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# SURFACE SCIENCE AND HETEROGENEOUS CATALYSIS

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#### SURFACE SCIENCE AND HETEROGENEOUS CATALYSIS

This is the subject of the lecture presented to the Chemical Society in Zurich on May 14, 1980

by

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# Introduction

Catalysis, and heterogeneous catalysis in particular, lies at the heart of most chemical technologies. We would like to acquire a molecular level understanding of the important heterogenous catalytic processes and scrutinize the atomic details as they occur in the surface monolayer that is composed of approximately 10<sup>15</sup> atoms/cm<sup>2</sup>. In the past 15 years modern surface science has undergone an explosive development that provided the techniques for investigations of the surfaces and processes that occur on surfaces on the atomic scale. Electron scattering techniques, low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HREELS), Auger electron spectroscopy (AES), ion scattering spectroscopy (ISS), secondary ion mass spectroscopy (SIMS), and atom scattering (helium diffraction and molecular beam-surface reactive scattering) can determine the structure and chemical bonding of atoms and molecules at surfaces and the rate parameters of elementary surface reaction steps.<sup>1</sup> The surface composition can be determined with a sensitivity of less

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than 1% of a monolayer with some of these techniques, and the oxidation state of surface atoms can be readily verified, using X-ray photoelectron spectroscopy (XPS), for example. We no longer need large surface area (100 meter sq. per gr.) catalysts to be able to determine reaction parameters (rate constants, activation energies, and preexponential factors). A l cm<sup>2</sup> area of a crystal surface is adequate for most catalytic studies.<sup>2</sup>

Among the important parameters of the catalytic process we are concerned with most frequently are the specific rate (or turnover frequency), the selectivity, and the lifetime. The turnover frequency is defined as the number of product molecules formed per surface site per second. Since most heterogeneous catalytic reactions occur far from equilibrium, this rate is usually much lower than the maximum obtainable rate near equilibrium. Selectivity is defined as the fraction of reacting molecules which are converted to the desired products. In the application of platinum for hydrocarbon " reforming" we aim to convert alkanes (n-heptane, for example) to toluene by selective dehydrocyclization, a reaction path which has to compete with hydrogenolysis, dehydrogenation, and isomerization. The lifetime of the catalyst is all important as it is frequently poisoned rapidly by undesirable side reactions or by impurities.

In order to develop the surface science of catalysis, we should scrutinize the structure and the composition of the surface that is catalytically active and then correlate this information with the catalytic reaction rates, selectivity, and catalys: lifetime. In order to achieve this goal, my studies use about 1 cm<sup>2</sup> surface area single crystals or polycrystalline foils that are well characterized in ultrahigh vacuum (UHV) by the modern techniques of

surface science. Then the crystal is enclosed in an isolation cell in the center of an UHV chamber. The isolation cell and a recirculation system can be pressurized to about 1-100 atm, and product distribution from the catalyzed reaction that occurs under these high pressure conditions is then monitored as a function of time using a gas chromatograph.<sup>3</sup> The structure and composition of the active surface is characterized directly, *in situ*, before and after the high pressure reactions using LEED and AES. Such an apparatus, shown in Figure 1, — car carry out reaction rate studies from 10<sup>-8</sup> Torr to 100 atm at low pressures, a mass spectrometer is used to determine the-product distribution and to monitor the rate. In this manner the kinetics of hydrocarbon reactions, catalyzed over crystal surfaces at high and low pressures, can be correlated.

We also systematically vary the structure of the single crystal strfaces. Often additives are deposited on these surfaces, such as alkali metals (electron donors) or oxygen or halogens (electron acceptors) to modify the valency of surface atoms or block some of the surface sites. Reaction studies on crystal surfaces so modified reveal the molecular ingredients of heterogeneous catalysis and the complexity of many of the industrial catalyst systems.

The catalytic reactions that I am studying include hydrocarbon conversion over platinum, the transition metal-catalyzed hydrogenation of carbon monoxide, and the photocatalyzed dissociation of water over oxide surfaces.

Our method of combined surface science and catalytic studies are similar to those used in synthetic organic chemistry. The catalysts that are used in the chemical technologies are small particles and are composed of many crystal faces. By investigating the catalytic behavior of each crystal face separately, we explore all the structural ingredients and additives which control the catalytic behavior, and thus we synthesize the catalyst. Of course, when using

single crystal models for the working catalyst we should constantly compare their activity to that of the real catalysts to establish credibility for the models. These have been accomplished by comparing the rates of cycloprogane ring opening on platinum and the hydrogenation of carbon monoxide on rhodium single crystal surface with those on practical commercial catalyst systems. Excellent agreement was obtained for these reactions.

We review below what we have learned about heterogeneous catalysis from these surface science approaches over the past 15 years and present models of the active catalyst surface that emerge from these studies.

# A. The Surface Is Heterogeneous on the Atomic Scale

The heats of chemisorption of diatomic molecules have been measured over tansition metal surfaces of for the chemisorption of carbon monoxide and hydrogen in Figures 2a, 2b, 3a, and 3b. On polycrystalline surfaces  $\Delta H_{ads}$  decreases rather smoothly from left to right across the periodic table. For single crystal surfaces, the experimental data indicates that there are many heats of adsorption values for a given crystal face of a transition metal. Also, there are marked variations of the heat of adsorption from crystal face to crystal face. For example, there is a 14 kcal difference between the highest and lowest binding energy state of CO on platinum crystal surfaces. Thus the surface appears to be heterogeneous on the atomic scale. There are various sites on a given crystal face which are distinguishable by their bonding strength, and the binding energies also vary greatly from crystal face to crystal face. A model of such a heterogeneous surface is shown in Figure 4. There are several even on a smooth (111) crystal face of an fcc metal. There sites that are distinguishable / are at least three binding states on this particular surface. The molecule may be located on top of a surface atom in a bridge site, or in a 3-fold site. CO

seems to prefer the on-top and bridge sites, while other species (oxygen, carbon, sulfur, and sodium) appear to like the highest coordination number (a 3-fold site in most cases) as determined by surface crystallography, LEED, or other techniques that have determined the site symmetry.<sup>7</sup> High resolution electron loss spectroscopy (HREELS) clearly shows that two binding sites of CO exist on the rhodium (111) crystal face where CO has different stretching frequencies.<sup>8</sup> This is shown in Figure 5. The electron energy loss at 2070 cm<sup>-1</sup> number corresponds to CO stretching vibration for a molecule located on top of a rhodium atom, while the lower frequency peak corresponds to a CO molecule located at a bridge site. Figures 6a and 6b show CO molecules on a top and a bridge site, respectively, on two different surfaces as their structures were determined by surface crystallography.<sup>9</sup>,10

Large change in the binding strength of a given molecule occurs when it is located at different sites of lower coordination, such as at steps or a kink.<sup>11</sup>In general, the heats of adsorption of the molecules or transition metal surfaces increase when bound to such a surface irregularity<sup>2,13</sup> ften the molecule dissociates more easily at such a site while only with difficulty at sites with higher numbers of nearest neighbors.<sup>14</sup> It is possible to prepare single crystal surfaces with periodic arrays of steps, one atom in height, or stepped surfaces which have a large concentration of kinks in the steps.<sup>15</sup> Several of these high Miller index surfaces are displayed in Figures 7 and 8. By cutting crystal surfaces appropriately, both the average terrace width and the step or kink densities can be systematically varied. LEED studies permit the determination of both the average step separation and the step heights as long as these steps are ordered.<sup>15</sup>

17 The dissociation of hydrogen and carbon monoxide on platinum crystal surfaces serves as a demonstration of the structure sensitivity of chemical bonding. Molecular beam surface scattering studies of H2-D2 exchange indicate that stepped platinum surfaces are almost an order of magnitude more 15,18 active in forming HD upon a single scattering than the Pt(111) surface. The reason for this difference is due to a small 0.5-1.5 kcal activation energy necessary to dissociate the hydrogen molecules to atoms on the (111) crystal face. The dissociative adsorption of  $H_2$  or  $D_2$  at the step edges requires no such activation energy. Photoelectron spectroscopy studies of CO adsorption on platinum surfaces which have a high density of kinks indicate that CO dissociates at the kink sites while absorb as intact molecules on the terrace sites and in the steps. Studies of hydrocarbon reactions on single crystal surfaces at low and at high pressures show the structure sensitivity of both the 19,20 C-H and C-C bond breaking processes. By monitoring simultaneously the dehydrogenation and the hydrogenolysis of cyclohexane and cyclohexene, it was found that kinks are more active in dissociating C-C bonds than the other surface sites and are the sites most active for hydrogenolysis

Kinetic studies on single crystal surfaces magnify the effects of small changes of binding or small changes in activation energies for bond breaking at the different surface sites if the bond formation or breaking at that site is rate\_determining. In this circumstance the activation energy of the chemical process that is to take place at that site appears in the exponent of the Arrhenius rate expression, thereby magnifying the effect of changing bond strength in an exponential manner. Thus minor changes in bonding strengths from site to site can give rise to orders-of-magnitude changes in chemical reaction rates that occur at the site accompanied by large variations in selectivity.

# B. The Surface is Covered

Oudar <u>et al</u>. have correlated the heats of adsorption of sulfur on transition metal surfaces with the heats of formation of metal sulfides.<sup>21</sup> The correlation is good and indicates that the heats of adsorption are larger by 5-10 kcal/mole. Thus the combined strength of the metal-sulfur bonds at the surface has to be greater than in the bulk. This difference provides a thermodynamic driving force for sulfur segregation at the surface. Surface segregation is frequently observed for carbon, oxygen, or silicon on transition metal surfaces. In the case of binary alloys, the surface is enriched with that metal constituent that lowers the total surface free energy of the system.<sup>22</sup> As a result of the different bonding at the surface, as compared to that in the bulk, surfaces are likely to have different chemical compositions. This is verified for many alloy systems; particularly important is the formation of the strong metalcarbon and metal-hydrogen bonds which form between the hydrocarbon reactants and the metal surface under reducing conditions or between the oxygen and the metal during oxidation reactions.

As a consequence of the strong surface forces for bonding, the surface usually stores a large concentration of mobile hydrogen atoms during hydrocarbon reactions that can readily be transferred to and from the various reaction intermediates. Under these circumstances the surface is usually covered with a carbonaceous deposit that is held tenaciously during the catalytic surface reaction of hydrocarbons, while the surface is oxygen covered during oxidation reactions.<sup>23</sup> The residence times of these strongly held adsorbates can be much longer than the reaction: time. Therefore, they may provide the surface sites on which the reaction occurs instead of the clean metal surface, or may block certain surface sites to prevent or poison

reactions which require the blocked sites.

# C. <u>Temperature Dependence of the Character of the</u> Surface Chemical Bond

A great deal of evidence has been accumulated over the past several years indicating sequential bond breaking of molecules with increasing temperature. In order to demonstrate this process, we consider the chemical adsorption of acetylene (C<sub>2</sub>H<sub>2</sub>) on the Pt(111) crystal face. LEED and HREELS studies indicate that the molecule adsorbed at 300 K (its structure is displayed in Figure 9) is bonded mostly to one platinum atom and the platinumcarbon distance is that characteristic of a covalent bond as determined by surface crystallography. The carbon-carbon distance in the adsorbed molecule is similar to that in ethylene. Upon heating this adsorbate to 370 K in the presence of small amounts of hydrogen, a rearrangement of the molecules takes place and they are converted to ethylidyne species that is shown in Figure 10. The C-C bond axis is perpendicular to the surface plane, and the C-C bond distance is stretched to a single bond. Both HREELS and LEED experiments indicate that similar species with different amounts of hydrogen are also stable (CH-CH3, C-CH<sub>2</sub>). The ethylidyne molecule forms also at a temperature that is below the range where most hydrocarbon catalytic reactions occur (450-700 K). When this molecule is heated to the catalytically important temperature range, it decomposes. HREELS studies show the presence of CH species on the Rh(111) surfaces. The surface is catalytically active in hydrocarbon reactions while it is covered with the carbonaceous fragments in this manner. Upon heating to over 700 K, the C-H species lose their hydrogen and the carbon atoms form a graphitic layer with the basal plane parallel to the surface as shown by LEED studies. This graphite layer renders the surface inactive during hydrocarbon

reactions. The regeneration of the platinum surfaces requires a complete removal of the inactive carbon coating by oxygen or by other means (ion sputtering, for example). Such a sequential bond breaking of molecules with increasing temperatures has been observed on many transition metal surfaces which include iron, nickel, rhodium, and platinum. The active carbonaceous fragments change with the changing surface structure of nickel from CH to C2 species. In fact, early in the history of surface chemistry such temperature dependent changes have been detected and gave rise to the classification of physical adsorption and chemisorption where the transition of weak to strong chemical bonding of the adsorbate occurs as the temperature is increased. (N2 dissociations to N atoms on iron surfaces with increasing temperatures.) One may take any reactive molecule, like diazomethane  $(CH_2N_2)$  and place it on a very reactive transition metal surface, like iron, where it remains intact as long as the temperature is low enough. With increasing temperature, sequential bond breaking occurs with small changes of thermal energy kT. The thermal energy changes needed to bring about bond breaking is much smaller than the broken-bond energy. Only at high temperature, above 700 K, does the thermodynamically most stable surface species form. Nevertheless, the molecular fragments that form in the intermediate temperatures, although metastable, remain unchanged on the surface in their temperature range of stability and keep the surface catalytically active and selective in hydrocarbon reactions.

# D. The Importance of Additives for Selective Catalyzed Reactions

We have discussed the role of surface irregularities - steps and kinks - as markedly influencing the rate and reaction path of catalytic reactions. Usually additives of various types are employed to prepare the active catalyst that plays an important role in carrying out surface reactions selectively and at high rates or to increase the catalyst lifetime. Let us

consider two types of catalyst additives, (1) one is deposited by a reaction mixture, and the other (2) that is added to the catalyst before the onset of the catalytic process during the preparation of the catalyst.

the turnover frequency for 1. In Figure 11, we show hydrogenation, and dehydrogenation of cyclohexene over Pt that was measured over 10 orders of magnitude reactant pressure range. As expected, the reaction rate increases with pressure. Perhaps a more important parameter, however, is the reaction probability, i.e. how many product molecules form per incident molecule at the various pressures. This is obtained by dividing the turnover number with the incident flux of the reactant. As seen in Figure 11, the reis quite high at low pressures, but it drops to less than action probabili 10<sup>-6</sup> at high pressures which are normally employed in the chemical technology. This is due to the long surface residence time of the molecules as compared to their frequency of collisions with the surface. Adsorbed hydrocarbon molecules may stay on the surface for seconds or longer, while collisions with the surface occur in every  $10^{-5}$  seconds/cm<sup>2</sup> near atmospheric pressures. The residence time of the adsorbed hydrocarbon depends on its strength of binding and the temperature. It appears that at a given temperature the higher the molecular weight of the reactant, the longer it stays on the surface. For a given organic reactant molecule, temperature greatly influences the residence time. By  $^{14}C$ labeling of the reactants, one can determine the time required for complete exchange for adsorbed organic layers by other adsorbates. These studies defined three temperature regimes that are distinguishable for a given molecule. At low temperatures (below 400 Kfor platinum) the organic molecule adsorbs and then readily desorbs in excess hydrogen. In the temperature range of 400-700 K, strongly bound molecular fragments form and a catalytic reaction takes place on

top or in exchange with these fragments. The residence times of the strongly adsorbed fragments are 100 to 1000 times the turnover frequencies to form the product molecules. Thus in the first approximation we can assume the organic fragments are part of the active, stable catalytic surface. It is interesting to note that while the carbon atoms in the organic fragments do not readily exchange with the incident reactants, the hydrogen atoms contained in the fragments exchange well, as indicated by hydrogen-deuterium exchange studies. At about 700 K the organic fragments lose hydrogen and graphitize which renders the surface catalytically inactive. These changes are shown schematically in Figure 12.

These results indicate that the reactants deposit their own catalytically active and selective surface during the first few milliseconds of the reaction at high pressures. This layer often introduces selectivity, i.e. it reduces the probability of facile competing reactions (hydrogenation or dehydrogenation) that compete with the much slower isomerization or dehydrocyclization. This way reactions that become much lower reaction probabilities can win out when competing with the more facile reactions. Future studies will have to verify the unique metal-carbon coordination and molecular structures of the active organic fragments that appear to act as necessary additives to the surface to carry out many important hydrocarbon conversion reactions selectively.

2. We present several examples to show how additives that are introduced during the preparation of the catalyst influence the rates, selectivity, and lifetime of catalytic reactions. Additives that are electron donors, such as potassium or sodium, or electron acceptors, like oxygen or chlorine, are frequently part of the catalyst formulation.

# a. Effects of porassium on iron during the hydrogenation of CO and NH<sub>3</sub> Synthesis

During the catalytic hydrogenation of CO over oxidized iron, the initially rapid formation of hydrocarbons decreases within a few hours. AES studies show that the decline in the reaction rate is due to the rapid reduction of the oxide and the buildup of a multilayer of carbonaceous deposit on the surface that poisons the catalyst.<sup>31</sup> When potassium is added to the oxid zed surface, an iron-oxygen-potassium phaseforms that is stable in the reducing  $H_2/CO$  mixture. The presence of potassium prevents the buildup of carbon on the surface of the catalyst, and the catalyst remains remarkably active and stable for long periods. It appears that potassium catalyzes the removal of the surface carbon through a reaction cycle that is likely to involve the formation and decomposition of KOH and  $K_2CO_3^{32}$  to produce the net reaction,  $C+H_2O \rightarrow CO+H_2$ .

When potassium is added to the iron surface during ammonia synthesis, it increases the heat of chemisorption of N<sub>2</sub> from about 9 kcal/mole to 13 kcal/mole; that, in turn, increases the surface cc...centration and residence time of these molecules.<sup>33</sup> Simultaneously, the activation energy for dissociation to nitrogen atoms is decreased by 3 kcal which results in a higher rate of dissociation. Since the dissociation of N<sub>2</sub> to atoms seems to be the rate limiting step in the formation of NH<sub>3</sub>, the rate of the reaction is increased.

b. The effect of oxygen on the selectivity of platinum catalysts in hydrocarbon reactions.

When platinum is heated in oxygen at elevated temperatures, a surface oxide forms with the oxygen atoms located just below the metal surface.<sup>34</sup> The Pt-O bond is so strong in this surface compound that the oxide remains

stable indefinitely during high pressure hydrocarbon reactions that are always carried out in excess hydrogen. Single crystal studies indicate that when this oxide is produced on platinum surfaces with a high density of kinks, a large change in the selectivity of hydrocarbon reactions occurs.<sup>35</sup> The rate of C-C bond breaking hydrogenolysis reactions are accelerated at the expense of dehydrogenation reactions that require only C-H bond scission or at the expense of dehydrocyclization. It appears that a combination of strongly bound oxygen and surface irregularities of certain types can greatly influence the course of hydrocarbon reactions on platinum on account of the electronic changes that are induced at these surface sites.

# c. The effects of sulfur, oxygen, and chlorine in changing the surface structure of catalysts.

When sulfur is deposited on nickel crystal surfaces in amounts much less than a monolayer, a restructuring of the surface occurs.<sup>37</sup> In the absence of sulfur, the clean Ni(111) crystal face has the lowest surface energy and is, therefore the most stable. On this metal surface sulfur would occupy a 3-fold site to form three M-S bonds. Sulfur forms a stronger chemical bond with the metal on the (100) crystal face where it is located in a high coordination 4-fold site (four M-S bonds). As a result, the (100) crystal face becomes thermodynamically more stable when sulfur is introduced. This provides the driving force for the gross restructuring of the surface. Simultaneously, the catalytic activity declines rapidly. Strongly bound oxygen or the presence of carbon also causes restructuring of the clean metal surfaces.<sup>15</sup>Often the surface can regain its original structure when the adsorbate is removed. Chlorine is known to facilitate the redispersion of small metal particles that are deposited on high surface area oxide supports. While

the mechanism of this redispersion process is not well understood, vapor transport is likely to be involved.

It is apparent that the surface structure of a catalyst does not remain unchanged during the chemical reaction. It may be different in the presence of hydrocarbons and in oxiding environments. Additives can serve to stabilize the surface structure or to alter it to obtain better selectivity for structure sensitive reactions or higher surface area for higher rates.

d. The effect of NaOH to catalyze the Photodissociation of  $H_2O$  on  $SrTiO_3$ 

When SrTiO<sub>3</sub> crystal surfaces are illuminated by light of greater than band gap energy (v3.1 eV) at 300 K in the presence of water, H<sub>2</sub> and O<sub>2</sub> evolve. This reaction occurs only in the presence of NaOH, however.<sup>38,39</sup> Surface studies using electron spectroscopy indicate that alkali hydroxides catalyze the hydroxylation of the oxide surface under these conditions.<sup>40</sup> The photoreaction actually takes place on the hydroxylated surface. Once water is dissociated to OH<sup>-</sup> and H<sup>+</sup> in the dark, in a NaOH catalyzed reaction, illumination that creates electrons and electron vacancies at the oxide surface proceed to reduce and to oxidize the surface species to create OH and H. Light also helps to regenerate the Ti<sup>3+</sup> defect sites that have been oxidized to Tx<sup>4+</sup> during the dissociative adsorption of water on the oxide surface.<sup>41</sup>

e. The effects of IB metals, Cu, and Au on the catalytic activity of other transition metals.

The addition of Cu or Au to various transition metals influences markedly their selectivity in hydrocarbon conversion reactions. Sinfelt <sup>42</sup> reported that the rate of hydrogenolysis of ethane has decreased exponentially

upon the addition of copper to the nickel catalyst. The dehydrogenation activity of cyclohexane, however, has not been diminished by the addition of the IB metal. Similar results have been reported when gold was added to platinum.<sup>43</sup>As a consequence the selectivity for dehydrogenation or for isomerization reactions has greatly increased.

It was also reported recently that a monolayer of gold incyclohexene on creases the dehydrogenation rate of platinum by 5-fold. The addition of gold to palladium also increased the rate of oxidation of hydrogen to produce water by over an order of magnitude.<sup>45</sup> The presence of gold on platinum and iridium also increases the lifetime of the transition metal catalysts during hydrocarbon reactions. Thus it appears that the relatively inactive gold and copper change and greatly improve, in some cases, the activity, selectivity, and lifetime of several transition metal catalyst systems. While this effect is not fully understood, both electronic and structural changes that occur when gold or copper are added are considered important to produce the observed changes of catalytic behavior.

# The Building of High Technology Catalysts

Surface science studies identified many important features of the active and selective catalyst systems by scrutinizing the surface on the molecular scale. Various surface sites were identified with distinguishable chemical bonding and the role of surface irregularities, steps, and kinks in breaking large binding energy chemical bonds (C-C, C-H, C=O) have been verified. The influence of additives in catalyzing side reactions, or by blocking sites of undesirable chemistry, by increasing the adsorbate bond strength or in restructuring the surface have been recognized. By application

of this molecular level understanding of the working catalysts, we aim to build new catalysts with desired activity, selectivity, or lifetime. Thus we hope to convert the field of heterogeneous catalysis to high technology where the principles of surface science are employed to develop the next generation of catalyst systems.

There is already such a group of catalysts - the zeolites. These alumina silicates are synthesized with different Al-Si ratio and pore structure that permits systematic variation of their acidity and their ability to accept molecules of certain shape into their pores while rejecting others (shape selectivity). Intensive studies of bimetallic systems composed of a transition/metal and copper or gold will also likely lead to the design of a new generation of catalysts. Atomic scale surface studies of catalytic systems, the correlation of their surface structure, composition, and oxidation state, with their catalytic reaction rates, selectivity, and catalyst lifetimes seem to be a promising approach to build new catalysts.

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### Figure Captions

- Fig.1 Scheme of the apparatus for carrying out surface reactions at high and low pressures  $(10^{-8} \text{ Torr} - 10^5 \text{ Torr})$  using small area  $(\sim 1 \text{ cm}^2)$  samples that are characterized with various diagnostic techniques.
- Figs. Heats of chemisorption of CO for (a) polycrystalline surfaces of 2a, 2b elements in the Periodic Table, and (b) various single crystal surfaces.
- Figs. Heats of chemisorption of hydrogen for (a) polycrystalling
- 3a,3b surfaces of elements in the Periodic Table, and (b) various crystal surfaces.
- Fig.4 Schematic representation of the heterogeneous surface on the Atomic Scale. Terrace, step, and kink atoms as well as point defects (adatoms and vacancies) have been identified by experiments.
- Fig.5 High resolution electron loss spectra of CO chemisorbed on Rh(111) at 300 K as a function of pressure.
- Fig.6a The structure of CO on the Rh(111) crystal face. Molecules occupy on-top positions. The rhodium-carbon spacing is 1.95 Å and the CO spacing is 1.07 Å.
- Fig.6b The adsorption structure of CO on Pd(100) crystal face at a 1/2 monolayer coverage. The molecules are in the bridge positions.
- Fig.7 Structure of several high Miller index stepped surfaces with different terrace widths and step orientations.
- Fig.8 The surface structures of several high Miller index surfaces with deferring kink concentrations in the steps.
- Fig 9. Perspective view of a metastable C<sub>2</sub>H<sub>2</sub> molecule on the (111) crystal face of platinum.
- Fig.10 Perspective view of ethylidyne on the Pt(111) crystal face. A stable structure reached after acetylene adsorption with

the addition of hydrogen. The same structure is obtained upon the adsorption of ethylene.

Fig.ll Correlation of cyclohexene reaction rates and reaction probabilities over 10 orders of magnitude pressure range. The reactions were performed at 150°C over the scepped Pt(223) crystal surface with hydrogen to hydrocarbon ratio of 10.

Fig.12 The effect of the temperature dependent character of bonding with hydrocarbons on reactivity.

-20-



-21-

Fig.1

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XBL 773-5236

Fig.2a



XBL777-5699

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Fig.2b



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XBL777-5700

Fig.3a



Fig.3b



XBL708-1717A









Rh (III) + (/3x/3) R30°CO

Fig.6a



Pd (100) + (2√2×√2) R 45° 2 CO xBL794-6170





fcc (443)

30

fcc (331)

X8L799-7019



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Fig.8

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XBL 794-6168

Fig.9



Pt (III) + ethylidyne

XBL794-6167

Fig.10



Fig.ll

- 1. LOW T (< 440 K), HIGH H PRESSURES CLEAN METAL CATALYSIS REVERSIBLE ADSORPTION OF HYDROCARBONS
- MEDIUM T (440-700 K), H PRESSURES
  CATALYSIS BY ACTIVE C<sub>X</sub>H<sub>Y</sub> FRAGMENTS.
- 3. HIGH T (>700 K), H PRESSURES MULTILAYER CARBON BUILD-UP POISONING BY GRAPHITE.

FIGURE 12