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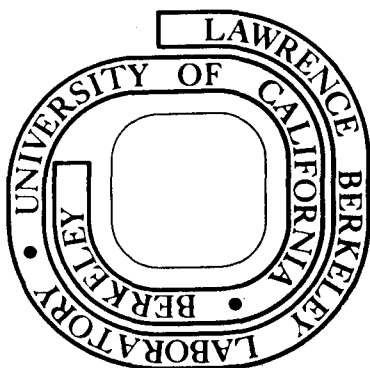G. A. Somorjai and D. W. Blakely

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# ON THE MECHANISM OF CATALYSIS OF HYDROCARBON REACTIONS
## BY PLATINUM SURFACES

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## ABSTRACT

Atomic height steps and kinks in steps have been identified on platinum surfaces as distinct catalytic sites where C-C, C-H and H-H bond scissions occur during the reactions of hydrocarbons. The active catalyst surface is covered with a carbonaceous overlayer whose properties affect both the reaction rates and the product distribution. A model for the catalysis of hydrocarbons on platinum surfaces is proposed which incorporates the effects of the low coordination number active sites and the atomic surface structure.

We have studied, over the past several years, the correlation between the activity of platinum crystal surfaces for carrying out a variety of catalytic reactions of hydrocarbons, and their atomic surface structure and surface composition. We would like to report the identification of distinct atomic sites on the platinum surface where H-H, C-H and C-C bond breaking predominantly occur. The hydrogen-deuterium exchange reaction[1] provided information about the H-H bond breaking while the C-H and C-C bond breaking activity was determined by monitoring simultaneously the rates of dehydrogenation and hydrogenolytic ring opening of cyclohexane to produce benzene and n-hexane, respectively.[2] Experimental evidence also indicates that the catalytically active surface is covered with a carbonaceous overlayer which forms as a result of partial dehydrogenation of hydrocarbons.[2,3] The overlayer is either ordered or disordered, dependent on reactant and clean platinum surface structure, the ordering influencing both the product distribution and the rate of surface reactions. As a result of these observations we shall propose a model of catalysis of hydrocarbon reactions by platinum surfaces.

The surface structures of the clean platinum single crystals and of adsorbed molecules were studied by low-energy electron diffraction and the surface composition by Auger electron spectroscopy.[4] The rates and product distributions in the various chemical reactions were measured by a quadrupole mass spectrometer at low pressures[3] and a gas chromatograph at high pressures.[5] The surface area of the single crystal catalyst samples is about 1.0 $cm^2$. Reaction rates as low as $10^{-15}$ moles of product per $cm^2$ of catalyst surface per second were readily detectable.

## ACTIVE SITES ON PLATINUM SURFACES

Three types of platinum surfaces which are distinguishable by their reactivities are shown schematically in Fig. 1. The low Miller Index Pt($\bar{1}$11) surface (Fig. 1a) has a very low density of surface imperfections, less than $10^{12}$ per $cm^2$, as compared to the number of surface atoms, $1.5 \times 10^{15}$ atoms per $cm^2$. The high Miller Index Pt($\bar{5}$57) surface (Fig. 1b) is characterized by a stable surface structure with 18% of the surface atoms in monatomic height steps.[6] The Pt($\bar{6}$79) surface (Fig. 1c) must have, in addition to high step density, a high density of kinks in the step or atoms of lower coordination since the ($\bar{6}$79) plane does not lie between two close packed planes as does the ($\bar{5}$57) plane [($\bar{1}$11) and ($\bar{0}$01)].[4] Thermal stability of high Miller Index surfaces has been systematically investigated and their relative stability as a function of crystal orientation and relative activities in various hydrocarbon reactions have been determined.[7] The surface sites on the different platinum surfaces are distinguishable by their coordination number, i.e., their number of nearest neighbors, ranging from kink atoms with only 6 nearest neighbors, to atoms in (111) orientation terraces with 9 nearest neighbors.

Molecular beam scattering studies in this laboratory indicate the reaction probability (number of reactive collisions per total collisions with surface) for hydrogen-deuterium exchange increases four orders of magnitude from less than $10^{-5}$ on the Pt($\bar{1}$11) surface to approximately 0.1 on a highly stepped platinum surface, Pt($\bar{3}$55).[1] The presence of a high concentration of atomic steps was necessary to detect the formation of HD on single scattering at low pressures and the amount of HD formed was proportional to the step density.

We have also found that the dehydrogenation of cyclohexane and cyclo-
hexene to benzene occurs only on stepped platinum surfaces in an appreciable
rate.[2,8] Figure 2 shows the step density dependence of the reaction rate
of cyclohexene dehydrogenation to benzene to demonstrate this effect.   The
rate of cyclohexane dehydrogenation to benzene is constant as long as there
are steps (tested as low as 7% steps) on the catalyst surface, but is
almost an order of magnitude lower on the Pt($\bar{1}$11) surface as seen in Fig. 3.
Thus, atomic steps appear to be the preferred surface sites for breaking
H-H and C-H bonds.

Cyclohexane undergoes dehydrogenation and hydrogenolysis on the stepped
platinum surfaces.   The relative rates of these two reactions can best be
monitored by the ratio of benzene to n-hexane in the reaction products.
As is demonstrated in Fig. 3, the rate of benzene production is independent
of step and kink density, while n-hexane production increases slowly
with step density and rapidly with kink density.   The rate of cyclohexane
hydrogenolysis to produce n-hexane per kink site is determined by the slope
of the line in Fig. 3b representing hydrogenolysis and is $3 \times 10^{-28}$ moles of
n-hexane per kink atom per second.   This is almost an order of magnitude
higher than the slope in Fig. 3a which is $4 \times 10^{-29}$ moles of n-hexane per
step atom per second.   The observed low hydrogenolysis activity on the type of
stepped surfaces represented by Fig. 1b may be caused by thermally generated
kinks in the steps.[9] Since n-hexane formation and the formation of other
hydrogenolysis products must be the result of C-C bond scissions, it appears
that kinks are very effective in breaking C-C bonds in addition to C-H and H-H
bonds.   Thus, we have been able to identify two active sites of lower

coordination number on platinum surfaces, steps with C-H and H-H and kinks in steps with C-C, C-H and H-H bond breaking activities.

## THE CARBONACEOUS OVERLAYER

During studies of hydrocarbon reactions on the various platinum surfaces, the catalyst surfaces were always covered with a carbonaceous overlayer.[2-4] The coverage was almost independent of the pressure in the range of $10^{-4}$ to $10^5$ N/m$^2$ (unpublished results of this laboratory) but varied markedly with temperature and the molecular weight of the saturated hydrocarbon reactant molecules.[2] The higher the temperature and the reactant molecular weight, the higher the coverage reaching monolayer amounts for cyclohexane at 725K or n-heptane at 575K. Unsaturated hydrocarbons such as ethylene or benzene form complete monolayers at all temperatures and pressures and double layers under certain conditions[7,10] of the reactant adsorbed on the overlayer. The reactant dissociates and the overlayer consists of partially dehydrogenated hydrocarbon species.[2-4] This carbonaceous overlayer may be ordered or disordered depending on the platinum surface structure, the nature of the reactant and the hydrogen to hydrocarbon ratio used in the reaction studies. Several reactions are very sensitive to the presence of ordering on the overlayer.[2] Cyclohexene conversion to benzene is poisoned unless the overlayer is ordered and n-heptane to toluene conversion occurs only in the presence of an ordered overlayer.[3] Other reactions like the hydrogenolysis of cyclohexane occur readily even in the presence of a disordered overlayer.

## MODEL OF THE ACTIVE PLATINUM CATALYST

As a result of these experimental observations we would like to propose an atomic scale model of the platinum surface that is active in

the catalysis of hydrocarbon reactions. This model is shown in Figure 4. The surface is heterogeneous both in atomic structure and in composition. The steps and kinks are the active sites where C-H and H-H and C-C, C-H and H-H bond breaking occur, respectively.[4]

Although steps and kink sites exhibit higher binding energy for both hydrogen and hydrocarbons, the greatly increased rate of dissociation of hydrogen at steps[1] may keep these sites active. Even though these sites are areas of high catalytic activity, the product desorption probably occurs from areas covered with the carbonaceous overlayer. Diffusion on and desorption from the areas covered by the carbonaceous overlayer is likely since the binding energy of products should be lower there. The structure of the carbonaceous overlayer is important in more complex reactions like dehydrocyclization of n-heptane to toluene and in reactions where rapid deactivation of the catalyst occurs. Thus, two types of structure sensitivity are to be distinguished, step structure sensitivity and overlayer structure sensitivity. Some of the catalytic reactions may be sensitive to both of these structural features. Some of them may be sensitive to one, and some of the reactions may be structure insensitive.

Since much of the structure sensitivity of the catalytic reactions reported in the literature has been deduced from the dependence (or independence) of the reaction rate on the mean particle size of dispersed catalyst particles[11,12], caution should be exercized in interpreting the mean particle size dependence of the reaction rate in terms of our model. Some of the structural features may vary in proportion to changes of particle size (perhaps step density) while other structural features (step to kink site ratio, overlayer structure) may not. Our experimental

observations give foundation to the active site concept originated by Taylor[13] for the importance of the heterogeneity of atomic surface structure in catalysis. Our model also accommodates the structure sensitivity-insensitivity reaction classification proposed by Boudart.[12]

It should be noted that in our studies of platinum catalytic activity, the effect of the porous material used to support the highly dispersed metal particles/ in actual catalysts has not been taken into account. The support may influence the concentration and structure of the atomic steps and the carbonaceous overlayer. However, most of the catalytic reactions that are attributed to the platinum in supported platinum catalysts[14] have been reproduced on the single crystal surfaces in the absence of the support. Thus, we do not expect that our model of the platinum catalyst is markedly changed when any effects of the support are taken into account.

Although many of our reaction studies on single crystal surfaces are carried out at both low[2,3] ($10^{-4}$ N/m$^2$) and at high[5] pressures ($10^5$ N/m$^2$) the rate determining steps in mechanisms of the surface reactions might be expected to change with the over eight orders of magnitude change in pressure. We do not expect, however, that the structural features that control the platinum catalysis of hydrocarbon reactions will be less influential at high pressure than at low pressures.

The causes for the unique bond breaking activity of low coordination number sites (steps, kinks) on surfaces has been the topic of theoretical concern recently.[15-18] The extent to which the variation of chemical behavior at surface irregularities is the property of transition metals other than platinum is yet to be determined. While palladium stepped

surfaces exhibit higher heats of hydrogen chemisorption than the low
Miller Index surfaces,[19] gold exhibits oxygen and hydrocarbon chemi-
sorption properties that are identical on both stepped and low Miller
Index surfaces.[20]

The model of the catalytically active platinum surface also explains
the effect of selective poisoning that influences the product distribution
in hydrocarbon reactions so markedly. An impurity, a second metal com-
ponent or a poison like sulfur, present in small concentrations, will
block first the kink sites that are of the highest binding energy on the
heterogeneous surface; drastically reducing the C-C bond breaking
activity (hydrogenolysis rate), and only moderately affecting the catalytic
reactions where only C-H and H-H bond breaking is required (dehydrogenation
or hydrogenation). This way selectivity in product distribution may be
achieved.

It should be pointed out that the two important structural features
that characterize the heterogeneous platinum catalyst surface -- atomic
steps and carbonaceous overlayers -- also emphasize the relationship
of heterogeneous catalysis to homogeneous and enzyme catalysis. The
catalytic activity or bond breaking ability of clusters of atoms along
steps or near kinks on the heterogeneous metal surface may be correlated
with the reactivity of homogeneous systems with a single metal atom or
metal clusters surrounded by ligands. The metal-ligand catalysts will
break and form H-H and C-H bonds as do the metallic clusters, but
generally lack the ability to break C-C bonds which is possessed by
the highly uncoordinated kink atoms on metallic clusters. The presence
of ordered carbonaceous overlayers which apparently are necessary to

perform the complex rearrangement of large molecules, for example the dehydrocyclization of n-heptane to toluene, or to prevent catalyst deactivation may be correlated with the structure sensitivity and specificity so important in complex enzyme reactions.

## ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Fig. 1.   Low-energy electron diffraction patterns and schematic repre-
sentations of the mean surface configurations of three repre-
sentative platinum single crystal catalyst surfaces; (a) Pt($\bar{1}$11)
surface containing less than $10^{12}$ defects/cm$^2$, (b) Pt($\bar{5}$57) surface
containing $2.5 \times 10^{14}$ step atoms/cm$^2$ with an average spacing
between steps of 6 atoms, and (c) Pt($\bar{6}$79) surface containing
$2.3 \times 10^{14}$ step atoms/cm$^2$ and $7 \times 10^{13}$ kink atoms/cm$^2$ with an
average spacing between steps of 7 atoms and between kinks of
3 atoms.

Fig. 2.   Initial rate of cyclohexene dehydrogenation to benzene on platinum
single crystal catalysts with (a) increasing step density and
(b) increasing kink density at a constant step density of
$2.5 \times 10^{14}$ step atoms/cm$^2$.   The reaction conditions are
$5 \times 10^{-6}$ N/m$^2$ of cyclohexene, $1.0 \times 10^{-4}$ N/m$^2$ of hydrogen and
423 K catalyst temperature.

Fig. 3.   Initial steady state rates of cyclohexane dehydrogenation to
benzene (-0-) and hydrogenolysis to n-hexane (--$\Delta$--) on platinum
single crystal catalysts with (a) increasing step density and
(b) increasing kink density at constant step density of
$2.4 \times 10^{14}$ step atoms/cm$^2$.   The reaction conditions are
$5 \times 10^{-6}$ N/m$^2$ of cyclohexane, $1.0 \times 10^{-4}$ N/m$^2$ of hydrogen and
423 K catalyst temperature.   The rate of dehydrogenation is
constant at $2.8 \times 10^{-14}$ moles/cm$^2$/sec with steps present on the
surface, but is less ($0.3 \times 10^{14}$ moles/cm$^2$/sec) on the Pt($\bar{1}$11)
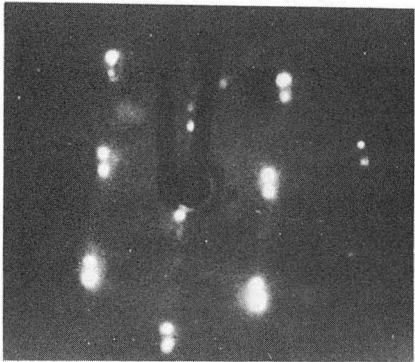surface (0.0 step density).   The rates of hydrogenolysis per

Fig. Cap., contd.

surface site are the slope of the lines representing hydrogenolysis

and are $3 \times 10^{-28}$ moles/kink atom/ sec and $4 \times 10^{-29}$ moles/step atom/sec.

Fig. 4.    Model of active platinum catalyst surface with a full carbonaceous
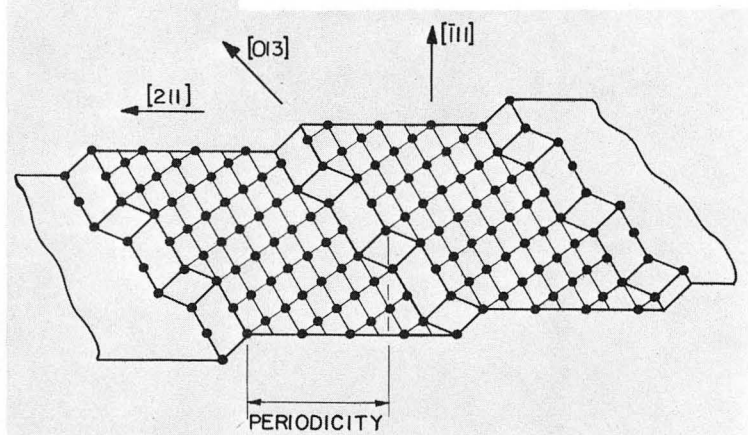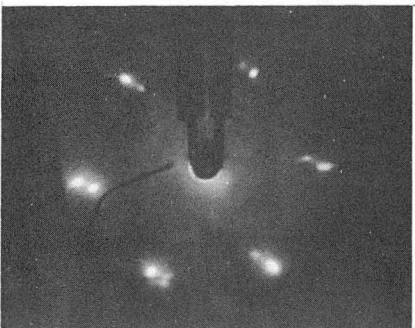
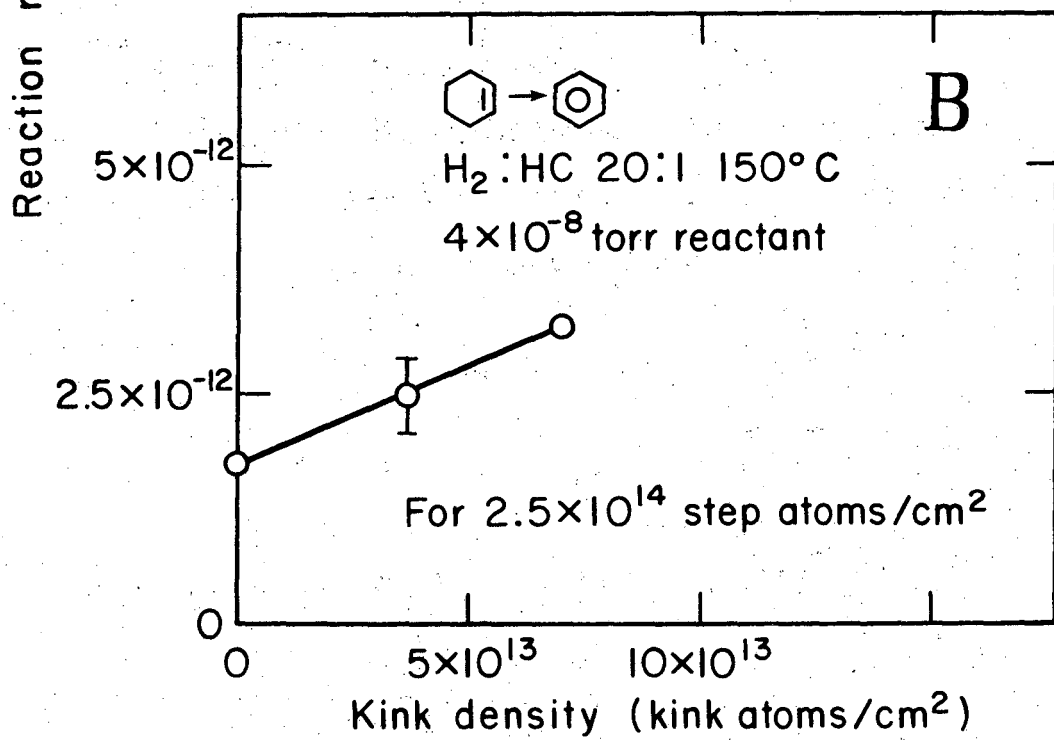overlayer showing exposed catalytic sites.
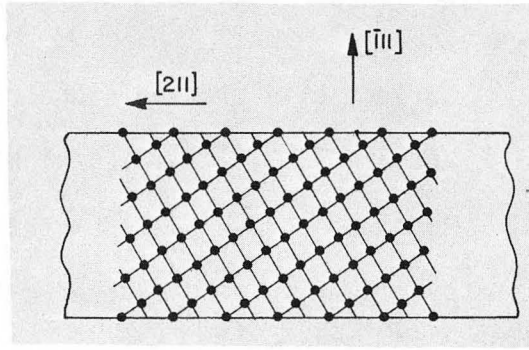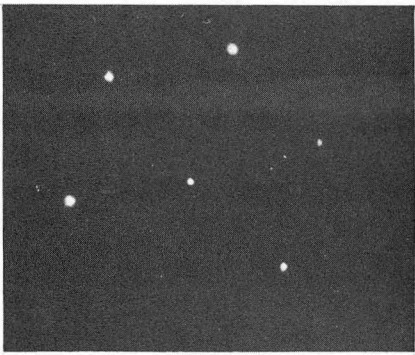
a) Pt - (1̄11)

b) Pt - (5̄57)

c) Pt - (6̄79)

XBB 758-5903

Fig. 1

Fig. 2

Fig. 3

Ordered Overlayer

Step

Kink

Terrace

Disordered Overlayer

Step

Kink

Terrace

XBL 733-5908

Fig. 4