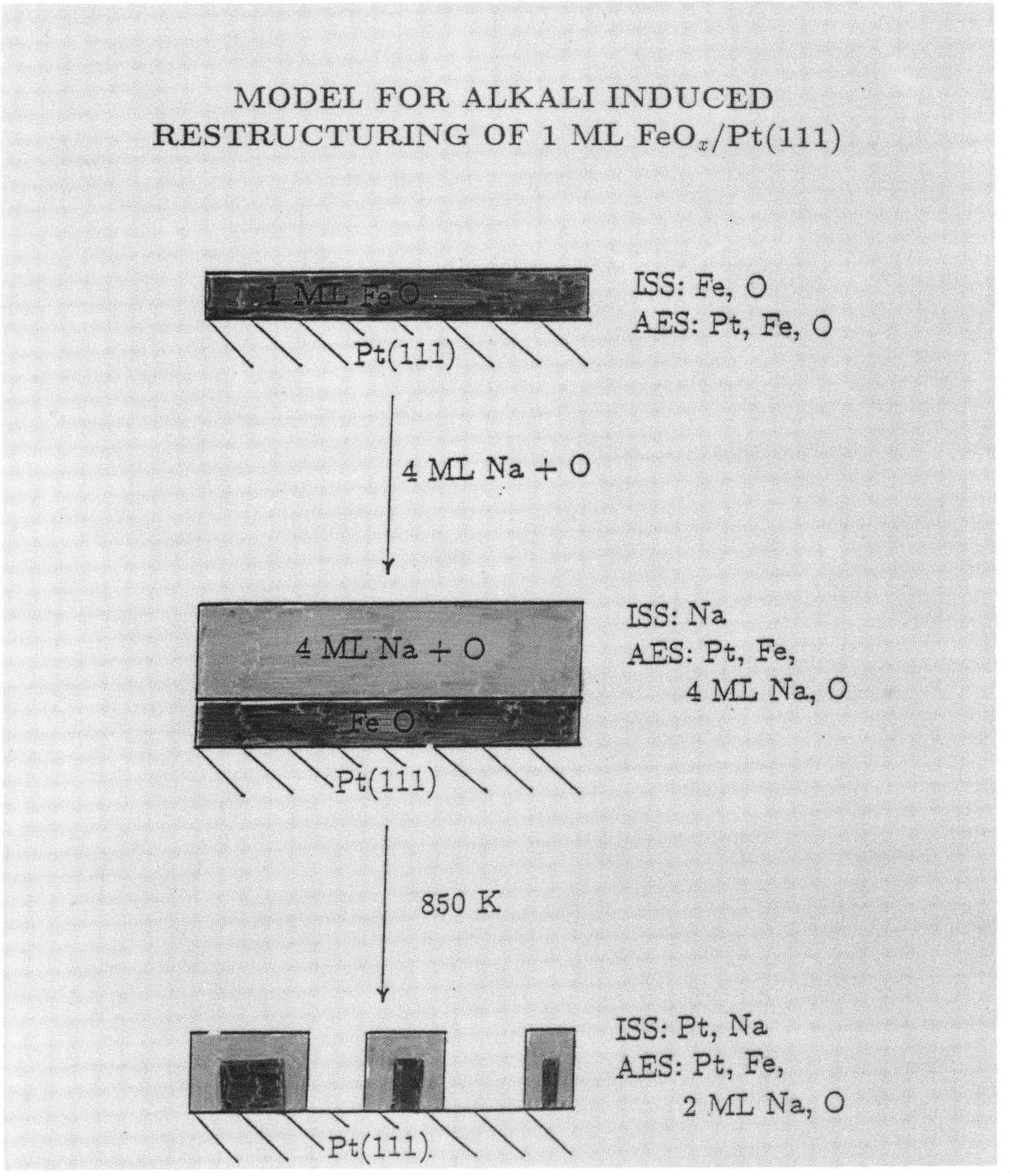
Fig. 14



Rh(111) + c(4×2) CO + Ethylidyne(CCH_3)

XBL 877-7004

Fig. 15



XBC 884-3012

Fig. 16

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