

## Hydrocarbon Conversion Catalyzed by Platinum Surfaces.

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### Introduction.

Hydrocarbon conversion, specifically catalytic reforming is one of the most important industrial applications of catalysis. In the reforming process, saturated hydrocarbons are converted to aromatic hydrocarbons and linear alkanes are converted to branched alkanes as selectively as possible, because of the high antiknock quality of aromatic and branched hydrocarbons. Platinum metal catalysts are employed under reducing conditions for this conversion of aliphatic straight chain hydrocarbons to aromatic molecules (dehydrocyclization) and to branched molecules (isomerization), and also for hydrogenation on a large scale in the chemical and petroleum refining industries. Dehydrogenation involves C-H bond breaking only, while hydrogenolysis necessitates the breaking of C-C bonds. Dehydrocyclisation must involve the complex process of dehydrogenation and ring closure. The turnover frequencies of the hydrogenation and dehydrogenation reactions are about  $0.1$  to  $10 \text{ sec}^{-1}$  under usual conditions of  $400$  to  $600 \text{ K}$ , atmosphere pressures of reactant and excess hydrogen, and those of the dehydrocyclisation and isomerization reactions are about  $10^{-4}$  to  $10^{-2} \text{ sec}^{-1}$ . After suitable preparation the Platinum catalyst selectively catalyzes the complex low turnover frequency reactions while blocking the simpler high rate dehydrogenation and hydrogenation reactions, and the slower but unwanted hydrogenolysis reaction. Platinum single crystals with various crystal faces, can be prepared with uniform and ordered surface structures. Surface science techniques like Low-Energy Electron Diffraction can be used to determine the structure of these single crystals. The idealized atomic surface structures for the flat Pt(100) and Pt(111), the stepped Pt(755) and the kinked Pt(10,8,7) surfaces is shown in figure (1). Two closest packed Platinum crystal faces of the highest atomic density, are the flat surfaces where each Platinum atom is surrounded by six and four neighbors. Stepped crystal faces show close packed terraces several atoms in width, separated by one atom high atomic steps. The lowered coordination of the step atoms accounts for several catalytic features. These steps can have kinks, and atoms at these ledges can have even lower coordination.

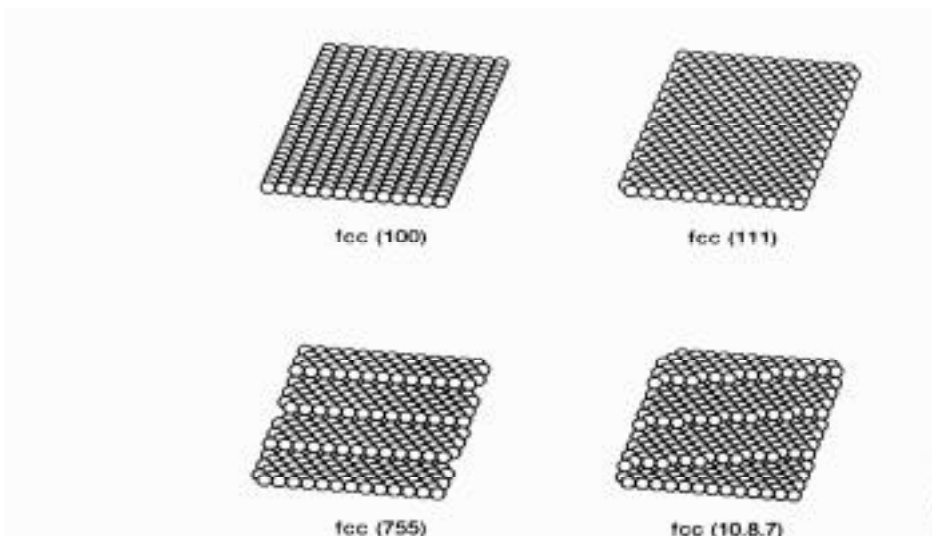


Figure 1

Worth mentioning is the fact that by suitable surface preparation, the structure and concentration of steps and kinks, along with the structure and width of the terraces can be varied.

### **Structure Sensitivity of Catalytic Reactions.**

Different platinum surfaces show different activities for the same hydrocarbon reactions. In figure (2a), the flat (111) and (100) surfaces are compared for the dehydrocyclisation of n-heptane. The hexagonal crystal face is 5 times more active than the square (100) face for this reaction. In figure (2b), the selectivity of the stepped platinum surface is compared with the (111) surface under identical conditions. The stepped surface with terraces at least five atom rows wide was found to be the most active for dehydrocyclisation. The difference in the activities between the best and least active platinum surfaces that were studied is at least ten-fold. The hexagonal surface structure enhances the rate, and the presence of steps increases the activity further by facilitating the C-H bond breaking, one of the elementary steps of this complex reaction.

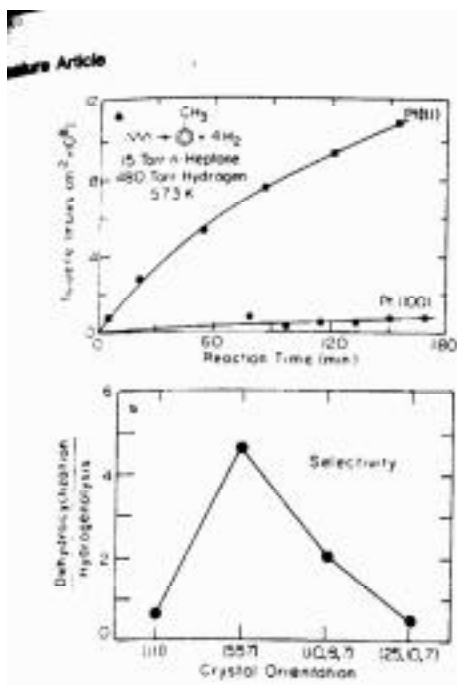


Figure 2a

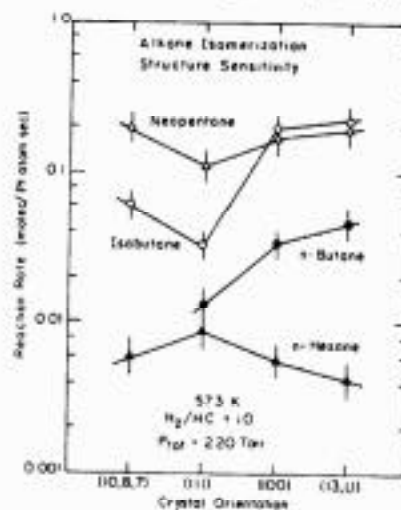


Figure 5. Structure sensitivity of alkane isomerization reactions catalyzed over platinum single-crystal surfaces.

Figure 2b

It was observed by researchers that kinks promoted both C-C and C-H bond scission and were detrimental to dehydrocyclisation. The C-C bond scission enhances hydrogenolysis activity, which competes with dehydrocyclisation. If the terraces are narrower than four atomic widths thus neither the reactants nor the product molecules can fit, and so the activity declines. Also if the terraces are wider than six atoms, the activity declines probably because neither the reactants nor products can fit. In another reaction, the isomerization of iso-butane, the square and flat (100) surfaces were found to be more active, than the flat hexagonal (111) crystal face. Steps again seemed to further improve catalytic activity. Because molecular rearrangements must also occur in addition to bond breaking, it is not surprising that terrace structure exerts such an important influence on the reaction path that the adsorbed molecules are likely to take. In summary the order of magnitude variation between crystal faces with the best and worst activity is almost an order. It is obvious that preparation of catalysts with appropriate surface structures allows a high degree of reaction selectivity and optimum activity for hydrocarbon conversion. Also important to understand is that the difference in chemical behavior of terrace, step and ledge atoms arises not only from their different structural environment but also from

their different electronic charge densities that result from a variation of the local atomic structure.

### **The Reactivity and Composition of the Strongly Adsorbed Carbonaceous Deposits on Platinum.**

When the working platinum catalyst surface is examined after carrying out any of the hydrocarbon conversion reactions, it is always covered by a near - monolayer amount of carbonaceous deposit. Restart reaction studies and reaction rate studies using Platinum surfaces precovered with carbonaceous over layers containing carbon-14 were used to investigate the catalytic activity and selectivity of carbon covered Platinum in hydrocarbon hydrogenation, dehydrogenation and skeletal rearrangement. As shown in figure (3), Carbon -14 labeled ethylene was chemisorbed as a function of temperature on the flat Pt (111) crystal face. Carbon -14 is a  $\beta$ -particle emitter. The  $\beta$ -particle detector was used to monitor its surface concentration as a function of time during the catalytic reaction. The hydrogen content of the adsorbed organic layer is determined by detecting the amount of desorbing hydrogen with a mass spectrometer. The (H/C) ration of the adsorbed species was determined from hydrogen thermal desorption. The amounts of preadsorbed alkenes that could not be removed by subsequent treatment in 1 atm of hydrogen represents the irreversibly adsorbed fraction. The adsorption reversibility decreases markedly with increasing adsorption temperature, as the surface species becomes more hydrogen deficient. The irreversibly adsorbed species have long residence times, of the order of days. Quantitative hydrogen thermal desorption studies were carried out as a function of surface structure and reaction temperature to determine the composition and the energetics for sequential dehydrogenation of carbonaceous deposits derived from a variety of adsorbed hydrocarbons including isobutane, neopentane, n-hexane, and cyclohexene.

Figure 3

Carbon monoxide adsorption - thermal desorption methods were developed to titrate uncovered Platinum surface sites ,before and after reaction rate studies. The uncovered -

site concentrations were correlated with the total surface carbon coverage as determined by Auger electron spectroscopy and the catalytic activity and selectivity of carbon-covered Platinum. These experiments together with results from related structure sensitivity, thermal desorption, deuterium exchange and radiotracer studies revealed that the primary role of the disordered carbon deposit is that of a non selective poison which blocks platinum surface sites from incident reactant molecules. The carbonaceous deposit stores and exchanges hydrogen with reacting surface species and provides desorption sites for product molecules. The growth mechanism of this carbonaceous deposit is sensitive to the structure of the reacting hydrocarbon and its morphology appears to vary continuously from two dimensional at temperatures less than 550 K to three dimensional for temperatures higher than about 600 K.

#### **Molecular Working Model of the Platinum catalyst.**

As a result of studies a molecular model of the working Platinum catalyst was proposed as shown in figure (4).

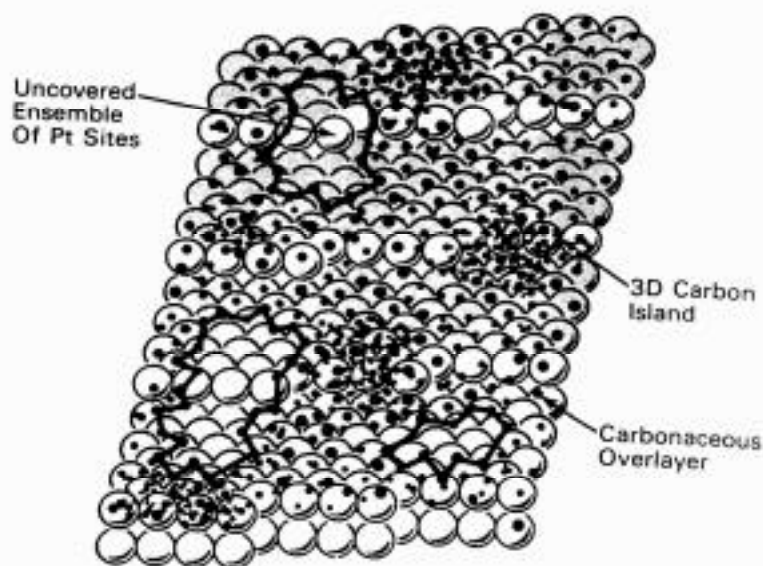


Figure 4

Auger electron spectroscopy revealed that during steady state hydrocarbon conversion, platinum surfaces always become covered with about one or more monolayers of strongly bound carbonaceous deposits. In the absence of other chemical additives, the formation of this carbon deposit must be considered as a fundamental feature of the catalytic hydrocarbon chemistry. The deposit resulted from the activated nucleation and growth ( $E_a \sim 10\text{-}20$  kcal/mole) of unreactive polymeric species with an average hydrogen content of about 1.0-1.5 hydrogen atoms per surface carbon atom. Since the binding energies of chemisorbed hydrocarbons appear to be lowered on carbon covered Platinum surfaces, it is likely that the deposit can also provide desorption sites for product molecules. Thus, the presence of carbonaceous deposit makes a catalyst out of Platinum that readily exchanges hydrogen with reacting species and facilitates the release of product molecules. Most catalyzed reactions could not occur either on the bare metal surface or on the surface that is completely covered by the irreversibly deposited organic layer. Hydrocarbon conversion must occur on the bare metal islands that are kept clean by the presence of hydrogen in the reaction mixture. However the intermediates or the products which form may not readily desorb from the bare metal sites because they are too strongly bound. It is likely that these species diffuse over onto the carbonaceous overlayer from which desorption commences perhaps with the additional transfer of hydrogen. By providing sites at which the reaction products are bound only weakly, the carbonaceous overlayer facilitates the desorption of the organic molecules. It should be noted that the active carbonaceous deposit that contains CH and CH<sub>2</sub> fragments stores about 10 times more hydrogen than the clean metal surface, which could be made available by promoters or by other transition metals that were used as alloying agents. Carbon monoxide adsorption-desorption studies revealed that a small concentration of uncovered Platinum sites always persisted in the presence of the carbon deposit. The uncovered sites appeared to exist in the form of patches or ensembles that contained several contiguous surface atoms. The concentration of these sites decrease with increasing reaction temperature. The existence of these exposed, multi-atomic sites is essential to rationalize the high selectivities for hydrogenolysis and aromatization, which are displayed by carbon covered Platinum. Another important feature of the catalyzed hydrocarbon reactions was the long surface residence times of the dissociatively

chemisorbed intermediates that were of the order of seconds. Within this residence time the adsorbed species could diffuse over long distances (*e.g.*  $10^{-8}$  -  $10^{-3}$  cm) and visit many different types of surface sites. All sites that are contained in an uncovered patch can therefore become available for sequential bond breaking and skeletal arrangement. It may even be possible for the adsorbed species to visit adjacent ensembles by diffusing over, around, or through the strongly bound carbonaceous deposit.

### Catalysis in the Presence of a strongly Adsorbed Overlayer.

The structure of the adsorbed hydrocarbon monolayers was studied in detail using LEED and HREELS. In the temperature range of 300-400 K, adsorbed alkenes form alkylidene molecules that are shown in figure (5).

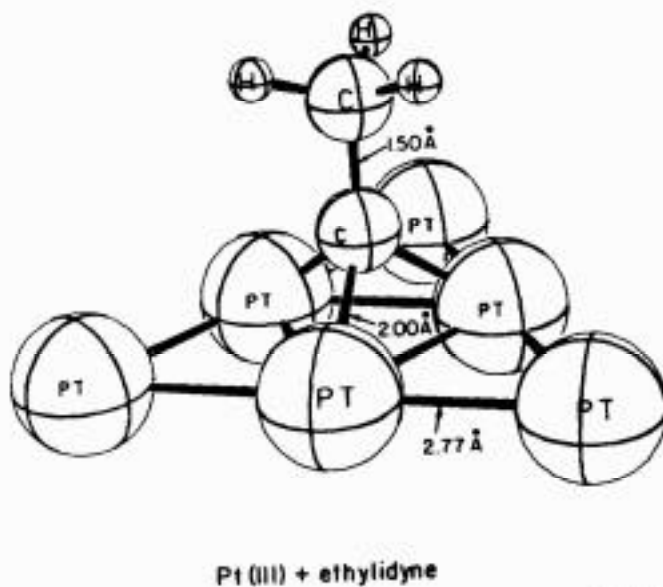


Figure 5

The C-C bond closest to the metal is perpendicular to the surface plane, and its 1.5 Å length corresponds to a single bond. The carbon atom that bonds the molecule to the metal is located in a threefold site equidistant 2.0 Å from the nearest metallic neighbor. This bond is appreciatively shorter than the covalent metal-carbon bond, and is indicative of multiple metal-carbon bonds of the carbene or the carbyne type. An example of this

type of reaction where the metal is covered by an overlayer is the hydrogenation of ethylene. This reaction is structure insensitive. One model that explains these results has been proposed. The hydrogen atom is transferred to the ethylene molecule that is weakly adsorbed on top of the ethylidene and in the second layer perhaps by forming an ethylidene intermediate. Thomson and Webb first proposed this model of the hydrogen transfer from hydrocarbons to ethylene. This mechanism is of the Eley-Rideal type and is characterized by low activation energy and structure insensitivity. There are other mechanisms that have also been proposed. At higher temperatures the rate of rehydrogenation of  $C_2H_3$  is significant and the bare metal becomes available in part for  $C_2H_4$  hydrogenation. During the electrochemical hydrogenation of  $C_2H_4$ , the Platinum surface is covered by a layer of hydrogen atoms that react rapidly with the approaching  $C_2H_4$  and do not permit the formation of ethylidene.

The organic overlayer may also serve as a template to orient or align the molecules. LEED surface crystallography and HREELS studies of the structure of these monolayers indicate that their structural integrity is preserved at temperatures as high as 400 K, thus their presence only allows us to carry out various specific reactions below this temperature.

#### **Implications for Alloy Catalysis with Platinum.**

As compared to pure platinum, bimetallic alloys such as Pt-Re, Pt-Au, Pt-Ir, offer superior activity, selectivity and poison resistance in catalyzed hydrocarbon reforming reactions. The improved stability of the Group VIII - Group IB alloys can be easily rationalized in the context of the model of the working metal catalyst. Since Group IB metals do not form strong bonds with hydrocarbon adsorbates, the concentration of carbonaceous fragments with high-metal organic bond multiplicity is reduced.

Polymerization of the adsorbed species that is required for the formation of carbonaceous deposits probably still can and probably does occur at exposed group VIII sites. However since these sites are isolated and mostly surrounded by a matrix of inactive metal sites, the removal of carbonaceous deposit by rehydrogenation can be accelerated. The influence of gold on hydrocarbon conversion catalysis was recently studied by evaporating gold on Platinum single crystals. This Pt -Au alloy shows different activity and selectivity for the conversion of n-hexane as shown in the figure(6).

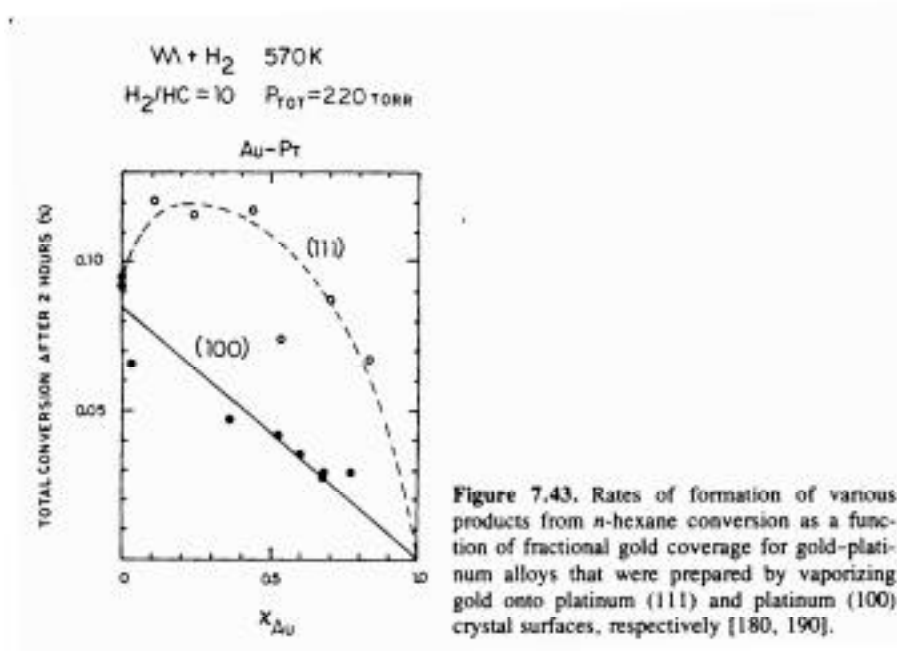


Figure 6

Isomerisation activities increase substantially as compared to those for clean platinum, whereas the aromatization and the hydrogenolysis rates decrease exponentially with increasing gold surface concentration. The geometric distribution of the Platinum sites that are present in the Pt (111) surface can explain this. Substitution of gold atoms dilutes the surface Platinum atoms such that the high coordination threefold Platinum sites are eliminated much faster than the twofold bridge and single atom top sites. This change in the distribution of the available reaction sites is frequently called the ensemble effect. As a result, catalyzed reactions that involve adsorption and rearrangement at threefold sites are eliminated, whereas reactions that require one or two atom sites are attenuated much more. This is called the high -coordination site elimination model. The surface structure sensitivity of alloying is obvious when the Pt (100) crystal face is used with gold. The (100) surface has a square unit cell that contains fourfold bridge and top sites, and unlike the (111) surface it does not have threefold sites. As shown in the figure above, when this surface is alloyed with gold, all reaction rates decline in proportion to the concentration of inactive gold on the Pt (100) surface when *n*-hexane was used.

### **Building of Improved Platinum Catalysts.**

The process of atomic scale catalysis by Platinum is fairly well understood. A lot of researchers are now trying to build improved catalyst systems. Additives are being used

to alter the surface structure beneficially, to reduce the amount of carbon deposit and to slow down its conversion to the graphitic form. As mentioned above, the addition of transition metals enables the catalytic systems to be operated at higher reaction temperature to obtain higher reaction rates. They show slower rates of deactivation and can be more selective for a given chemical reaction than the one component catalyst. Also, one of the major challenges in preparing these scientifically tailored metal catalysts is to deposit the metal particles with the specific surface structure needed to obtain optimum reaction selectivity. The structural and chemical interactions of the support with the metal are important parameters in this direction and could induce charge transfer toward or away from the metal that could beneficially alter its catalytic properties. There are attempts to prepare metal catalyst particles with uniform size and equal distances of separation by using microelectronic circuitry fabrication technology. Using electron beam lithography, metal particles can be deposited in ordered arrays on silica or alumina substrates.

In conclusion I would like to say that the building of new high technology catalysts using a molecular level understanding of the process is becoming very popular with researchers at large. The fuel and chemical industries depend largely on the development of new catalysts for tapping new materials to produce fuel or chemical feedstocks.

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