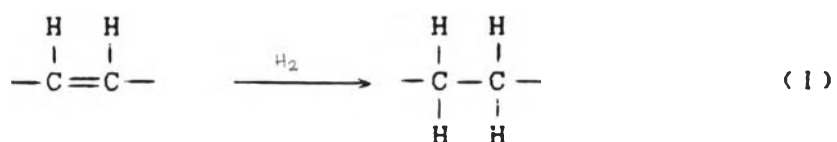# CHAPTER III

## THEORY

### 3.1 Introduction

The hydrogenation of fats and oils came rapidly to be of great econocmic importance when it was understood that here existed a practical means of modifying the character of one oil so as to enable it to be substituted for others. The hydrogenation is the most useful method for preparing alkanes. It is not limit to the synthesis of alkanes but is a general method for t he conversion of a carbon-carbon double bond into a carbon-carbon single bond. Using the same apparatus, the same catalyst, and very nearly the same conditions, we can convert alkene into an alkane, an unsaturated alcohol into a saturated alcohol, or an unsaturated ester into a saturated ester. Since the reaction is generally quantitative, and since the volume of hydrogen consumed can be easily measured, hydrogenation is frequently used as a analytical tool ; it can, for example, tell us the mumber of double bonds in a compound. The reaction consists of the direct addition of hydrogen at double bonds in molecules, according to the following scheme (6).

$$
\begin{array}{ccc}
\overset{\displaystyle H}{\underset{\displaystyle |}{}} \ \overset{\displaystyle H}{\underset{\displaystyle |}{}} & & \overset{\displaystyle H}{\underset{\displaystyle |}{}} \ \overset{\displaystyle H}{\underset{\displaystyle |}{}} \\
-C = C- & \xrightarrow{\ H_2\ } & -C-C- \\
& & \underset{\displaystyle H}{\underset{\displaystyle |}{}} \ \underset{\displaystyle H}{\underset{\displaystyle |}{}}
\end{array}
\qquad (1)
$$

The addition of hydrogen to alkenes is the presence of metallic catalysts, e.g. Ni, Pt, Pd, etc., is usually a cis addition. This cames about because reduction take place when the alkene is adsorbed at the metallic surface ; approch of active hydrogen occurs from one side of the alkene only, i.e. from the interier of the metal where the hydrogen is readily adsorbed, probably as reactive free atoms, in resonable concentration : metal that are effective hydrogenation catalysts have the capacity of adsorbing quite large amounts of hydrogen. The alkene is probably bound to the metal surface by an interaction involving its electrons for, after reduction has taken place, the reduced product, becomes desorbed very readily and so leaves the catalyst surface free for adsorption of more alkene.

Hydrogenation of the ethylenic linkage in glyceride oils, fatty acids, and fatty esters, to produced products of improved properties is one of the major processing operations in the fat and oil industry. There are two reasons to hydrogenate oils. First, since the number of double bonds is reduced, the opportunity for oxidation is decreased, and thus the flavor stability is increased. Second, physical characteristics are changed such as the melting point is raised.

## 3.2  Chemistry of Hydrogenation

### 3.2.1  The Hydrogeration Reaction

The basical hydrogen of an unsaturated carbon-carbon double bond appears to be very simple but is extremely complex from reaction (I).

$$\text{—CH} = \text{CH—} \quad + \quad H_2 \quad \xrightarrow{\text{catalyst}} \quad \text{—CH}_2 \text{—CH}_2 \text{—}$$

Hydrogenation is exothermic : the two bonds (C-H) being formed are, together, stronger than the bond (H-H) and bond being broken. The quantity of heat evolved when one mole of an unsaturated compound is hydrogenated is called, the heat of hydrogenation (6).

The hydrogenation of the usual vegetable oil results in an increase in temperature of the oil of 1.6-1.7 °C for each unit decrease in iodine value. The heat of hydrogenation ($\Delta Hh$) for methyl esters of the common unsaturated fatty acids is shown in Table 3.1 (7).

Table 3.1   Heats of hydrogenation of methyl ester

| Methyl ester | $\Delta Hh$ (Kcal/mole) |
|---|---|
| Palmitooleate | $- 29.30 + .24$ |
| Palmitelaidate | $- 32.43 + .60$ |
| Oleate | $- 29.14 + .26$ |
| Elaidate | $- 28.29 + .15$ |
| Linoleate | $- 58.60 + .39$ |
| Linoelaidate | $- 55.70 + .13$ |
| Linolenate | $- 85.40 + .58$ |

Thus the heat of hydrogenation of fatty esters is not very different from that of other aliphatic compounds in the liquid phase 28-29 Kcal per double bond. This heat of hydrogenation is used by industrial operators to supply heat to the reactor. The reactant is heated to some minimum

temperature and the hydrogen admitted. The heat of reaction is used to heat the reactants to some maximum temperature where the temperature is controlled.

For hydrogenation to take place, gaseous hydrogen, liquid oil, and the solid catalyst must be brought together at a suitable temperature. In ordinary practice it may be assumed that the hydrogen is first caused to dissolve in the oil, with the hydrogen-ladden oil then brought into contact the catalyst by mechanical means. In the usual type of equipment, reaction is brought about by agitating the suspension of catalyst and oil in a closed vessel in an atmosphere of hydrogen. Agitation of the catalyst-oil mixture serves the double purpose of promotion solution of hydrogen in the oil and continuously renewig the oil at the catalyst surface. The solubility of hydrogen and other gases in oil increases linearly with temperature and, of course, pressure.

When vegetable oils are hydrogenated, at least three different types of reduction can occur. The first type is the reduction of carbon-carbon double bonds in the fatty acid chains and which results in the reduction of the iodine value (I.V.). In all cases, isomerization accompanies the type of hydrogenation being considered, therefore, any discussion of the mechanism must explain both. During reduction of the I.V., the color and odor of the triglycerides are improved, indicating that it least some of trace quantity materials are being hydrogenated. These materials contain carbonyl, quinone-type, etc. structures. The mechanism for this second type of hydrogenation is not well understood, partly because of the large and probably variable number of trace materials present in the oils or fats. Although hydrogenation processes for reduction of the

I.V. are some what effective in improving the color and odor, processes for getting, primarily, color and odor improvements without significant reduction of the unsaturation in the fatty acid chains are known. The third type of hydrogenation that is possible for oils or fats involves the production of fatty alcohols and glycerine (This type of reduction is sometimes called hydrogenolysis).

Hydrogenation of the carbon-carbon double bond as practiced commercially generally involves a nickel catalyst. Palladium catalyst is apparently used to a limited extent commercially, and platinum is sometimes used in the laboratory. The approximate range of commercial operating variables is as follow (9) :

Temperature, 110-190 $^{o}$C

Pressure, 0-300 psig.

Catalyst concentration, 0.01-0.15% by weight nickel

Agitation, mechanical or gas bubles through liquid

The rate of hydrogenation under the condition just outlined depends on the temperature, the nature of the oil, the activity of the catalyst, the concentration of the catalyst, and the rate at which hydrogen and unsaturated oil molecules are supplied together to the active catalyst surface. The composition and the character of the hydrogenated product may vary according to the positions of the double bonds, which are hydrogenated as well as certain isomerizing influences accompanying the reaction, and are highly dependent on the conditions of hydrogenation.

The hydrogenation process is equally applicable to glycerides, fatty acids, nonglyceride esters and other unsaturated fatty acid derivatives. The hydrogenation of

fatty materials is accomplished to produce a more oxidatively
stable product and/or change a normally liquid oil to a semi-
solid or solid fat with melting characteristics designed for
a particular product. Thus to prepare a consistent product
with the desired characteristic, the reaction parameters must
be controlled.

### 3.2.2 The Heterogeneous Catalysts

The type of catalysis that is the most important
in industry, and the type that operates in fat hydrogenation,
is heterogeneous catalysis. By definition, a heterogeneous
system is one in which the catalyst and the reactants exist
in different physical states. Heterogeneous catalysis is to
be some what sharply distinguished from homogeneous catalysis,
in which the catalyst and the reactants comprise a single
phase. In homogeneous catalysis the catalyst function in the
form of individual molecules, which are uniformly distributed
throughout the reacting system. Thus the quation of catalyst
physical structure or of surface phenomena does not enter.
On the other hand, in heterogeneous catalysis it is the
catalyst surface that performs the catalytic function ; hence
the nature of the surface is of extreme importance. A
catalyst operating in a homogeneous system is defined simply
in terms of its chemical constitution and its concentration
in the system. With all other factors controlled, the effect
of a homogeneous catalyst of definite composition is exactly
predictable on the basis of its concentration. If the
catalyst is an immiscible solid, however, its behavior will
depend not only on its chemical composition, but also to a
very large degree on both the nature and the extent of its
surface. The fact that the characteristics of a solid
catalyst are determined so largely by the submicroscope

character of its surfaces renders the study and the control of such catalysts very difficult. Apparently similar catalysts may differ enormously in their activity and specific action (7).

### 3.2.3 Catalysis in Relation to Activation Energy

Chemical reactions, catalyzed or uncatalyzed, do not occur instantaneonsly principally because of a pattern of molecular distribution of energy that ensures that at any instant only a few molecules of the reacting substances will be at a sufficiently high energy level. The critical energy for a specific reaction, known as the energy of activation (7).

Although hydrogenation is an exothermic reaction, it preceeds at a negligible rate in the absence of a catalyst, even at elevated temperatures. The uncatalyzed reaction must have, therefore, a very large energy of activation. The function of the catalyst is to lower the energy of activation (Eact) so that the reaction can proceed rapidly at room temperature. The catalyst does not, of couse, effect the net energy change of the overall reaction ; it simply lowers the energy hill between the reactants and products. The energy of activation is represented graphically in Figure 3.1 (6).

The fact that a catalyst cannot initiate reaction does not mean that the introduction of a catalyst into a reacting system may not influence the composition of the reaction products ; or that difference catalyst may not yield different products. In many eases reaction follows a number of alternative course ; hence the composition of the

final products will depend on the relative rate of the various alternative reactions. Where a number of different reaction occur together, the addition of a catalyst to the system may accelerate some of them to a for greater extent than others.
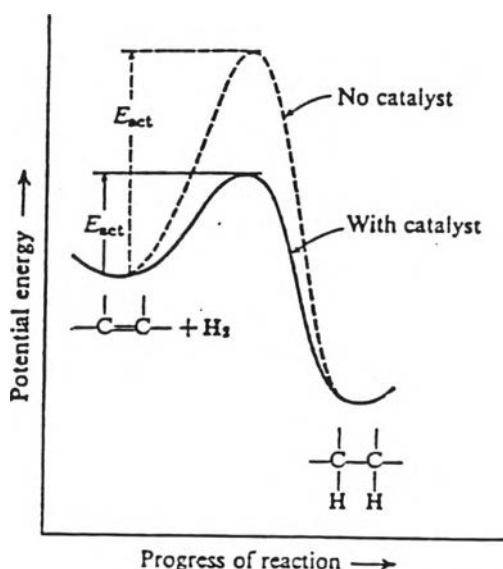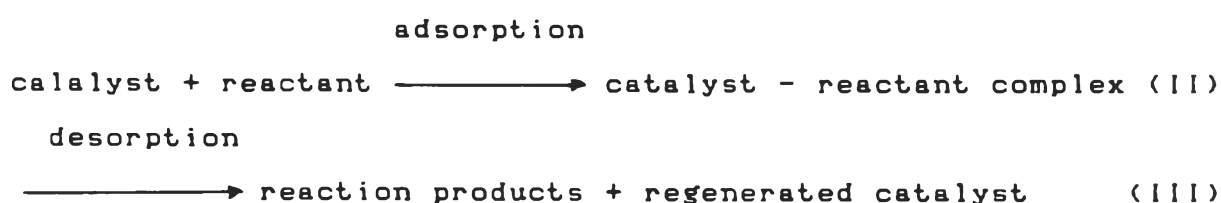


Figure 3.1 Potential energy changes during progress
of reaction effect of catalyst

In heterogencous catalysis it is now gernerally assumed that reaction proceeds through the formation of unstable intermediate compounds or adsorption complexs, in which the catalyst is temporarily combined with one or more of the reactants. A catalyst lower Eact by permitting reaction to take place in a different way that is by a different mechanism. In this case, the reactants are adsorbed on the enormous surface of the finely divided metal, where reaction actually occurs. Reaction between the adsorbed molecules is very different from the reaction that would

have to take place otherwise ; it is believed that stongly
bound molecules of the reactant are held to the catalyst
surface by secondary valence forces or by complexing.

In any event, it is essential that they be unstable,
that is, capable of being either decomposed or desorbed, to
permit reaction to proceed according to the following scheme (7).

adsorption

calalyst + reactant ⟶ catalyst - reactant complex (II)

desorption

⟶ reaction products + regenerated catalyst    (III)

The rate a chemical reaction k is determined by the
integrated Arrhenius equation

$$k = a \ e^{-Eact/RT}$$   (3.1)

Where T is the absolute temperature, a is a factor
related to the concentration of the reactants, and Eact
represents the activation energy. Because of the exponential
character of this equation, a relatively slight change in
activation energy will have a large effect on the reaction
rate.    Catalyst increase the reaction rate through their
influence on the activation energy. From exponential relation
outlined previously, it is readily apparent that the catalyzed
reaction may proceed at a rate that very greatly exceeds that
of the uncatalyzed reaction.

Lowering the energy hill, as we can see, decreases
the activation energy of the reverse reaction as well, and
thus increases the rate of dehydrogenation. We might expect,

therefore, that platinum, palladium, and nickel, under the proper conditions, should serve as dehydrogenation catalysts; this is indeed the case. Hydrogenation is favored by an excess of hydrogen under pressure and dehydrogenation is favored by sweeping the hydrogen in a stream of inert gas (6).

### 3.2.4   Theory of Catalyst Structure

Since heterogeneous catalysis is a surface phenomena, an essential requirement in an active catalyst is a highly extended surface. With all other factors being equal, the smaller the individual catalyst particles, the more active the catalyst will be (7).

In spite of the obvious relationship of surface area to catalyst activity, it does not follow that the activity is determined solely by the magnitude of the surface area. The latter may be made very large without the catalyst necessarily being very active. In fact metallic nickel dispersed to the colloidal state may be virtually devoid of catalytic activity. All evidence indicates that the activity of a hydrogenation catalyst is due to a certain degree and kind of heterogeneity in the catalyst surface. The development of this heterogeneity will not occur under all conditions but must be achieved by special methods of catalyst preparation.

The various phenomena associated with heterogeneous catalysis are best explained on the basis of the "active spots" Theory of Tylor (10). This theory assumes that the metal atoms on the surface of the catalyst posses varying degree of unsaturation, according to the extent to which they are elevated above the general catalyst surface, or otherwise released from the mutually restraining influence of their neighboring atoms. The relatively few metal atoms

which are thus highly unsaturated are to ones which are
capable of entering into temporary combination with the
hydrogen and the unsaturated oil, in this way furthering the
hydrogenation reaction. Each unsaturated atom or concentration
of unsaturated atoms constitutes an active spot or center. The
catalytic activity of each unsaturated atom corresponds to the
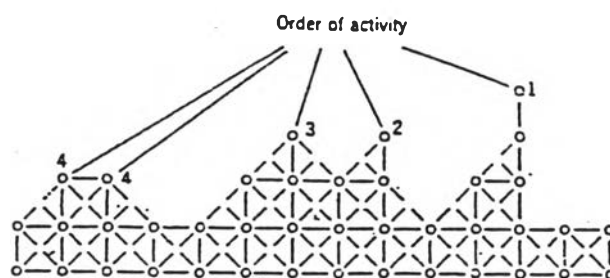extent of its unsaturation, see Figure 3.2 (7).



Figure 3.2   Schematic representation of a catalyst surface

An alternative theory of catalyst structure
envision the active portions of a catalyst as areas where
the normal crystal lattice of the metal is slightly expanded
to fit more exactly the dimensional requirements for
two-point adsorption on either side of a double bond. In
the case of nickel, the mormal interatomic spacing of 2.47 $\overset{o}{A}$
is actually a little smaller than the theoretical optimum.
Expansion may occur as metallic nickel is produced by the
reduction of a nickel compound (an expansion of 0.16 $\overset{o}{A}$ has
been reported in Raney nickel) or simply from reduced
interatomic attraction in very small crystallites.

Hydrogenation catalysts are seldom prepared
directly from massive nickel, but are made by first combining
the nickel with other elements, as in nickel oxide, nickel

hydroxide, nickel carbonate, nickel formate, nickel-aluminum
alloy, etc., and then reducing the resulting compound to regain
the niokel in metallic form. The efficacy of this procedure,
in producing active nickel atoms relatively free from restraint
by   neighboring  atoms,   is  evident  from  the   schematic
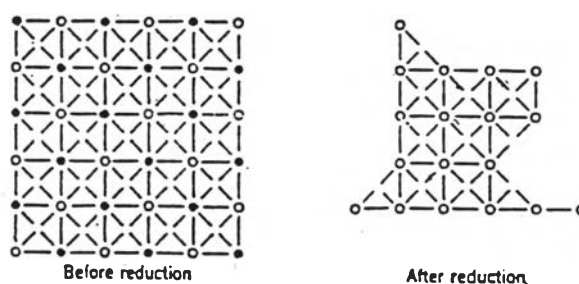representation of catalyst reduction in Figure 3.3 (7).



Before reduction              After reduction

Figure 3.3  Schematic representation of effect of
            reduction on nckel catalyst
            (White circle = nickel atom ; black circle
            = atom of oxygen, aluminum, etc.)

     According  to the active-spot theory,  the  most
active nickel atoms, which are attached to the surface by the
minimum of constraint, are but one step removed from a gaseous
state.  Armstrong and Hilditch (7) have considered it probable
that  such atoms are actually momentarily detached from  the
catalyst during the period of their catalytic fanction,  and
that  the nickel thus actually operates in a  gaseous  form.
The subseqent migration and attachment of the nickel atom to
the most exposed part of the catalyst surface is assumed  to
maintain  a  state  of average similarity  to  the  original
catalyst.

     There is considerable evidence that the hydrogenation

of an ethylenic compound must be preceeded by two-point adsorption of the carbon atoms on either side of the double bond. This requirement would impose certain dimensional limitations upon the space lattice of all effective in hydrogenation of double bonds (nickel, cobolt, iron, copper, platinum and palladium) all have interatomic spacing close to that (2.73 $\overset{\circ}{A}$) calculated as optimum for such two-point absorption.

Twigg and Rideal (11) have correlated the catalytic activity of various metals with their interatomic distances. Using the distances 2.47 $\overset{\circ}{A}$ for Ni-Ni, 1.52 $\overset{\circ}{A}$ for C-C bond, and 1.82 $\overset{\circ}{A}$ for C-Ni, they showed that for adsorption of the C-C group the valence angle for the bond would have to be 105 $\overset{\circ}{4}'$, see Figure 3.4, which is considerably less than the tetrahedral angle 109 $\overset{\circ}{28}'$. For the valence angle if the bond to equal the tetrahedral angle the interatomic distance for the metal would have to be 2.73 $\overset{\circ}{A}$. Significantly, the inter-atomic distances for platinum and palladium are 2.76 and 2.74 $\overset{\circ}{A}$, respectively. They should fit the C-C group without appreciable strain and probably are very good catalyst for that reason.
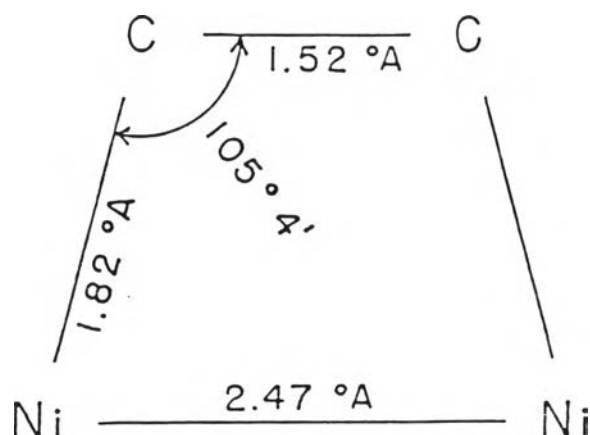
Figure 3.4 Interatomic distance and valence angle for C=C adsorbed on nickel surface.

For a number of other good reasons platinum and palladium are not used for the hydrogenation of fats and oils, except in the laboratory. A most important consideration is that they are much more expensive than nickel. Also, they are relatively unselective. Because all unsatarated bonds which are apparently hydrogenated with relatively equal facility, there is no marked preferential hydrogenation of the more unsaturated components of an oil. Finally, the noble metal catalysts are said to become poisoned easily. Therefore nickel catalyst has been widely used in industry for the hydrogenation of fats and oils.

### 3.2.5 Theory of Carbon-Carbon Double Bond

#### 3.2.5.1 Carbon-Carbon Double Bond

In ethylene, each carbon atom is bonded to only three other atoms, two hydrogens and one carbon. Strong $\sigma$ bonds are formed with these three atoms by the use of three hydride orbitals derived by hybridising the 2s and this time, two only of the carbon atom's 2p atomic orbitals-an atom will normally only mobile as many hybride orbitals as it has atoms or groups to form strong $\sigma$ bonds with the resultant $sp^2$ hybride orbitals all lie in the same plane and are inclined at $120°$ to each other (plane trigonal orbitals). Informing the molecule of ethylene, two of the $sp^2$ orbitals of each carbon atom are seen as overlapping with the 1s orbitals of two hydrogen atoms to form strong $\sigma$ C-H bonds, while the third $sp^2$ orbital of each carbon atom is used to form a strong $\sigma$ C-C bond between them.

This then leaves, an each carbon atom, one unhybridised 2p atomic orbital at right angles to the plane containing the carbon and hydrogen atom. These two 2p atomic orbitals are parallel to each other and can themselves overlap to form a molecular orbitals, spreading over both carbon atoms and situated above and below the plane containing the two carbon and four hydrogen atoms (dotted lines indicate bonds to atoms lying behind the plane of the paper and ◀ to those lying in front it (12) :



(IV)
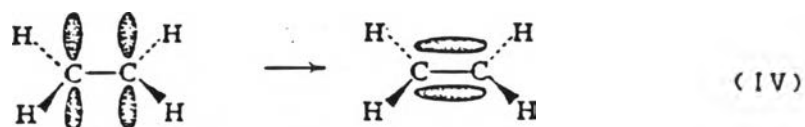
The electrons occupying this new molecular orbital are known as $\Pi$-electrons and the orbital itself as a $\Pi$ orbital. The new $\Pi$ bond that is thus formed has the effect of drawing the carbon atoms closer together thus the C = C distance in ethylene is 1.33 Å compared with a C-C distance of 1.54 Å in ethane. The lateral overlap of the $p$ orbitals that occurs in forming $\Pi$ bond is less effective than the linear overlap that occurs in forming a $\sigma$ bond and the former is thus weaker than the later. This is reflected in the fact that the energy of a carbon-carbon double bond, though more than that of a single bond is, indeed, less than twice as much thus the C-C bond energy in ethane is 83 kcal/mole, while that of C=C in ethylene is only 143 kcal/mole.

### 3.2.5.2  Addition to Carbon-Carbon Double Bond

A carbon-carbon double bond consists of a strong $\sigma$ bond plus a weaker $\pi$ bond, in a different position (V) (12) :



(V)          (VI)                (VII)
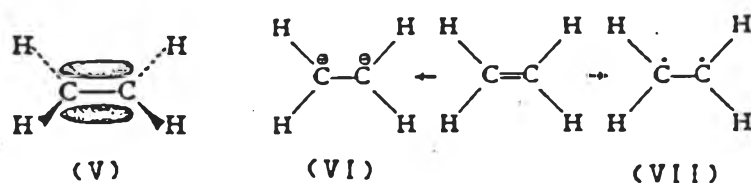
The pair of electrons in The $\pi$-orbital are less firmly held between the carbon nucli and so more readily polarisable than those of the $\sigma$ bond, leading to the characteristic reactivity of such unsaturated compounds. Addition to such compounds can proceed through ionic (VI) or free radical (VII) mechanisms, depending on the way in which the electrons becomes polarised either by the approching reagent or other causes. Thus the former tends to predominate in polar solvent, the latter in non-polar solvents, especially in the presence of other radicals or of light.

### 3.2.6  The Hydrogenation Mechanism.

### 3.2.6.1  Mass Transfer Step in Hydrogenation

When a heterogeneous catalytic reaction occurs, several physical and chemical process must take place in proper sequence transfer of the reactants to the

catalyst surface and of the products away from the catalyst, has long been recognized as being important in the reaction (13).

The step that occur on a molecular scale in the following manner :

1. Mass transfer of reactants from the main body of the fluid to the gross exterior surface of the catalyst particle.

2. Molecular diffusion and/or knudsen flow of reactants from the exterior surface of the catalyst particle into the interior pore structure.

3. Chemisorption of at least one of the reactants on the catalyst surface.

4. Reaction on the surface (This may involve several steps.)

5. Desorption of (chemically) adsorbed species from the surface of the catalyst.

6. Transfer of products from the interior catalyst pores to the gross external surface of the catalyst by ordinary molecular diffusion and/or knudsen diffusion.

7. Mass transfer of products from the exterior surface of the particle into the bulk of the fluid.

As practice commercially, this hydro-genation involves three phases : the gas phase (hydrogen), the liquid phase (triglycerides or fatty ester) plus dissolved hydrogen and the solid phase (metallic catalyst). The three phases of the system are brought together in a heated stirred reactor with hydrogen available under pressure in

the headspace of the reactor. The hydrogen must be
dissolved in the liquid-solid phase before reaction can
occur since the dissolved hydrogen is the only hydrogen
available for reaction. The hydrogen and unsaturate group
may then diffuse through the liquid to the solid surface of
catalyst. In general, at least one of the reactants must be
chemisorbed on the surface.

The chemical reaction on or near the
catalyst surface between unsaturated hydrocarbons and
hydrogen proceeds by way of surface organometallic
intermediates. Such reactions include adsorption of
reactants, surface reactions and desorption of product of
both hydrogenation and isomerization. After desorption from
catalyst surface, the product diffuses to the main body of
liquid (9).

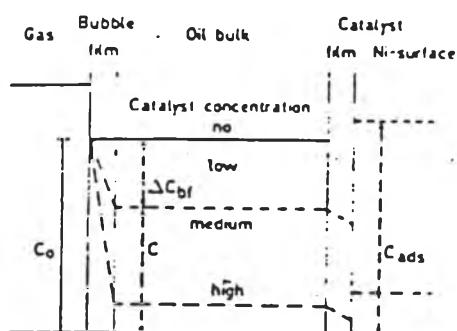Several of these step are shown in
schematic fashion in Figure 3.5 (2).



Figure 3.5   Concentration of hydrogen at different stagesin
the mass trasport of gas buble to catalyst surface
surface.

Of course, if the catalyst is non porous, step 2 and 6 are absent. Step 1, 2, 6, and 7 are obviously physical process, while step 3 to 5 are basically chemical in character. The rates of various step depend on a number of factor in addition to the concentration profiles of the reactant and product species.

In last step (#7) needs some discussion since several alternatives are possible. In the case of hydrogenation of an oleic group, the stearic acid group would be transferred. If one of the double bonds of a linoleic acid group is hydrogenate, however, the monounsaturated acid group can be transferred to the main body of oil. As alternative, the monounsaturated acid can remain at the catalyst surface until it is hydrogenated or isomerized ; then the stearic acid group or the isomer is transferred to the liquid phase. Of couse, the isomer can remain near the catalyst surface until it is reduce. In the case of just isomerization the positional or geometrical isomers is transferred to the liquid.

### 3.2.6.2 Mechanism of Hydrogenation and Isomerization.

It will greatly help our understanding of the several effects that obtained from hydrogenation if we now look closely at what are understood to be the different posibilities open when either a solitary double bond is adsorbed at the surface of an active nickel catalyst, the nickel atoms are about 2.5 $\overset{o}{A}$ apart. The ideal spacing of about 2.7 $\overset{o}{A}$ corresponds to the spacing between

the carbon atoms of a double bond. Metal which catalyse the hydrogenation of these double bonds, such as nickel, copper, palladium and platinum, all have atomic spacings close to 2.7 $\overset{o}{A}$.

The mechanism for hydrogenation and isomerization of triglycerides which really complicated olefins is in the same of light olefin in order to model the reactions leading to the various isomers and hydrogenation products, we can use a simple scheme such as that in Figure 3.6 (14). When the double bond is adsorbed at the surface of active metal, carbon chain containg one cis double bond between the $C_9$ and $C_{10}$ atoms has formed links to the metal surface. The first step undoubtedly involves the $\pi$-bonding interaction of the double bond and a metal atom very much like one in the famous Zeise's salt. The next step can be written in analogy with what is beleived to occur in the case of simple coordination catalyst systems, e.g., the well known Wilkinson complex, $(Ph_3P_3)RhCl$. This means that a hydrogen atom from on M-H bond (activated hydrogen atom, H*) in the neighborhood is transferred to one of the carbons of the olefinic bond (Figure 3.6 a). While this bond is simultaneously sliding off sideways so that a $\sigma$ M-C bond is formed to produce an unstable partially unsaturated complex (Figure 3.6b).

If a high concentration is present of hydrogen is present on the surface, the complex will probably react with another activated hydrogen atom to complete the hydrogenation. If a low concentration of hydrogen is present on the catalyst surface one of the
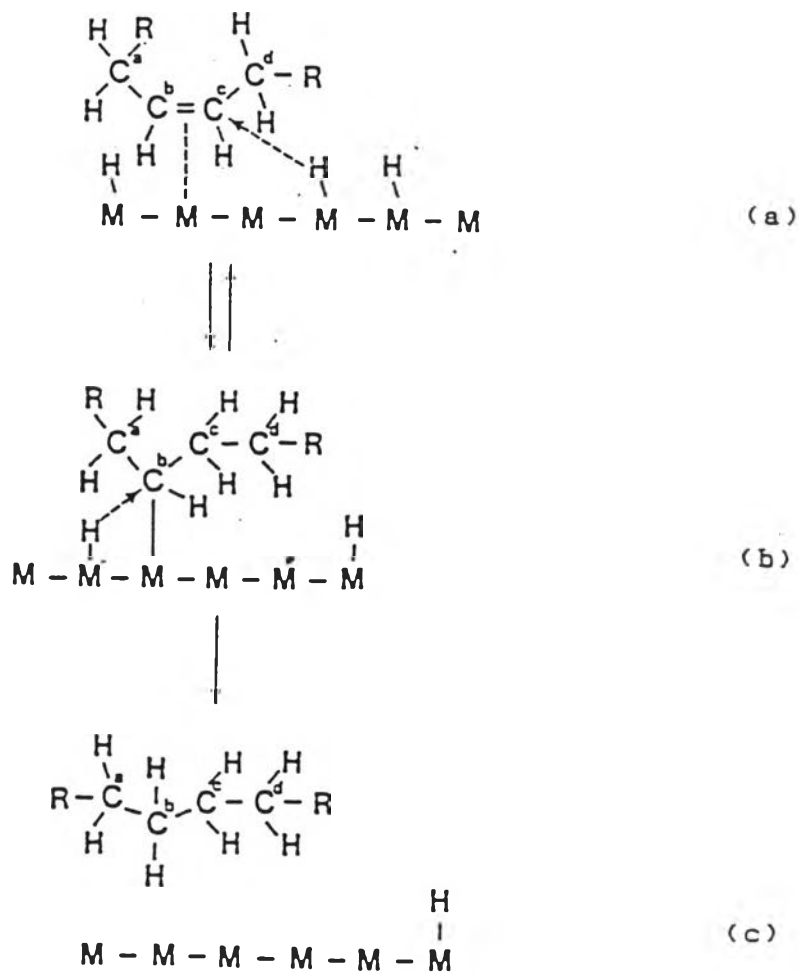
Figure 3.6   Formation and reaction of the alkyl
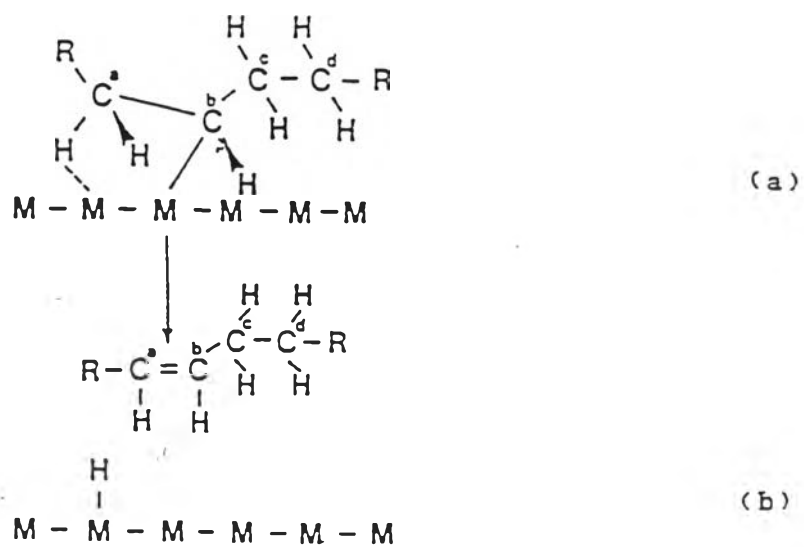intermediate on a metal surface



Figure 3.7   Bond shift resulting from reaction of
the alkyl intermediate

hydrogen atoms of the complex will probable dissociate from the complex to reform a double bond.

So the resulting metal-bonded ethyl group has now various possibilities of reaction :

1. There may be a reverse reaction to product the original cis-configurated species. The same H atom is lost by $C_9$ before $C_{10}$ can acquire one ; the original $C_{9-10}$ cis-bond reforms and is desorbed. Thus nothing has really happened.

2. There may occur a twisting or rotation around the C-C axis and thereafter a reverse reaction back to the $\pi$-bonded state and finally to the unbonded initial situation. It is the other H atom on $C_9$ which is lost, hence a trans bond forms and is desorbed. This sequence produces a trans-configuration (geometric) isomer.

3. A hydride transfer from an M-H group to the metal bonded carbon. $C_{10}$ captures on H atom whilst $C_9$ still holds two ; the bond is therefore saturated and is desorbed.

4. A reversal as in point (1) and (2) may take place, but now involving the (M-)C-C bond on the other side of the metal-bonded carbon. This situation is illustrated in Figure 3.7. Depending on which of the two H-atoms are closest to an empty M-site, an H-atom is lost from $C_8$ and a cis- or trans-olefin bond will be produced. It must be stressed that the double bond $C_9 = C_{10}$ of Figure 3.6 and 3.7 could equally well be shifted to a $C_8 = C_9$ position as the attack of hydrogen might have occured at position "10" and the carbon at position "9" would then have been bonded to a metal site

In hydrogenation practice the concentration of dissolved hydrogen may vary within wide limits. When an oil has a low iodine number and hence a low concentration of unsaturated fatty acids, or when an oil contains very little catalyst, the concentration of dissolved hydrogen may obviously approach saturation closely if the agitation is reasonably good. On the other hand, if agitation is relatively poor, the unsaturation of the oil relatively high and the catalyst concentration likewise high, the concentration of dissolved hydrogen can doubtless fall very low. Such a condition is particularly likely to occur when a high concentration of catalyst is employed in laboratory hydrogenation. It may be recognized by failure of the reaction to accelerate when the amount of catalyst is increased, and also by the rate of reaction remaining constant over a wide range of iodine number, rather than continuously decreasing as the degree of unsaturation falls. The hydrogenation rate depends, under these conditions, simply upon the rate at which hydrogen can dissolve in the oil, and hence is independents, within limits of the concentration of either of the other two reactants.

The question of hydrogenation in the oil is important not only with respect to the reaction rate, but also in relation to the course of hydrogenation and the consequent composition of the hydrogenated product. As was implied above, and as will be developed in a later section, there is evidence that agitation, pressure, catalyst concentration, and temperature are interrelated in their influence on the course of hydrogenation, and that the latter is possibly to be interpreted in term of the concentration of hydrogen adsorbed on the catalyst.
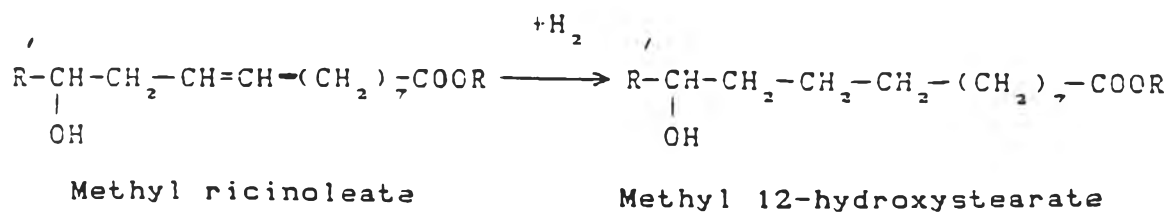
## 3.3  Theory of The Hydrogenation of Methyl Ricinoleate

Fully hydrogenated methyl ester of high hydroxyl content has a number of desirable properties ; medium range metting point, low solubility in organic solvents, non-toxicity, oxidation stability, etc. Methyl ester wax has the above desirable properties only when the ethylenic linkage of the ricinoleate ester molecule is reduced without appreciable dehdroxylation taking place during the hydrogenation process.  The simple double bond hydrogenation give methy 12-hydroxystearate.
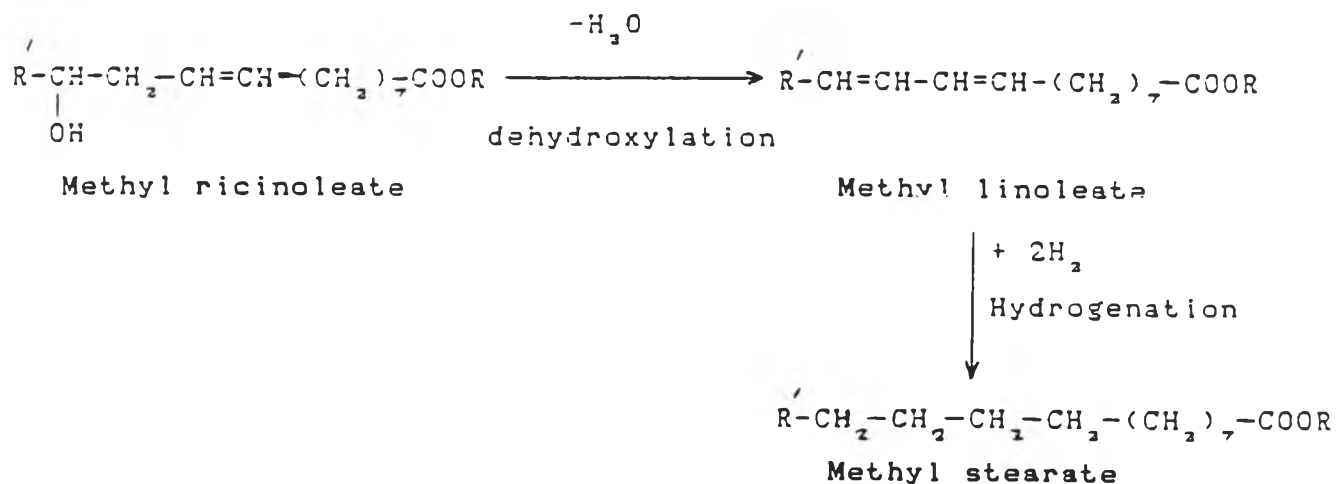
### 3.3.1  Nature of the Reaction

The double bond and the hydroxyl group of methyl ricinoleate are the two centers which are affected during hydrogenation.   While saturatin of the double bonds of the ricinaleate ester chain is undoubtedly the major reaction that occur when methyl ricinoleate is hydrogenated, it must be pointed out that as number of other reactions can occar even under comparatively mild conditions.  These reactions include conjugated hydrogenation, dehydroxylation, isomerization, hydrolysis, estolide formation, etc. (4,9,15).

- Hydrogenation.   The hydrogenation of methyl ricinoloate saturation of the double bonds of ricinoleate ester chain to give methyl 12-hydroxystearate which can be commercially achieved using of nickel catalyst at about 150 $^{\circ}$C and 150 psig. hydrogen pressure. The hydrogenation reaction occurs according to the following reaction.

$$R-\underset{\underset{OH}{|}}{CH}-CH_2-CH=CH-(CH_2)_7-COOR \xrightarrow{+H_2} R-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-CH_2-(CH_2)_7-COOR$$

Methyl ricinoleate               Methyl 12-hydroxystearate

- <u>Dehydroxylation</u>. The dehydroxylation or dehydration of methyl ricinoleate gives diene products. Methyl ricinoleate is dehydrated by reacting the hydroxyl group of the ricinoleate ester with an adjacent hydrogen to form water molecule. The products are unsaturated ester with two double bonds of the 9-12 and 9-11 linoleate ester type. The reaction is caused by high temperature during hydrogenation. Temperature above 150$^o$C are avoided to minimize dehydroxylation. Finally, the diene products one hydrogenated to stearte by the folowing reactions.

$$R-\underset{\underset{OH}{|}}{CH}-CH_2-CH=CH-(CH_2)_7-COOR \xrightarrow[\text{dehydroxylation}]{-H_2O} R-CH=CH-CH=CH-(CH_2)_7-COOR$$

Methyl ricinoleate                              Methvl linoleate

$$\downarrow \begin{array}{l} + 2H_2 \\ \text{Hydrogenation} \end{array}$$

$$R-CH_2-CH_2-CH_2-CH_2-(CH_2)_7-COOR$$
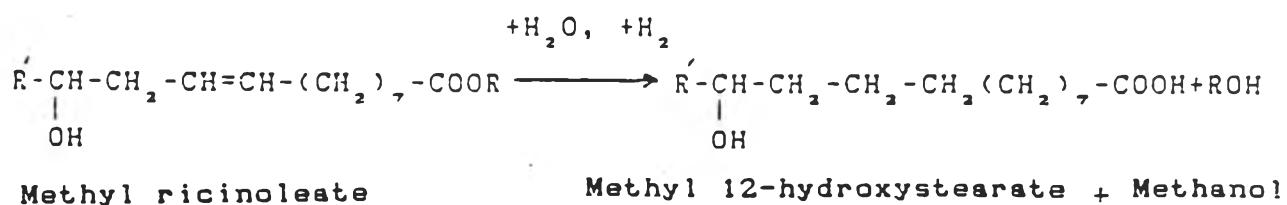
Methyl stearate

- <u>Isomerization</u>. The isomerization is the formation of isomeric unsaturated fatty ester with properties different from the naturally occuring forms. Such isomers
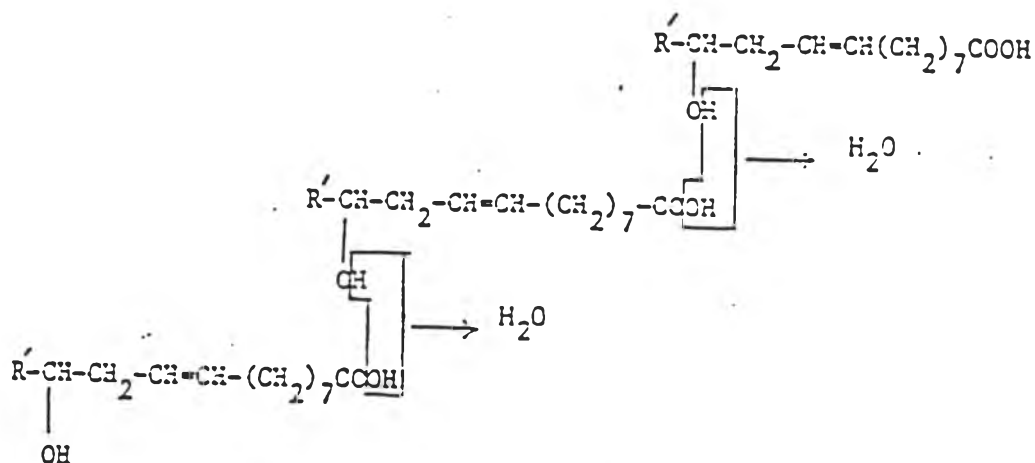
may originate from (a) the addition of hydrogen at a double bond which is normally not saturated by natural process, (b) the migration double bonds, (c) conversion of natural cis-forms to trans-forms. In the fully hydrogenation of methyl ricinoleate, the isomerization reaction is negligible.

- <u>Hydrolysis</u>. The hydrolysis is caused by splitting of fat molecule to fatty acid and alcohol. The reaction is occured when there are water and acid catalyst. During hydrogenation, water form the dehydroxylation and acidity of the catalyst cause the hydrolysis. Therefore, increasing the dehydroxylation increases the hydrolysis which is showed by increase in acid value of the hydrogenated product. The reaction is the following.

$$R-CH-CH_2-CH=CH-(CH_2)_7-COOR \xrightarrow{+H_2O, +H_2} R-CH-CH_2-CH_2-CH_2(CH_2)_7-COOH+ROH$$
$$\quad\ |\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\quad OH \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad OH$$

Methyl ricinoleate        Methyl 12-hydroxystearate + Methanol

-- Estolide formation. The estolide formation is caused by condensation of the carboxyl end of one molecule of ricinoleic acid with the hydroxyl group of another. The reaction can be hastened by heating. The structure of estolide trimer is shown the following.

$$R-CH-CH_2-CH=CH(CH_2)_7COOH$$
$$| \atop OH$$
$$R-CH-CH_2-CH=CH-(CH_2)_7-COOH \longrightarrow H_2O$$
$$| \atop OH$$
$$R-CH-CH_2-CH=CH-(CH_2)_7COOH \longrightarrow H_2O$$
$$| \atop OH$$

Note :   $R' = CH_3-(CH_2)_5$

OR $= -O-CH_3$

## 3.4  Operating Variables

While hydrogenation tends to be naturally selective, the plant operator has four variables under his immediate control which he can manipulate to change the selectivity to a marked extent. The variables are temperature type and concentration of catalyst, hydrogen pressure, and agitation.

These variables exert their influences in a complex maner by controlling the following six steps involved in hydrogenation (7,11) :

1. Solution of hydrogen in the oil.
2. Adsorption of dissolved hydrogen on the catalyst.
3. Prior, simultaneous, or latter adsorption of an unsaturated bond.
4. Formation of a hydrogen-nickel unsaturated bond complex.
5. Decomposition of the complex.
6. Desorption of the saturated bond.

The observed effect of temperature on the hydrogeration is the sum of all the effects on the many steps of the reaction. An increase in temperature increases the solubility of Hydrogen in the oil. Also, the higher temperature will lower the viscosity of the oil, thus increasing the agitation, and the hydrogen may diffuse from the bubble through the surface to the oil phase. Higher temperatures cause a faster reaction on the catalyst surface, so with increased agitation and pressure, hydrogen is kept supplied to the catalyst surface for the saturation. However, if the temperature alone is increased, although more hydrogen is supplied to the catalyst surface, the reaction is very rapid and the hydrogen on the catalyst may be partially depleted. This would account for the increased isomerization at higher temperatures. There is not enough hydrogen on the catalyst surface to complete the saturation, so the catalyst takes back a hydrogen and a geometrically isomeric double bond results (7).

This choice of an operating temperature is usually limited to those between 80 and 200°C. Below this range the nickel catalyst employed posseses insufficient activity, and above this range these is danger of damaging the oil. Also above 200°C the rate of reaction which at first inereases with temperture begins to decrease. Between 135 and 175 °C the rate of reaction is approximately doubled for an increase of 22°C. Increasing the temperature at which a hydrogenation is performed increases the selectivity of the reaction or side reactions; the dehydroxylation, hydrolysis, estolide formation and also isomerization.

Increasing hydrogen pressure results in a large driving force to solubilize the hydrogen in the oil. As a result, the hydrogen concentration in the liquid and at the catalyst surface is always increased regardless of the degree of agitation. At low pressures, the hydrogen dissolved in the oil does not cover the catalyst surface, but at high pressures especially at low temperatures, an increases in pressure does not change the formation of isomers because the catalyst surface is already covered and the pressure is sufficiently high to supply all the hydrogen needed to increase the rate of saturation, but the rate of side reactions do not change. At low pressure, the rate of hydrogenation is almost directly proportional to the absolute hydrogen pressure. The hydrogen pressure used in the reaction vessel is generally between atmospheric and 200 pounds per squareinch gage, within which range the reaction rate is roughly proportional to the pressure. Below atmospheric pressure the reaction rate is generally too small to be useful.

Agitation helps overcome the resistance for the transfer steps of the reactants and products in the mixture. Since hydrogen transfer is generally a controlling step, increased agitation results in higher hydrogen concentrations at the catalyst surfaces. Consequently in such a case, the overall rate of hydrogenation inereases but selectivity, isomerization and side reaction decrease. At very high rates of agitation in which the resistances for all transfer steps are eliminated, further increases of agitation have no effect on the rate, selectivity, or isomerization since there are no changes in the concentrations at the catalyst surface. And also, the agitation must dissipate the heat of the reaction and not allow any over heating or hot spots in the surface of catalyst. Increasing agitation not only decreases external diffusion effect in the interparticle fluid between the bulk of the fluid and the surface of the catalyst particle but also decreases the dehydroxylation caused by hot spots or exothermic heat of reaction on catalyst surface and subsequently decrease the hydrolysis caused by water molecule from the dehydroxylation.

As the amount of catalyst used is increased, the overall rate of hydrogenation always increases (assuming a relatively good suspension of the solid catalyst in the oil). When a hydrogen diffusion step is controlling, the rate of hydrogenation per unit weight of catalyst decrease. However, since the hydrogen concentration at the catalyst surface decreases, consequently, selectivity, isomerization and side reaction increase. When no diffusion steps are controlling, the concentration at the catalyst surface is

unchanged. Consequently there are no changes in selectivity, isomerization, side reaction, or rate of hydrogenation per unit weight of catalyst (i.e., the overall rate is directly proportional to the amount of catalyst). Generally, a catalyst concentration between 0.02 and 0.25% nickel is used in the hydrogenation reaction.