CHAPTER III

THEORY

3.1 Introduction

The concept of catalysis as a method of controlling the rate and direction of a chemical reaction has captured the imagination of scientists and technologists. Ideas of what constitutes a catalyst and the mechanism of catalytic activity have undergone continuous refinement since, spurred by the enormous industrial importance of catalysts as illustrated by the variety of catalytic processes characteristic of modern petroleum refineries and of the chemical industries. Most of these processes involve solid catalysts, and an understanding of catalysis from both the theoretical and practical point of view is essential to chemical engineers and chemists.

A basic concept is that a catalyzed reaction involves the transitory adsorption of one are more of the reactants onto the surface of the catalyst, rearrangement of the bonding, and desorption of the products. This leads to three groups of theories of catalysis [25] :

1. The geometrical theories emphasize the importance of the correspondence between the geometrical configuration of the active atoms at the surface of the catalyst and the arrangement of the atoms in the portion of the reacting molecule that adsorbs on the catalyst. An aspect of the geometrical approach of great usefulness is the observation that reaction selectivity may be markedly altered by the number and arrangement of sites required for competing reactions, which leads to the concepts of the importance of "ensembles" or specific grouping of atoms at the catalyst surface and structure sensitivity as affected by particle size, alloying, and other variables.

2. The electronic theories proceed from the fact that chemisorption involves the distortion or displacement of electron clouds, and they attempt to

2. The electronic theories proceed from the fact that chemisorption involves the distortion or displacement of electron clouds, and they attempt to relate activity to the electronic properties of the catalyst. This may be in terms of the electronic structure of the solid as a whole, or in terms of the orbitals around individual atoms. More recently attention has been directed to the properties of atoms as individual entities and to the electronic effects caused by the nearest neighbors in the solid rather than by the solid as a whole. In many cases it is difficult to separate geometrical effects from localized electronic effects.

3. The above two theories represent primarily a physical approach in that the catalyst is regarded as essentially a static material having the property of converting reactant to product. The chemical approach on the other hand regards the catalyst as a chemical intermediate that forms an unstable, surface, transitory complex with the reactants. The rates of these processes and the structures formed are assumed to obey chemical principles. This leads to the concept that the maximum rate is obtained when the bonds between the adsorbed complex and the catalyst surface are neither too strong nor too weak. This is a useful concept but limited in that the energetics are generally unknown, more than one intermediate is frequently involved, and one is more generally concerned with selectivity rather than activity as such.

3.2 <u>The role of catalyst surface morphology in activity and selectivity [26]</u>

Over 30 years ago it was conventional to describe the differences in performance between similar catalysts in terms of "electronic" and " geometric" factors. To avoid ambiguities, because these terms were tacitly narrowed down to imply only collective parameters as used in physics of electrical conductivity or magnetism, a convenient classification of crystallite requirements of relevance to catalyst selectivity was developed.

Bond Strength : The formation of chemical bonds between atoms of the substrate and the catalyst surface and their rupture at a later stage are essential steps in all heterogeneously catalyzed reactions ; that is, if the bond is too weak, no chemisorption will take place, and if too strong, the desorption step will become too slow. For a given reactant, the main variables on the catalyst side that influence the bond strength are the chemical identity and the valence of the adsorbing atom (s). The enormous differences in catalytic performance between platinum and gold illustrate the effect or electronic configuration on the bond strength and thus on the activity. For a given metal atom and a given adsorbate, the bond strength is to some extent also influenced by the environment, in particular the chemical nature of the nearest neighbors. This is the essence of the ligand effect in catalysis, which is important in bimetallic catalysts or catalysts with adsorbed compounds such as sulfur or carbon.

Coordination : The coordination requirement of a reaction catalyzed by an isolated surface atom is defined as the minimum required number of coordination sites per surface atom. Blakely and Somorjai [27] showed with single metal crystals that flat faces have a significantly lower activity than terraces, since atoms in step, kink, edge, and corner sites exhibit a higher degree of coordinative unsaturation. These effects are partly responsible for the fact that crystallite faces are efficient in C-C bond breakage, while C-H and H-H bond scissions are more effective on crystallite corners and edges ; for example, several atomic ligand sites necessary for the cyclization are available on corner and edge atoms of low coordination number.

Ensemble (site): The ensemble requirement is the minimum required number of contiguous surface atoms of the element able to form bonds with the end adsorbate. This definition accepts the conjecture that for a specific reaction mechanism, the required active center on the catalyst surface can be either a single metal atom or an ensemble of several adjacent atoms as shown in Fig. 3.1. The ensemble requirement for a certain reaction can be studied by diluting the metal in an alloy with a chemically inert metal, thus reducing the concentration of large ensembles of the active metal. An example is that for Pt-Sn alloys. At low temperatures (<450 °C), multiple site reactions such as isomerization, hydrogenolysis, and 1, 5 - dehydrocyclization do not occur because the majority of ensembles comprise single atoms, hence the product aromatic content is low. But at higher temperatures (500 °C), 1,6-

dehydrocyclization, which has a lower site requirement than the former reactions, occurs at a sufficiently fast rate , thus improving aromatic yields.

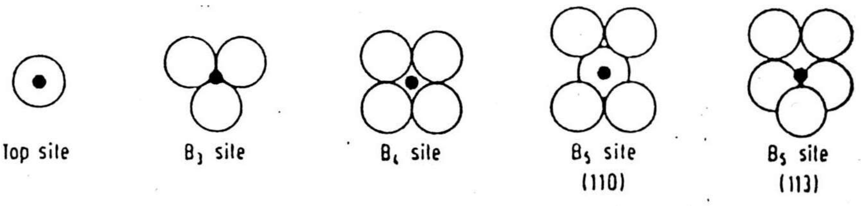


Figure 3.1 Examples of adsorption sites: black dot represents adsorbate (26).

Template: This describes the stereochemical conditions a catalytic center must fulfill in order to render the reaction " stereo specific " or " shape selective, " that is, capable of preferentially producing one of several isomers: The general consensus now is that the ensemble effect is more important than the others . Although the coordination requirement is extremely important because different reactions are favored on different parts of the crystallite surface (i.e., corner and edge or face atoms) - that is, at positions of minimum activation energy - the selective adsorption of poisons on these sites may have important effects on selectivity.

Let us assume that a molecule interacting with a catalyst surface can react along different reaction paths resulting in different products, and that each of these paths is known in every atomic detail. We should then be able to define for each path the requirements with respect to the chemistry and geometry of the catalyzing sites for the reaction to proceed. If the catalyst fulfills the requirements of only one of these paths, it is clear that only this reaction will take place.

3.3 Supported metal catalysts [28]

Metal catalysts are of particular interest for reactions involving hydrogen, such as hydrogenation, hydrogenolysis, and catalytic reforming. The relative rates of parallel or sequential reactions are affected by the number and arrangement of sites on the catalyst. These in turn may be affected by particle size ; by the use of alloys; by kinks, steps, and other crystal imperfections; and by the blockage of some of the sites by deliberately added poisons or by accumulation of carbonaceous deposits. There is also a possible role of the support in influencing the properties of the metal.

3.3.1 Metal activity

Maximum catalytic activity is associated with rapid but not too strong chemisorption of reactants. The heat of adsorption of gases such as oxygen, nitrogen, hydrogen and ammonia, ethylene, and acetylene on metals decreases in a continuous manner as one proceeds across groups VB, VIB, VIIB, and $VIII_1$, $VIII_2$, and $VIII_3$ of the metals in either the first, second or third transition series. Group IB metals do not readily adsorb some gases, e.g., hydrogen, since the dissociation of hydrogen is the rate-limiting process and this has a high activation energy. Hydrogen atoms can be chemisorbed under conditions where molecular hydrogen is not chemisorbed.

Hydrogenation reactions are carried out with a wide variety of reactants. the most active metallic catalysts are those in group VIII. This is readily rationalized in terms of adsorption effects; the strength of adsorption on, for example, group IB and VIB metals is too strong, that on IB metals is too weak or nonexistent. Within group VIII relative activity differences vary with the nature of the reaction and require a more detailed examination of the mechanism.

3.3.2 Alloy catalysts

Studies of alloy catalysts were of considerable interest in the 1950s in conjunction with the burgeoning electronic theories of catalysis, but then fell into disfavor. More recently they have been revived, stimulated by the industrial importance of bimetallic catalytic reforming catalysts and a more sophisticated fundamental understanding of the structure of alloys and the factors affecting the distribution of alloy components between the surface and the bulk. Of particular interest have been studies of a binary alloy of an active metal and of an essentially inert metal such as nickel-copper alloys and, more generally, of a mixture of a group VIII metal and a group IB metal.

3.3.2.1 Reactions on alloys

Some of the early work with alloy catalysts was based on the concept that an alloy might exhibit some type of averaged property of its components. More specifically, in the rigid-band electronic model of binary alloys it was assumed that a common band would be formed from the two constituents. At an alloy composition at which holes in the d band became filled, there might occur a sudden shift in catalytic properties since the adsorption characteristics of the alloy might change markedly at this point. This view point is now clearly incorrect, at least for those systems most widely studied, such as nickel-copper, palladium-silver, and palladium-gold, and most probably for group VIII-group IB systems in general. This is shown by alloy spectra and a variety of reaction studies.

In these alloys the atoms do not lose their individuality, and it is more fruitful to consider the structure as a group of individual atoms, at least as a first approximation. With nickel-copper, for example, the activity is ascribed to the arrangement of nickel atoms only, and the copper is regarded as an inert diluent. This essentially geometrical concept may be modified to some extent, to consider that the nearest neighbors to a nickel atom may influence its adsorptive properties and hence catalytic behavior; i.e., there may be an electronic effect. Sachtler terms the first the ensemble effect and the second the ligand effect. In many cases it is difficult to separate the contributions of the two. The effects observed with alloy catalysts can be rationalized primarily in terms of ensemble (geometrical) effects, but it seems necessary to involve ligand effects to explain some of the changes observed in reactivity.

3.3.2.2 Site - Number Requirements (Geometrical effects)

An underlying concept in catalysis for the last several decades in that some reactions require adsorption on a group of sites or a " multiple site" in order to occur. Such a group of sites has been termed an ensemble by Kobozev and Dowden and a multiplet by Balandin, and the concept has been visualized and developed in a variety of ways by different investigations. Of great significance is that this allows a rational approach to the tailoring of catalysts to achieve high selectivity when more than one reaction pathway may occur; it also explains a variety of poisoning effects on selectivity. If geometrical considerations are the predominant effect, then dilution of an active metal with an inactive metal should decrease the rate of those reactions requiring the greatest number of nearby sites relative to the rate of a reaction requiring the least number of sites.

3.3.2.3 Factors influencing ensemble effect in bimetallic catalysts [26]

The catalyst activity, stability, and selectivity of some bimetallic catalysts usually deviate from additive behavior predictable from the individual metal properties. Guczi [29] reviewed the factors controlling hydrocarbon reactions catalyzed by supported and unsupported alloys, emphasizing that ensemble effects are usually dominant, arising from the necessity to have a critical size of the assembly of atoms in the active "landing" site for the incoming and reacting molecules; thus alloying is the main controlling factor for different reaction routes.

A classic example of the ensemble effect in alloy catalysis is given by Sachtler and Somorjai [30], who showed that cyclohexane dehydrogenation goes through a maximum at an intermediate composition of Au (inert) in Pt (active) under atmospheric conditions on a single crystal. For pure platinum the activity is low due to carbonaceous deposit formation, which, like hydrogenolysis, is fast due to the availability of ensembles for multiple bond formation [29]. Addition of Au reduces the self-poisoning reaction, which cannot occur on small ensembles, thus causing an increase in reaction rate. At high Au compositions, the activity declines because ensembles become too few and too small to catalyze cyclohexane dehydrogenation. From a deactivation viewpoint, it has been suggested that the role of the second metal is to reduce ensemble sizes below that necessary for C-C bond fission and "deep hydrogenation," which produce coke precursors . Another example is the increase in isomerization and dehydrocyclization selectivity (relative to hydrogenolysis) on alloyed catalysts because of the smaller site requirement for these reactions .

Ensemble effects can be modulated by several other factors (Fig. 3.2). Surface segregation of one metal and site elimination by blocking are two well-known effects . Matrix and strong metal-support interaction effects (SMSI) influence the state of dispersion and stability of bimetallic catalysts under reaction or rejuvenation conditions [29]. The effects of dispersion and alloying are two of the more important factors. As mentioned previously, ensemble sizes on single metal crystallites generally decrease with increasing dispersion; consequently the proportion of multiply bonded intermediates (which can be coke precursors), the catalyst experiences lower metallic coking rates. The increase in the amount of lower coordination number metal atoms causes an increase in the turnover number (TON) of hydrogenolysis, whereas the TONs for exchange and dehydrogenation rates remain constant.

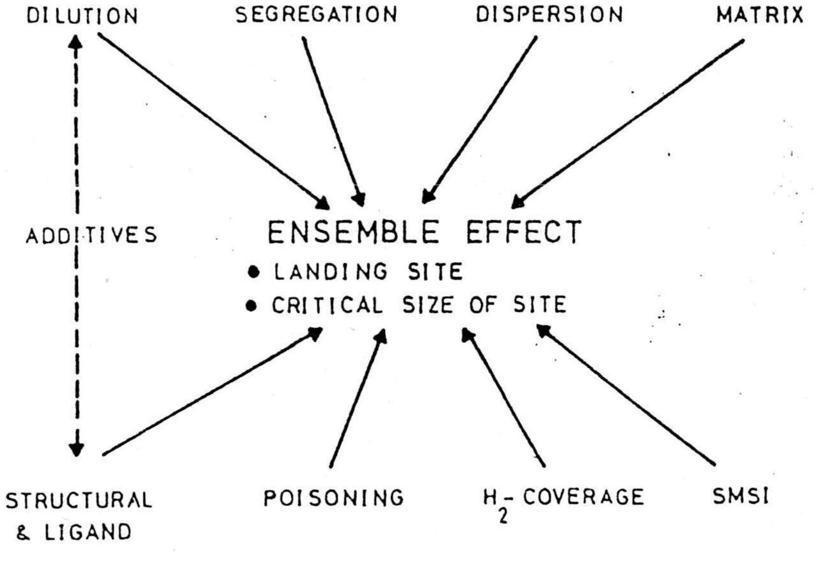
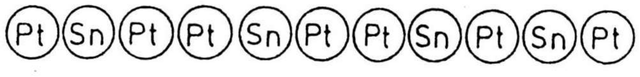


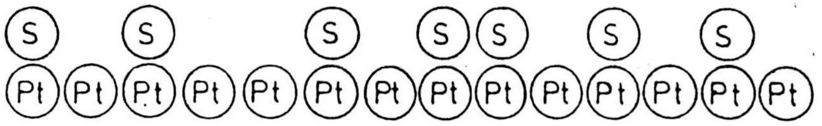
Figure 3.2 Factors affecting the ensemble effect in bimetallic catalysis (26).

However, when alloying is performed, the surface will contain atoms of an inactive metal; hence the active metal ensemble size will diminish, sometimes without any serious change of the surface geometry, crystallite size, etc., and consequently the rates of hydrogenolysis and metal site coking drastically decrease . Thus, the change in ensemble size caused by Increased dispersion or alloying in an inactive metal leads to opposite effects on hydrogenolysis TON.

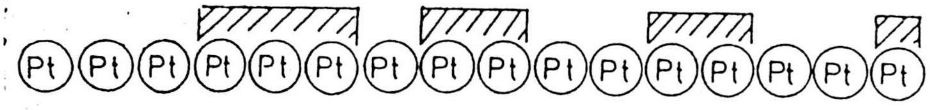
The surface geometry of a Pt/Al_2O_3 catalyst is shown in Fig. 3.3. It shows the intimate relationship between ensemble size, selective poisoning by an additive, and deactivation by carbonaceous fragments. In each case, the result is a dilution in the number of large active ensembles of platinum. The decrease in hydrogenolysis reaction rates due to



A. Alloying with inactive metal (tin).



B. Poisoned by sulfur.



C. Deposits of coke.

Figure 3.3 The surface geometry of a Pt/Al_2O_3 catalyst (26).

coke has been noted by Barbier et al. , Trimm , and Parera et al.. The decrease in hydrogenolysis rate due to sulfur has been noted by Hayes et al. , Apesteguia et al. , and Van trimpont et al. . This advantageous hydrogenolysis suppression is used industrially on Pt-Re/Al_2O_3 catalysts (Fig. 3). Sulfur, firmly bound to Re, blocks the cracking power of Re and dramatically diminishes the size of platinum ensembles . This leads to an observed enhancement of all reactions running as and through dehydrogenation (e.g., single-site dehydrocyclization and isomerization) ; thus Pt-Re+S alloys behave similarly to Pt-Sn alloys because the sulfided rhenium acts as an inert diluent .

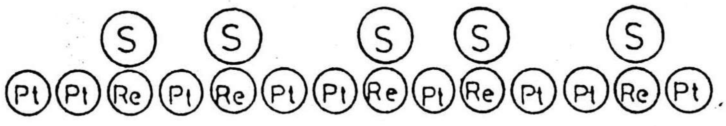


Figure 3.4 Schematic illustrating the stabilization of the catalytic activity of Pt-Re catalysts in the presence of sulfur (26).

In the case of Pt-Ir alloys, both components are very active. The improved activity (aromatic yield) of these catalysts over the Pt-Sn or Pt-Re+S (sulfided Pt-Re) alloys is due to the high dehydrocyclization activity of the iridium component . The higher hydrogenolytic activity due to the iridium component is controlled by continuous addition of sulfur in the feed (0-10 ppm), thus reducing the Pt-Ir ensemble sizes on the catalyst , but still improving the selectivity for the single-site 1,6-dehydrocyclization reactions.

3.4 Role of bimetallic catalysts in catalytic hydrogenation [31]

In the 1950s there was a strong interest in heterogeneous catalysis by alloys, due to the alleged validity of the Rigid Band Model (RBM). According to this model, upon alloying, the holes in the d-band of transition metals could be filled and as a consequence the chemisorption and adsorption would be considerably influenced. This interest ceased as results contradicting the RBM model were accumulated.

Since the late 1960s there has been a renaissance of interest in alloy catalysis due to the discovery of the superior properties of the Pt-Re/Al_2O_3 catalyst. At the same time, considerable progress was achieved both in the characterization of alloy surfaces and in the quantum theory of alloys. The catalysis by alloys has been reviewed by many groups of researchers [32-35].

The present status of knowledge about catalysis by alloys can briefly be summarized as follows:

1. The composition of the surface of equilibrated alloys can differ substantially from that of the bulk, and chemisorption or the catalytic reaction itself can induce additional changes in the surface composition.

2. The selectivity patterns are mainly determined by the ensemble size effect, but a ligand effect may also occur simultaneously. It is now generally accepted that the individual surface atoms retain their character in alloys, and their catalytic properties are mainly determined by their nearest neighbors.

3. Alloys often exhibit catalytic activity than either of their constituents because of a lower degree of poisoning. This can result in higher catalyst stability and in a change in selectivity for a given reaction. Typically, hydrogenation is not significantly suppressed by alloying.

If metal atoms are supported on an "inert" carrier, some additional factors become operative. The particle size is normally diminished, thus the ensemble size is generally decreased [29]. As a consequence, the small particles easily interact with the coordinatively unsaturated sites (CUS) resulting in an incomplete reduction of the metals. Furthermore, the texture of the metal particles also changes since the number of kinks and step sites increase as compared to the terraces. Finally, in a highly dispersed system, the d-band structure also changes due to the small number of metal atoms in the particles.

In a bimetallic system, in addition to the dispersion effect, there is a further narrowing of the d-band structure. Another important factor is that the ensemble size can be further diminished at a given particle geometry and, finally, dispersion of a bimetallic catalyst can be achieved nearly on the atomic scale if one component is "grafted" onto the support [27].

In the context of supported alloys, the following factors should be considered:

1. ensemble size variation
2. particle size effect, dispersion
3. matrix effect
4. change in hydrogen coverage and in the structure adsorbed hydrogen
5. separation of bimetallics into components
6. metal-support interaction (MSI)
7. suppression of self-poisoning reactions

3.5 Ethylene [36]

Ethylene, in the Geneva nomenclature "ethene" ($H_2C=CH_2$), is the lightest olefinic hydrocarbon. At ambient conditions it is colorless, flamable gas of the same density as nitrogen with aslightly sweet odor. ethylene does not freely occur in nature and yet represents the organic chemical consumed in the greatest quantity worldwide. It is the basic chemical raw material for a large variety of industrial products especially polyethylene.

The importance of polyethylene for the chemical industry is founded on its reactivity due to the double bond in its molecular structure. Although less reactive than acetylene but simpler, safer, and less costly to produce and further convert, ethylene has largely replaced acetylene as the basic building block for an entire branch of industrial organic chemistry.

3.6 Selective hydrogenation of Acetylene

The field of petrochemicals has undergone considerable expansion since the early 1950s. The replacement of natural products such as cotton, word and rubber by plastics, synthetic fibers and synthetic rubbers, has required the production of larger and larger quantities of raw materials. A substantial proportion of these raw materials, whose essential characteristic is their chemical reactivity and hence an unsaturated nature, is produced by steam cracking.

Steam cracking is a process that takes place at high temperature (about 800 °C) and in the presence of steam [37]. It is carried out at substantially atmospheric pressure, but the product is then compressed to about 15 MPa for fractionation, so hydrogenation is carried out at this pressure [28]. The effluent from steam cracking of hydrocarbons to produce ethylene, other olefins, and other products contains small amounts of acetylenic compounds. In some cases, acetylene and other species may be economically recovered; in others, acetylenes and dienes may be removed by selective hydrogenation, using a nickel or a palladium catalyst. The selective hydrogenation of acetylene over supported palladium catalysts is a process widely used to purify the ethylene produced by steam cracking of hydrocarbons. The ethylene to acetylene ratio in the stream to be treated is generally higher than seventy [38]. An economic operation of the plants requires a high conversion to ethylene of acetylene and a minimum hydrogenation of ethylene and/or acetylene to ethane. Typically the acetylene concentration can be reduced from an initial value in the region of 5000 to below 5 ppm with hydrogenation of no more than 1 percent of the ethylene, operating at temperature in the range of about 60-70 °C [28]. This can be achieved by a correct choice of the reaction conditions and also by the presence of a very small concentration of carbon monoxide in the feed or by promoted palladium on alumina catalysts. Carbon monoxide acts as a poison and increases the selectivity of the catalyst [38]. The plant operation is complicated by the aging of the catalysts. Frequent adjustments of reaction conditions and periodic regenerations are required to maintain a sufficient conversion of acetylene.

3.6.1 Catalysts

At the present time, practically all such catalysts are based on palladium supported on an alumina carrier. They have a low palladium content, about 0.04% on the average, because, by reducing the reaction rate, mass-transfer limitations are reduced, thus improving the selectivity and reducing the risk of a runaway [37].

Palladium-based catalysts promoted by a second metal are now available. The promoter improves selectivity or stability such as Procatalyse LT279 [3].

It has been found that, by studying the role of palladium-based bimetallic catalysts, hydrogen depletion is a possible reason for the effect of the addition of copper and tin to palladium catalysts in the selective hydrogenation of acetylene [39].

Palladium itself is one of the most important metals in hydrogenation. Its unique ability selectively to hydrogenate alkynes and alkadienes to olefins has formed the subject of many in-depth inverstigations [2, 5-8, 10, 13, 15, 21, 40-41].

Palladium hydride is one of the key intermediates which controls the selectivity of acetylene hydrogenation [15]. The rate of reaction increases in parallel with the formation of the β-hydride, whereas the selectivity defined as the ratio of the ethylene formed to the acetylene consumed is markedly decreased. This supports the mechanism proposed on unsupported palladium [10] according to which ethane is the initial product of the reaction and is directly formed from acetylene. The same mechanism is applicable on Pd/Al_2O_3, and it was established that three types of intermediates were sufficient to describe the mechanism as illustrated in Fig. 3.5.

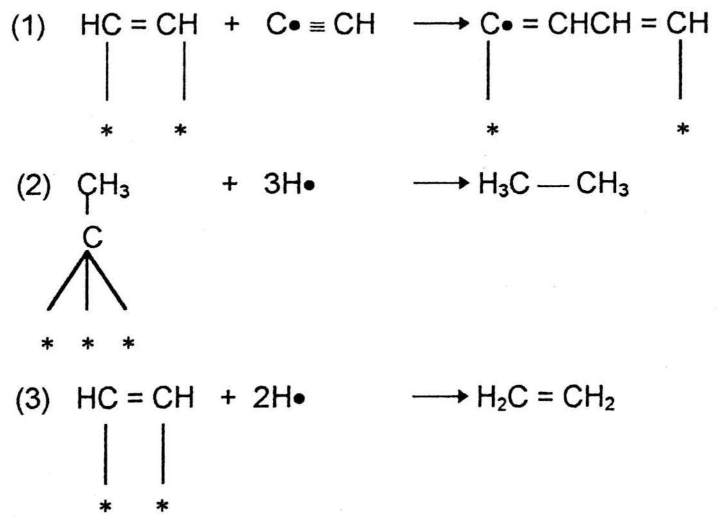


Figure 3.5 Surface intermediates in acetylene hydrogenation (31)

(1) dissociative adsorption of acetylene to form polymer species,
(2) reactive adsorption of acetylene to form ethane directly,
(3) associative adsorption of acetylene to form ethylene.

Laboratory scale investigations using a large excess of ethylene have shown that the initial selectivity for ethylene is always high, even in the absence of gas-phase CO, but it decreases with catalyst aging time, resulting in net ethylene consumption [22]. It has been shown [12] that the build-up of strongly bound carbonaceous material on the support is responsible for the change in selectivity. Recently, it has also been shown [21] that the intrinsic selectivity (the reaction routes of acetylene) does not change during aging, but the rate of ethylene hydrogenation from the gas phase increase as deposits are formed.The addition of trace amounts of CO (max. 100 ppm) hardly reduces the reaction rate of acetylene, but drastically suppresses ethylene hydrogenation [20]. At higher concentrations of CO a decrease in the overall reaction rate of acetylene has been found. $^{14}C_2H_2$ labelling [42] has demonstrated that the intrinsic selectivity is only marginally influenced by aging or by addition of CO which affect only ethylene hydrogenation from the gas phase. Obviously there are at least two different surface sites for acetylene and ethylene hydrogenation, the latter being most probably associated with hydrogen-deficient carbonceous deposits on the support [12]. Hydrogen migrating to the support seems to participate in the unselective process, in the hydrogenation of ethylene [43]. The effect of added CO is to reduce the rate of ethylene hydrogenation by blocking sites for hydrogen dissociation on the metal [12].

In order to improve the selectivity of the Pd/Al_2O_3 catalyst, Cu, Sn and Au have been added in the belief that they might:

- change the intrinsic product selectivities in the reaction of acetylene ;
- change the relative number of sites active for acetylene and ethylene hydrogenation;
- increase and stabilize the dispersion of Pd and thereby inhibit the formation of β-phase palladium hydride.

Results obtained by an American-Hungarian group [12, 20-22, 42-43] have clearly demonstrated that the addition of copper to palladium causes a significant decrease in the overall rate of ethane formation as shown in Fig. 3.6. At the same time there is a decrease in the catalyst activity as well as a marginal decrease in oligomer selectivity. $^{14}C_2H_2$ and $^{14}C_2H_4$ labelling show that the intrinsic selectivity does not change upon addition of copper. The products formed from acetylene are about 40-50 % ethylene, 40-50% C_4+ and 1-5 % ethane.

In contrast to the Pd/Al_2O_3 catalyst, the addition of gas-phase CO in trace amounts has practically no effect on the selectivity with copper-containing catalysts. However, when large amounts of CO have been added, the overall reaction rate decreases. Fig. 3.7 shows the effect of addition of CO to copper-free and copper-containing catalysts. It should be noted that the effects of CO are reversible.

It has also been shown that the rate of deposition of oligomers on the support is also reduced on addition of copper [12].

Replacing hydrogen with deuterium in the feed has no effect on the selectivity of copper-containing catalysts [42], while it has a pronounced effect on that of the Pd/Al_2O_3 catalyst [16].

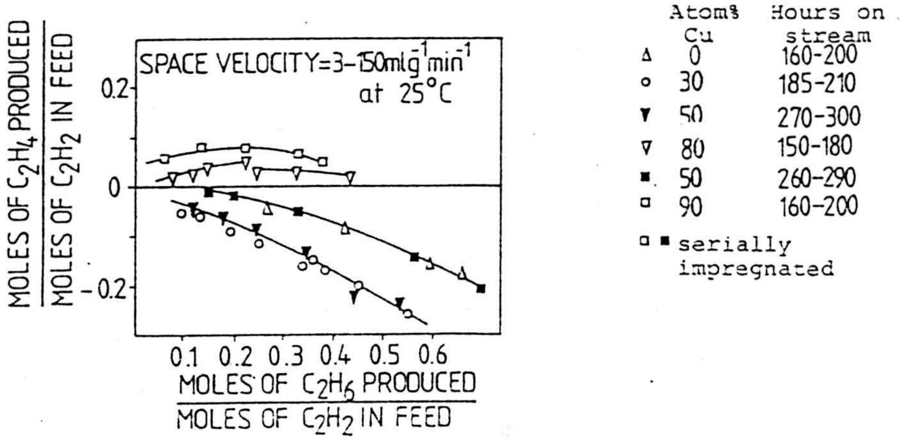


Figure 3.6 Reaction paths near steady state showing the selectivity improvement of 0.04 wt% Pd/Al_2O_3 impregnated with Cu (31).

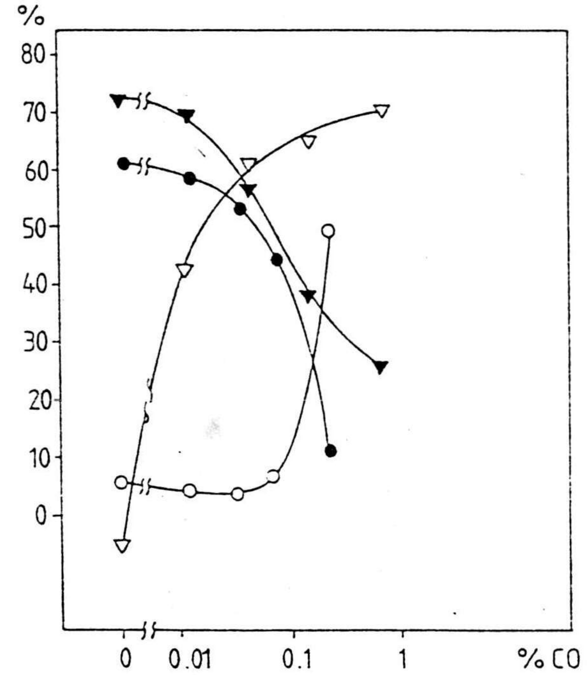


Figure 3.7 Effect of CO on acetylene conversion and ethylene selectivities on Pd/Al_2O_3 and $Pd\text{-}Cu/Al_2O_3$ catalysts. Open symbols: ethylene selectivity; closed symbols: acetylene conversion; (▽) 0.04 wt% Pd/Al_2O_3; (O) 0.04 wt% Pd/Al_2O_3 modified by 80 at. % Cu (31).

Based upon these results the following picture emerges. The addition of copper and of CO have similar effects on acetylene hydrogenation. Both reduce the unselective hydrogenation of gas-phase ethylene,most probably by reducing the hydrogen supply to the deposits on the support. CO blocks adsorption sites for adsorbed hydrogen. Part of the copper covers palladium (as does CO) resulting in a decrease in activity and in a suppression of acetylene dissociation. It stabilizes the palladium dispersion and in this way no β-phase palladium hydride can be formed. The remainder of the copper partially covers the support and hinders the formation of deposits, resulting in a decrease in ethylene hydrogenation and in a better overall selectivity. Obviously, with Pd-Cu/Al_2O_3 catalysts, the geometric effects and the hydrogen supply are the most important factors.

Similar conclusions can be drawn from results obtained on tin-modified Pd/Al_2O_3 catalysts [43]. Even the replacement of Al_2O_3 by SiO_2 and a simultaneous increase in the palladium load to 5 wt.% do not significantly affect the intrinsic selectivity. Alloying of Pd with Au in the Pd/SiO_2 catalyst has a similar effect to that of addition of copper to the Pd/Al_2O_3 catalyst. The data in Table 3.1 clearly shows that the intrinsic selectivity remains unchanged and there is a decrease in the hydrogenation of gas-phase ethylene resulting in an improved overall selectivity. In this system the geometric effects and the hydrogen supply are again the most important factors.

Table 3.1 The effect of the addition of Cu and Au to Pd/Al_2O_3 and Pd/SiO_2 catalysts on the overall and intrinsic selectivities for hydrogenation of trace amounts of acetylene in ethylene (31).

Catalyst	Overall selectivity (%)			Intrinsic selectivity[a] (%)		
	$S_{C_2H_6}$	$S_{C_2H_4}$	S_{C_4+}	$S'_{C_2H_6}$	$S'_{C_2H_4}$	S'_{C_4+}
0.04 wt.% Pd/Al_2O_3	90	-20[b]	30	6	67	27
0.04 wt.% Pd + 0.4 wt.% Cu/Al_2O_3	58	15	27	5	66	29
5 wt.% Pd/SiO_2	87	-23[b]	36	2	54	44
95 at.% Au + 5 at.% Pd/SiO_2 total metal load 5 wt.%	35	21	44	2	43	55

[a] Measured by ^{14}C labelling.

[b] C_2H_4 is consumed.

Acetylene hydrogenation on unsupported Pd-Au alloys has been studied by Visser et al. [44] in a pulse reactor. Besides the ensemble effect, a pronounced increase in the apparent activation energy was observed when d-band holes in palladium were filled (40% Au). Changes in the bond strengths and ligand effects were suggested to be responsible for this increase, as well as the elimination of side reactions leading to self-poisoning.

3.6.2 Reactor design, operating [45]

The selective acetylene hydrogenation reactors have been designed to operate adiabatically or isothermally. In most ethylene plants, adiabatic reactors are preferred on the basis of lower capital investment.

For normal gas streams containing up to 0.3 % acetylene, a two-bed reactor is needed with an intercooler to remove heat of reaction. A typical system is shown in Fig. 3.8.

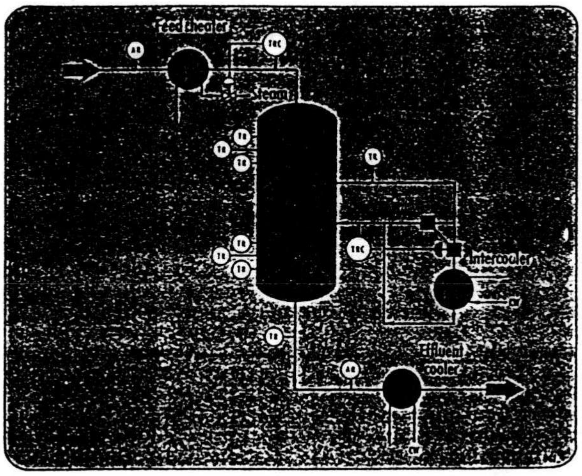


Figure 3.8 Typical two-bed reactor configuration (45).

With higher acetylene content in the feed gas, the number of beds and intercoolers is increased to handle the higher heat of reaction and to maintain the temperature rise per bed at less than 15 °C.

The most critical variable in reactor operation is the feed-gas inlet temperature because it controls the extent of acetylene hydrogenation. To achieve optimum selectivity, it is essential to have precise control of the inlet temperature to each catalyst bed. Some plants have employed sophisticated instrumentation for adjusting the inlet temperature to control the extent of acetylene hydrogenation across each bed.

The normal operating temperature lies in the range 65 to 85 °C. During start-up, the reaction can proceed at as low as 45 °C. After a short period when the catalyst has stabilized, the reactor temperature will reach the normal operating range and will remain constant throughout its life. the reactor heat-exchanger system must be designed to accommodate the start-up condition.

Space velocity is primarily a function of the acetylene content in the reactor feed. It is usually in the range of 5,000 to 12,000 scfh/cu ft catalyst. Other operating factors must also be considered in selecting the proper design.

The design linear velocity can vary between 0.4 to 2.0 fps. Lower linear velocity must be avoided because it will eventually affect gas distribution and interfere with the overall hydrogenation reaction.

The operating pressure of the acetylene reactor is largely dictated by the design of the ethylene-plant purification system. It is usually located downstream of a depropanizer or deethanizer. Reactors have been designed to operate from 100 to 550 psig.

3.6.3 Reactor feed.

Table 3.2 shows the typical composition of C_3-and-lighter and C_2-and-lighter feeds to the acetylene hydrogenation reactor. The various components can be classified into three types:

1. Type 1-Major reactive components-hydrogen,ethylene, and propylene. These components are present in large quantities and can enter into the catalytic reaction.

2. Type 2-Minor reactive components-acetylene, methyl acetylene, and propadiene. These components are present in small quantities. Their total concentration in the feed is less than 1.0 mol%. Selective hydrogenation of these components is the desired objective of the process.

3. Type 3-Inerts-methane, carbon monoxide, ethane, and propane. These components do not enter into the hydrogenation reaction.

Table 3.2 Typical feed composition to the selective hydrogenation reactor (45).

	C_3 and lighter mole %	C_2 and lighter mole %
Hydrogen	15.40	21.00
Carbon monoxide	0.20	0.28
Methane	22.20	12.30
Acetylene	0.24	0.20
Ethylene	30.80	37.30
Ethane	10.90	28.80
Methyl acetylene	0.15	—
Propadiene	0.21	—
Propylene	19.10	0.12
Propane	0.70	—
Butenes	0.10	—
	100.00	100.00

3.6.4 <u>Reactions.</u>

The primary desired reaction is hydrogenation of acetylene to ethylene:

$$C_2H_2 + H_2 \rightarrow C_2H_4 \quad \text{-----------------} \ (1)$$

Secondary desired reactions are hydrogenation of methyl acetylene and propadiene to propylene:

$H_3C - C = CH + H_2 \rightarrow C_3H_6$ -------------- (2)

$H_2C = C = CH_2 + H_2 \rightarrow C_3H_6$ -------------- (3)

Undesired reactions are hydrogenation of ethylene and propylene to ethane and propane respectively.

$C_2H_4 + H_2 \rightarrow C_2H_6$ --------------- (4)

$C_3H_6 + H_2 \rightarrow C_3H_8$ --------------- (5)

Reactions 4and 5 must be minimized because they destroy valuable products.

3.6.5 Reaction rate.

Selectivity cannot be explained if hydrogenation of acetylene and ethylene are competing reactions. According to Bond [41] the rate of ethylene hydrogenation is 10-100 times faster than the rate of acetylene hydrogenation.

If reaction rate were the controlling mechanism, then a considerable amount of ethylene would be hydrogenated before complete hydrogenation of acetylene could take place. A different mechanism is therefore needed to explain the preferential hydrogenation of acetylene in spite of its lower reaction rate.

3.6.6 Selectivity mechanism.

A theory was postulated that the only way acetylene can be selectively hydrogenated with no ethylene hydrogenation is by total exclusion of ethylene from all active sites on the catalyst. This is possible only if active sites are always saturated with components other than ethylene. Adsorption and desorption rates were then considered as the controlling kinetic mechanism.

The adsorption characteristics of acetylene, methyl acetylene on palladium and other group VIII metals have been studied extensively [41, 48].

The rates of adsorption for these components are reported to decrease in this order:

Acetylenes > diolefins > olefins > saturates

Desorption rates decrease in the reverse order. Furthermore, it has been suggested that the more strongly adsorbed components can displace weakly adsorbed components.

Methyl acetylene and propadiene present in the reactor feed gas may be considered as moderating components which exclude ethylene from active sites. Plant data shows that methyl acetylene and propadiene are partially hydrogenated across the reactor. This implies that these two components are adsorbed on active sites and contribute to selectivity.

In reactors where the feed contains only the C_2-and -lighter fraction of the cracked gas, methyl acetylene and propadiene are absent. Yet in commercial operation the same selective hydrogenation of acetylene occurred with no ethylene loss was achieved. This suggests that other moderators are present in the feed.

Carbon monoxide has been reported to retard the hydrogenation of acetylene so that higher reaction temperatures are required. Such an effect has also been observed in the various operating commercial reactors. Since carbon monoxide, it must also be adsorbed on active sites and can be considered as a selectivity moderator.

The role of carbon monoxide as a selectivity moderator is contrary to the past belief that it is an undesirable temporary poison on palladium catalyst.

3.6.7 Active-site coverage.

the catalyst surface coveraged by two components, S_1 and S_2 are related to their partial pressure in the gas phase by the Langmuir adsorption equation:

$$S_1 = K_1P_1/(1+K_1P_1+K_2P_2) \quad \text{-------------} \ (6)$$
$$S_2 = K_2P_2/(1+K_1P_1+K_2P_2) \quad \text{-------------} \ (7)$$

Where:

K_1 and K_2 = adsorption rate constant
P_1 and P_2 = partial presure

The free energy of adsorption is expressed in thermodynamic functions as:

$$G_1 = -RT \ln(K_1) \quad \text{------------} \ (8)$$
$$G_2 = -RT \ln(K_2) \quad \text{------------} \ (9)$$

The difference in free energy of adsorption between the two components is:

$$\Delta G = G_1 - G_2 = -RT \ln(K_1/K_2) \quad \text{-----------} \ (10)$$

The ratio of active-site coverage by the two components can be obtained by dividing Equation 6 by Equation 7 and substituting Equation 10.

$$S_1/S_2 = (P_1/P_2)\, e^{-\Delta G/RT} \quad \text{-----------} \ (11)$$

From Equation 11 we can see that a difference in the free energy of adsorption between the two components of only a few kilocalories per gram mole will result in a very high surface coverage of the more strongly adsorbed compoOnent. Conversely, if the difference in free energy of adsorption between the two components is small, the partial pressure becomes the controlling variable in competition for surface coverage.

Theoretically, if values of the free energy of adsorption of various components were available, Equation 11 could be expanded to explain the selectivity mechanism of the hydrogenation reaction quantitatively. Unfortunately such data are currently not available in the literature.

3.6.8 Effect of carbon monoxide.

It is difficult to define in advance the operating conditions for an acetylene-hydrogenation reactor because of uncertainty about the factors that will be encountered. Not least of the variables is the carbon-monoxide content of process gas. Carbon monoxide is formed by the reverse-shift reaction catalyzed by nickel present in the pyrolysis tubes.

The amount formed is dependent on the cracking severity, the age of the pyrolysis tubes, and the sulfur content of the feedstock. The required reactor-inlet temperature for complete acetylene hydrogenation is dependent on the carbon monoxide content in the feed. If carbon monoxide content changes, then a compensating increase or decrease of operating temperature must be made.

Data from 12 operating reactors with different carbon monoxide contents is plotted in Fig 3.9. It shows the correlation between the inlet temperature to the second bed, and the carbon monoxide content in reactor feed.

Two distinct curves, one for C_2-and- lighter one for C_3-and-lighter streams, can be drawn to show that operating temperatures are significantly

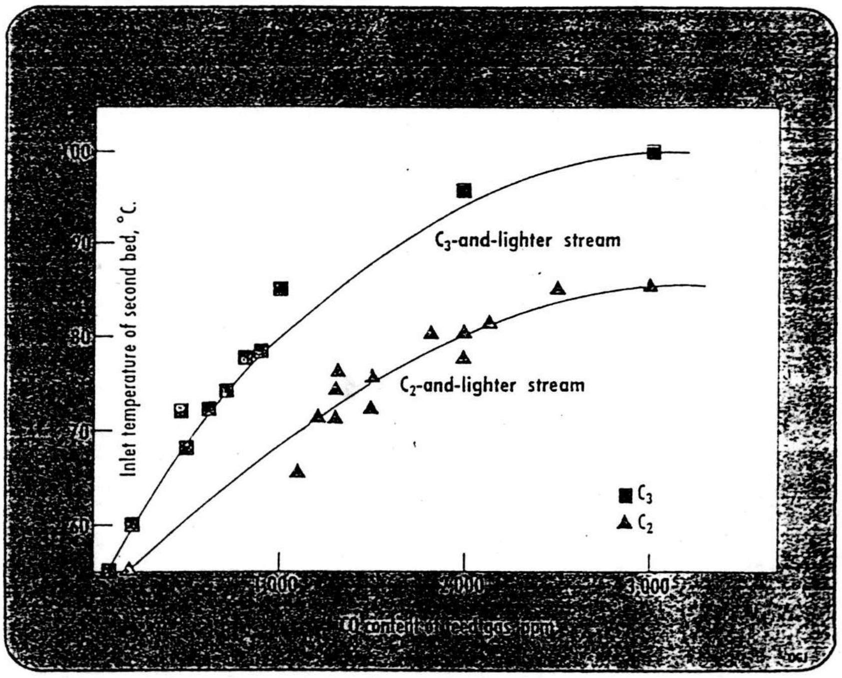


Figure 3.9 Effect of CO on operating temperature (45).

higher for C_3-and-lighter streams. For all points plotted on the curve, acetylene content in the ethylene product was less than 5 ppm.

Several experiments were conducted at the ICI research department to show that carbon monoxide is indeed a selectivity moderator. To eliminate the possible complicating effect of methyl acetylene and propadiene, a C_2-and - lighter stream similar to that shown in Table 2 was used as feed gas to the pilot reactor. To simplify analysis, nitrogen was substituted for methane and ethane.

With 1,000 ppm of carbon monoxide present in the feed gas, complete hydrogenation of acetylene with no ethylene loss was achieved at an operating temperature of about 65 °C. As soon as carbon monoxide was removed from the feed gas, ethylene hydrogenation took place immediately and the reactor temperature rapidly increased to 200 °C.

After the pilot reactor was cooled, selective reaction was again achieved when carbon monoxide was introduced in the feed gas. The same result was observed when methyl acetylene and propadiene were present in the feed gas.

These results have confirmed that carbon monoxide is an essential moderator for the selective hydrogenation of acetylene. Based on these findings, ICI instituted a modified start-up procedure which required preconditioning of the catalyst with carbon monoxide prior to introduction of the feed gas. Previously, occasional hot spots developed during start-up, when process gas first entered the reactor. The new procedure has minimized such incidents and permitted smooth commissioning of the reactor.

3.6.8 Polymer formation.

The displacement mechanism may be extended to explain why there is no polymer formation in commercial reactors using ICI 38-1 catalyst. Polymers are longchain hydrocarbons formed by polymerization reactions of C_2 or C_3 acetylenes. Their formation depends on their ability to remain on active sites and form longer chains by propagating the polymerization reaction.

The fact that acetylene adsorbs more strongly than methyl acetylene, suggests that short-chain molecules are more strongly adsorbed than longchain molecules. When polymerization of acetylene or methyl acetylene begins to form C_4 or C_6 chains, further propagation of the reaction is terminated because the long-chain molecule is displaced from the active site by other moderating components.

The reason for polymer formation has never been properly understood. Displacement of polymer-forming chains by the more strongly adsorbed components remains for now the most convincing explanation.

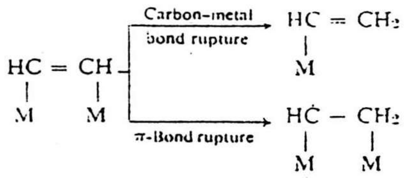
In tail-end hydrogenation reactors where moderating components are absent, polymer formation therefore remains an annoying operating problem that necessitates a spare reactor system to ensure continuous opeation.

3.7 Chemisorption of Acetylenes [46]

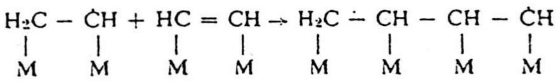
Not very much evidence exists concerning the chemisorption of acetylenes at metal surfaces. Infrared studies [49] have revealed that adsorbed ethyl radicals are present at silica-supported nickel catalysts and an associatively adsorbed form of acetylene has been reported [50] on alumina-supported palladium. At room temperature the heat of adsorption is independent of coverage until the molecules are sufficiently close to cause adsorbate-adsorbate interaction : this therefore implies and immobile adsorbed state. One important fact observed is that acetylene is much more strongly adsorbed than ethylene. If the latter is added to acetylene, it is the acetylene which adsorbs and reacts to the exclusion of the ethylene. This fact determines the fate of species adsorbed at the surface during acetylene hydrogenation, since any olefins formed are immediately desorbed to appear as gaseous products in the early stages of reaction. Thus the process of ethylene formation is a selective one and has been made use of in the commercial synthesis of ethylene and also the selective removal of acetylene form gases by hydrogenation.

Geometrical considerations of the associatively adsorbed state show that acetylenes are adsorbed with greater strain on platinum and palladium than on nickel. Further, it has been argued that acetylene is not to be expected to adsorb on the (111) plane of face-centred cubic metals, since the interatomic distances are too close. This latter hypothesis has been used to explain the inactivity of the metals Os and Ru, which have a close-packed hexagonal structure. Prossible arrangements for packing adsorbed acetylene on (100) and (110) planes of face-centred cubic metals have been proposed by Bond [51], and a staggered arrangement of molecules seems the most preferable, as this avoids excessive overlap.

The associative form of adsorbed acetylene is an ethylene-like structure and therefore has residual unsaturation. Depending on whether the π-bond or a carbon-metal bond is broken when hydrogen attacks adsorbed acetylene, either an adsorbed unsaturated vinyl radical is formed or a free

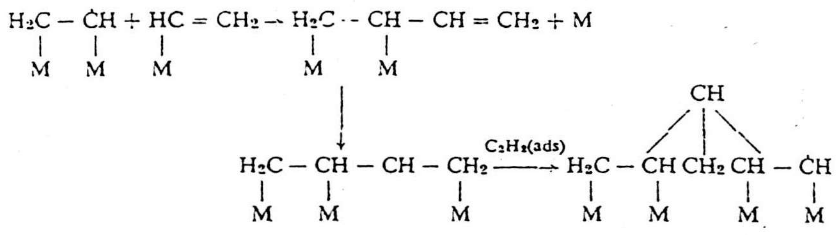


radical, The adsorbed free radical may then initiate a surface polymerization process in which the adsorbed acetylene is the monomer unit.



$$\underset{\substack{|\\ M}}{H_2C} - \underset{\substack{|\\ M}}{\dot{C}H} + \underset{\substack{|\\ M}}{HC} = \underset{\substack{|\\ M}}{CH} \rightarrow \underset{\substack{|\\ M}}{H_2C} - \underset{\substack{|\\ M}}{CH} - \underset{\substack{|\\ M}}{CH} - \underset{\substack{|\\ M}}{\dot{C}H}$$

Repetition of this process leads to surface polymer units containing an integral number of pairs of carbon atoms and such hydrocarbons do appear amongst the products of hydrogenation. It is more difficult to explain the appearance of branced chain polymers, but a s-butyl free radical could be formed as follows:



The latter process (equation (16) involves an intramolecular rearrangement of electrons in which a π - bond is broken and a new carbon-metal bond formed, and so only steric and geometric effects may be expected to hinder the formation of the branched chain polymer.

3.8 Reaction of Spill-over Hydrogen Produced on One Phase with a reactant Adsorbed on Another Phase [47]

The phenomenon of interest here is described in Figure 3.10. Essentially a hydrogen species is formed on one phase (usually a metal) and spills over to react on the other phase. From the many examples of this type we will consider herein the reactions of ethylene and acethylene over Pd/Al_2O_3.

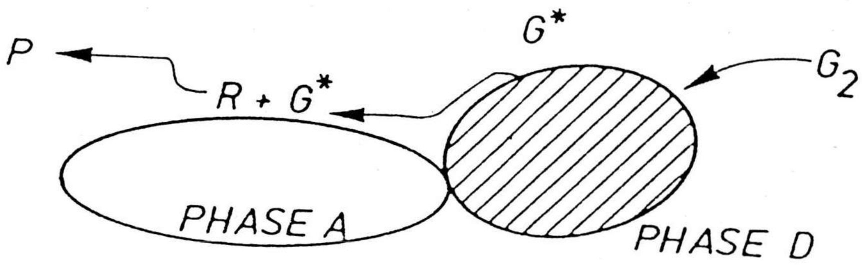
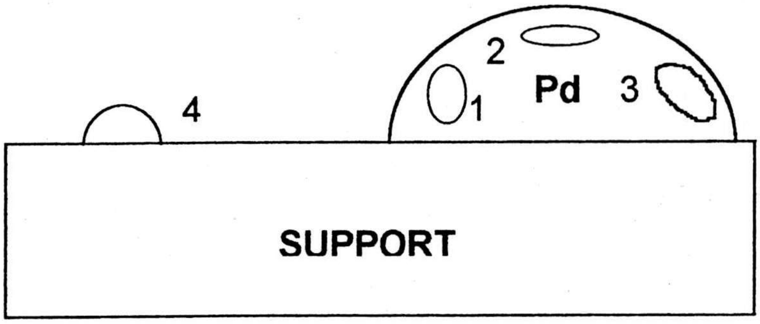


Fig. 3.10 Reaction between a species (G*), formed on phase D, then transfered to phase A by spill-over surface diffusion, where it reacts with an adsorbed molecule R (47).

Sarkany and coworkers [12] studied the hydrogenation of a mixture of 0.29 mole% C_2H_2, 0.44 mole% H_2 and C_2H_4 up to 100% , a so-called tail-end mixture, on palladium black and several Pd/Al_2O_3 catalysts. Hydrogenation of C_2H_4 increased with the time on stream for all the Al_2O_3-supported catalysts; the opposite behaviour was noted with palladium black. Polymer formation was noted for all catalysts studied and also increased with time. It was recognized that a small number of C_2H_4 hydrogenation sites were located on the metal but the majority were on the polymer-covered support. The authors proposed that C_2H_4 adsorbed on the support and was hydrogenated there. Spill-over hydrogen was tentatively identified as the source of hydrogen. Because of the parallelism between polymer formation and ethylene hydrogenation, it was proposed that the surface polymer served as a hydrogn pool or facilitated diffusion of hydrogen from Pd to the support.

3.9 Model representing the sites involved in the selective hydrogenation of acetylene

It can be concluded according to previous findings [6-9,13,14,16,21] that four main types of sites are associated in the selective hydrogenation of acetylene. Three types which are responsible for conversion of acetylene to ethylene, direct ethane formation from acetylene, and oligomer formation from acetylene are on the metal surface whereas the other which accounts for hydrogenation of ethylene to ethane is on the support. These types of sites can be represented as a model in Figure 3.11.



1 SITE FOR OLIGOMER FORMATION

2 SITE FOR DIRECT ETHANE FORMATION

3 SITE FOR ETHYLENE FORMATION

4 SITE FOR ETHANE PRODUCTION FROM ETHYLENE

Figure 3.11 Model representing the sites to be operative in the selective hydrogenation of acetylene