

## CHAPTER III

### THEORY



#### 3.1 Introduction

The hydrogenation of vegetable oils was discovered by Normann over eighty years ago and since then has developed into the major chemical process in fat and oil industry [11].

When vegetable oils or animal fats 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 of the triglyceride and which results in the reduction of the iodine value (I.V.). As practiced commercially, this hydrogenation involves with three phases: the gas phase (hydrogen), the liquid phase (triglycerides plus dissolved hydrogen), and the solid phase (metallic catalyst). In all cases, isomerization accompanies the type of hydrogenation being considered. Therefore, any discussion of the mechanism must explain both. In addition, selectivity is an important part of the reaction.

During the reduction of the I.V., the color and odor of the triglycerides are improved, indicating that at least some of the trace-quantity materials are being hydrogenated. These materials contain carbonyl, quinone-type, etc. structures. The mechanism of 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 and fats. Although hydrogenation processes for reduction of the I.V. are somewhat 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. For example, hydrobleaching processes have been patented [12,13]. This reaction uses metal oxide catalysts with hydrogen pressures up to perhaps 1500-2500 psi.

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.) The reduction occurs at high pressures from about 2500-4000 psi, at temperatures from approximately 250-400 °C, and in the presence of solid catalysts such as copper chromite [14]. The mechanism for this type of reaction is obviously considerably different than that for the reduction of the carbon-carbon double bonds.

This thesis will concentrate in the reduction of carbon-carbon double bonds.

From literature survey, the hydrogenation of rubber seed oil could not be found. The following theories of hydrogenation of vegetable oils are stated because it is found that the hydrogenation behavior of rubber seed oil and vegetable oils are similar.

## 3.2 Chemistry of Hydrogenation [15]

### 3.2.1 Mechanism

The basic hydrogenation of an unsaturated carbon-carbon double bond appears to be very simple but is extremely complex:



As this reaction shows, hydrogenation can take place only when the three reactants have been brought together - the unsaturated oil, a liquid, the catalyst (which is a solid), and hydrogen gas. Thus the physical mechanism of bringing the reactants together has been devised without understanding what happened when the reactants were together in the correct structure to cause reaction.

The reactants of three phases system - gas, liquid, and solid - 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 may then diffuse through the liquid to the solid catalytic surface. In general, at least one of the reactants must be chemisorbed on the surface of the catalyst. However, the reaction between unsaturated hydrocarbons and hydrogen proceeds by way of surface organometallic intermediates.

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 hydrogenation reaction. For example, Bailey [15], in 1949, outlined several transfer steps that must occur. Since hydrogenation and isomerization occur simultaneously and both on the catalyst surface, a restatement and enlargement of steps involved during hydrogenation seem necessary:

- (1) Transfer of hydrogen from gas to liquid phase.
- (2) Transfer of hydrogen from liquid phase to catalyst surface.
- (3) Transfer of unsaturated group (carbon-carbon double bond) from liquid phase to catalyst surface.

(4) Chemical reactions on or near the catalyst surface. (Such reactions include adsorption of reactants, surface reactions, and desorption of product from both hydrogenation and isomerization.)

(5) Transfer of product from catalyst surface to the main body of liquid.

The last step needs discussion since several alternatives are possible. In the case of hydrogenation of an oleic acid group, the stearic acid group would be transferred. If one of the double bonds of a linoleic acid group is hydrogenated, however, the monounsaturated acid group can be transferred to the main body of oil. As an alternative, the monounsaturate 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 course, the isomer can remain near the catalyst surface until it is reduced. In the case of just isomerization, the positional or geometrical isomer is transferred to the liquid [11].

Since there are several transfer steps, it is obvious that the amount of interfacial area is important plus the degree of agitation. Bailey [16] had indicated that the transfer of the hydrogen from the gas to the liquid phase was often the single most controlling step. Wisniak [17] has verified this postulate. Much of the hydrogenation data reported in the literature were obtained using operating conditions such that, transfer steps were controlling to at least a considerable degree. Such data frequently are not as valuable as would be liked in studying the kinetics and chemistry that occur at the catalyst surface.

If the mixture to be hydrogenated contains monoenes, dienes, and polyenes, there may be competition between the different unsaturated systems for the catalyst surface. Thus the dienes may be preferentially adsorbed from the oil to the catalyst surface and partially isomerized and/or hydrogenated to a monoene and then desorbed to diffuse to the main body of the oil. The di- and polyenes are preferentially adsorbed until their concentration in the oil is very low, and the monoenes then may be adsorbed and reacted [18].

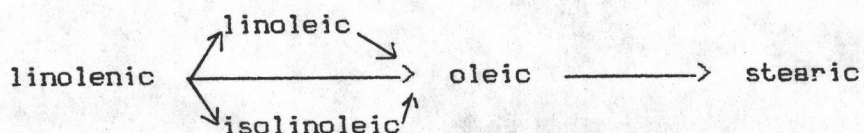
Since the oils that are hydrogenated are composed of a mixture of fatty acids, the selectivity of the reaction is very important.

### 3.2.2 Selectivity [15]

The term "selectivity" as used in the industry had two meanings as applied to the hydrogenation reaction and products. The term originally was defined by Richardson et al. [18] as the conversion of linoleic acid to a monoene, compared to the conversion of the monoene to stearic acid. This was also known as chemical selectivity since it compared the rates of chemical reactions.

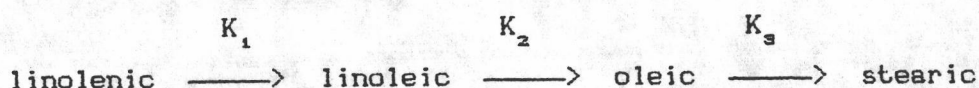
Another type of selectivity was applied to catalysts. If a catalyst was "selective", it produced an oil of softer consistency or lower melting point at a given iodine number (value) (I.V.). Since this could not be made a very quantitative term, this definition was at best somewhat value and the catalyst one called "selective" might be labeled something else by others. Since neither type of "selectivity" could be measured with any precision, the term was used only for comparisons.

In 1949 Bailey [19] demonstrated that the following model could be used to measure the relative reaction rate constants for each hydrogenation step during the batch hydrogenation of linseed, soybean, and cottonseed oil:



Using this model, Bailey considered each reaction to be first order and irreversible and thus developed the kinetic equations to represent the concentration of each acid group as a function of time. Relative reaction rate constants were calculated for several runs, and the ratio of the reaction rate constant for linoleic to oleic, divided by the reaction rate constant for oleic to stearic, was the selectivity (ratio) of the reaction. If the ratio was 31 or above, the hydrogenation was selective and below 7.5, nonselective. However, as the calculation of the reaction rate constants was very laborious, little use was made of the quantitative measure.

A simpler reaction sequence was proposed by Albright in 1965 [20]. Since the triene (linolenic acid) produces several different dienes (isolinoleic acids) when one double bond is hydrogenated and since there would be little difference in the rates of hydrogenation of the mixture of dienes, these were included in one term. Also, since the addition of 2 moles of hydrogen to linolenic acid to produce oleic acid directly has not been shown to occur, the shunt was eliminated from the model, and since geometric and positional isomers that are formed were believed to have almost the same reactivity, these were not included in the model. Thus, the model is simplified to



Many investigators have reported on the effect of operating variables on chemical selectivity. For example, when the degree of agitation is rather low (i.e. when mass transfer resistances are at least partially controlling), selectivity increases with decreased pressure and agitation, and increased temperature and amounts of catalyst [15]. When agitation rates are so high that mass transfer resistances are negligible, selectivity decreases with pressure; however, selectivity is unaffected by changes in catalyst concentration or increased agitation, and is essentially unaffected by temperature [17,21,22]. Selectivity has generally been characterized on a qualitative basis. Some attempts have been made to define it quantitatively but in general they were rather inadequate for the more complicated triglycerides. Albright and Wisniak [21] have reported a method which is based on a rather complicated hydrogenation sequence.

Because polyunsaturated groups hydrogenate preferentially to monounsaturated groups (and they do, even for quite nonselective hydrogenation) does not necessarily mean that the rate of hydrogenation for a double bond in a polyunsaturate acid group (such as linoleic acid) is faster than for the double bond in a monounsaturate acid group (such as oleic acid). In this respect, when a mixture of acetylene and ethylene are hydrogenated, the acetylene hydrogenates preferentially [22]. Yet the rate of hydrogen uptake is less while acetylene is being reduced than when ethylene is.

### 3.2.3 Isomerization

During the hydrogenation of fats the double bond may be saturated or isomerized while it is adsorbed on the catalyst surface. Both positional and geometric isomers are formed and are very important to the production of partially hydrogenated fats.

Since the trans form of octadecenoate has a higher melting point (trielaidin, melting point (m.p.)  $42^{\circ}\text{C}$ ) than the cis form (m.p.  $4.9^{\circ}\text{C}$ ), but lower than the saturated (tristearin, m.p.  $73.1^{\circ}\text{C}$ ), the level of trans double bonds and saturates determines the solids content of fats at various temperatures. The saturated octadecanoate determines the solids at high temperatures, and the trans form performs the same function at the lower temperatures.

Both geometrical and positional isomers are formed on the catalyst surface by reaction with a hydrogen atom, basically by way of the Horiute-Polanyi mechanism.

As the double bond is adsorbed on the catalyst surface, the first reaction is with a hydrogen atom. Since this leaves a very active intermediate, another hydrogen atom may add to the adjacent position, with the molecule desorbed as a saturated one. However, if there is not a hydrogen atom available, a hydrogen may be removed from a chain carbon atom by the catalyst. Since the hydrogens on either side of the "active center" are activated, either may be removed. If the original hydrogen is removed, the original double bond is reformed and the molecule is desorbed. However, if the other hydrogen is removed, the double bond is shifted one position from the original position. Which of the two hydrogens on the carbon are removed



determines whether the new double bond will be cis or trans. Also, the double bond in the original position may be converted to trans. The double bonds in the new position may also be shifted. As hydrogenation proceeds, the isomerized double bonds tend to be shifted further and further along the chain, and the trans isomer content will increase until the monoenes are saturated [23].

The methylene-interrupted system of double bonds found in linoleic, linolenic, and other acids may also undergo an isomerization step. However, the hydrogen on the methylene group between the double bonds are quite labile. As the pentadiene approaches the catalyst, one of the hydrogens may be removed by the catalyst, thus causing a shift of one double bond to the conjugated position and a hydrogen adds to the carbon at the end of the conjugated system. When the bond shifts it may be cis or trans (trans predominates). Evidently, the conjugated system is tightly chemisorbed to the catalyst surface since it is hydrogenated to a monoene very rapidly and then desorbed. The remaining double bond may be cis or trans and may be shifted one position from the original position [24]. Thus from cis, cis-9, 12- octadecadienoate, hydrogenation produces the 9, 10, 11, and 12 cis and trans monoenes. Most of the trans will be in the 10 and 11 positions.

#### 3.2.4 Reaction Order and Reaction Rates [15]

In view of the literature on oil hydrogenation kinetics, it can hardly be expected that any definite order can be assigned to the reaction as a whole. On the other hand, it would be somewhat remarkable if the reaction rate bore no relation to the extent of unsaturation in the oil. Actually under most conditions, hydrogenation will approach the character of a unimolecular reaction, where the rate of hydrogenation at any

instant is roughly proportional to the saturation of the oil. However, the character of the reaction is markedly influenced by various conditions of hydrogenation.

A number of typical hydrogenation curves of cottonseed oil are shown in Figure 3.1, with the logarithm of the iodine number of the oil plotted against hydrogenation time. When so plotted, a true unimolecular or first order reaction should yield a straight line, as in curve B. Curves similar to curve B are often obtained under average conditions of pressure, agitation and catalyst concentration at moderate or low temperatures, that is, below about 150 °C. At higher temperatures the shape of the hydrogenation curve resembles that of curve C since an increase in temperature accelerates the first stages of hydrogenation to a relatively greater extent than the latter stages; that is, it accelerates the conversion of linoleic to oleic acid to a greater extent than the conversion of oleic to stearic acid. In the case of curve A, hydrogenation more nearly approaches a linear rate. This type of curve is often obtained in the hydrogenation of

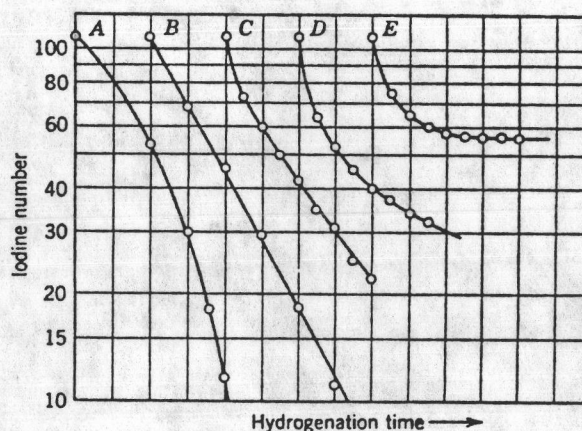


Figure 3.1 Typical cotton seed oil hydrogenation curves [15]

relatively saturated oils, such as tallow, and is also sometimes observed in hydrogenation at a low pressure with a high concentration of catalyst, where the rate of hydrogenation is determined by the rate of solution of hydrogen in the oil.

Curve D is characteristic of very high temperature hydrogenation, of hydrogenation with a very low concentration of catalyst, or of hydrogenation under conditions producing progressive slow poisoning of the catalyst during the reaction. Curve E represents a hydrogenation carried out with a self-poisoned nickel sulfate catalyst that was almost completely ineffective during the later stages of the reactions. Similar curves are obtained under conditions producing rapid catalyst poisoning.

### 3.2.5 Induction Period [11]

The induction period that occurs in many hydrogenation runs often occupies a major portion of the time the triglycerides are in the reactor. Wisniak and Albright [17] reported induction periods from 10-80 minutes for batch runs at 100-130 °C. The induction periods at these temperatures decreased with increased temperature, pressure and amount of nickel catalyst. A somewhat comparable run at 160 °C showed little or no induction period [25]. The cause of the induction period is not known definitely, but it is probably related to some extent at least with selective adsorption but slow hydrogenation of the trace-quantity polar materials of the oil such as those materials which are colored or odoriferous. Presumably more effective bleaching or refining operations would decrease the induction period. Any manufacturer contemplating low temperature hydrogenation should determine carefully if the induction period is an excessive portion of the residence time of the triglycerides

in the reactor system. Certainly more research attention needs to be devoted to the induction period and methods of eliminating it.

### 3.3 Effects of Process Conditions [15]

The four main reaction parameters are temperature, pressure, agitation, and catalyst concentration. Of course, the type of oil and the type of catalyst also determine the product produced by hydrogenation. Changes in the reaction parameters, using the same type of oil and catalyst, are made according to the type of product desired. Although these reaction parameters are all interrelated, they are discussed singly for better understanding.

#### 3.3.1 Effect of Temperature

Hydrogenation, like other chemical reactions, is accelerated by an increase in temperature. The effect of temperature on the reaction rate is somewhat less than in ordinary reactions but is variable, as shown in Figure 3.2. At high rates of agitation the rate, shown as I.V. drops per minute, steadily

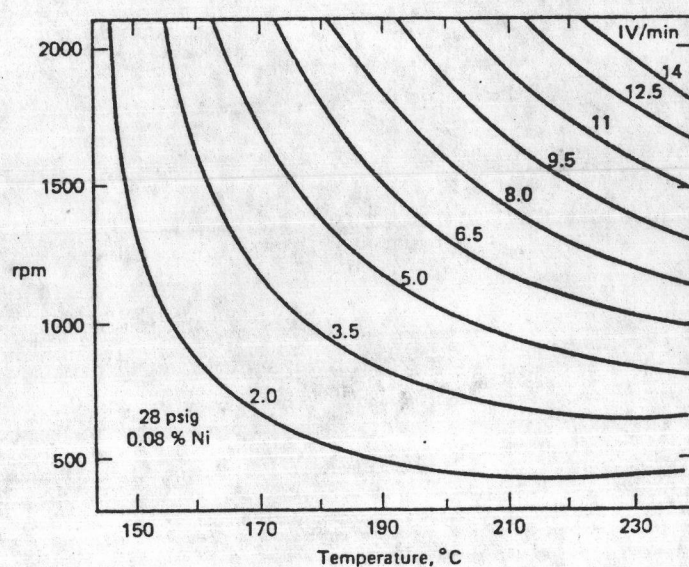


Figure 3.2 Effect of reaction agitation and temperature on rate of hydrogenation of soybean oil [15].



increase, but at low agitation the effect of temperature slowly decreases as the temperature increases, thus indicating that several factors are affecting the reaction rate.

Also, the formation of trans unsaturation is affected by temperature. As the temperature of reaction is increased, the formation of trans unsaturation increases almost linearly. However, as shown in Figure 3.3, the pressure also affects isomer formation. Temperature also increases the selectivity ratio value, and the increase is almost linear with temperature, pressure also affects the selectivity ratio.

The observed effect of temperature on the hydrogenation 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 [17]. 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 temperature cause a faster reaction on the

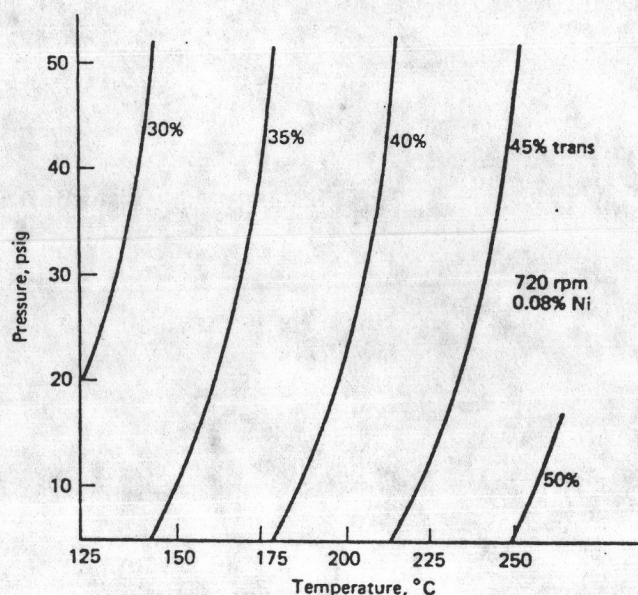


Figure 3.3 Effect of reaction temperature and pressure of trans unsaturation in 80-1.V. soybean oil [15].

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.

Hydrogenation is an exothermic reaction, and 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. Rogers and Siddiqui [26] determined the heats of hydrogenation ( $\Delta H_H$ ) of the methyl esters of the common unsaturated fatty acids (Table 3.1).

Table 3.1 Heats of hydrogenation of methyl esters [15]

Methyl Ester	$\Delta H_H$ (kcal/mole)
Palmitoleate	$-29.30 \pm 0.24$
Palmitelaidate	$-32.43 \pm 0.60$
Oleate	$-29.14 \pm 0.26$
Elaidate	$-28.29 \pm 0.15$
Linoleate	$-58.60 \pm 0.39$
Linoelaidate	$-55.70 \pm 0.13$
Linolenate	$-85.40 \pm 0.58$

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 reaction mass 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.

### 3.3.2 Effect of Pressure [11]

Increasing hydrogen pressures results in a larger driving force to stabilize 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. The overall rate of hydrogenation increases; at lower pressures, the rate of hydrogenation is almost directly proportional to the absolute hydrogen pressure [15,17,25]. Selectivity and isomerization always decrease with increased pressure.

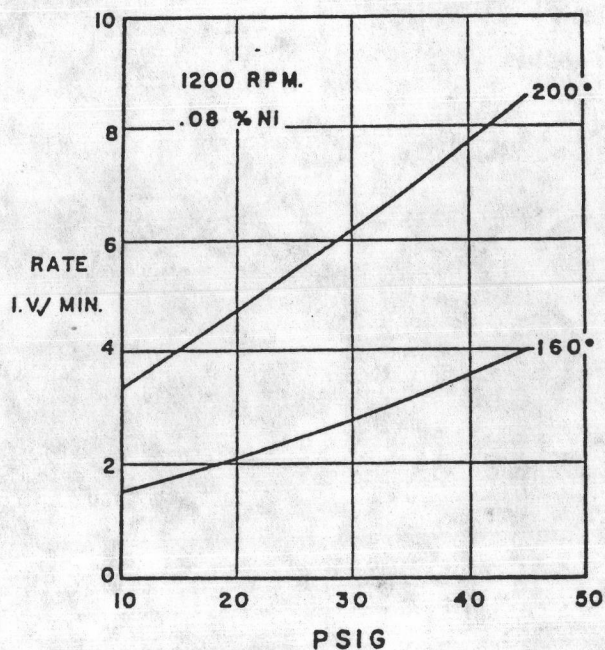


Figure 3.4 Effect of reaction pressure and temperature on the rate of hydrogenation of soybean oil [15].

Most industrial hydrogenation of oils are performed under hydrogen pressure of 10-60 psig. Although this is a very limited range of pressures, changes in pressure have a profound effect on the products produced.

Figure 3.4 shows the effect of pressure on the rate of hydrogenation of soybean oil at two different temperatures. If the pressure is doubled, the rate approximately doubles at both temperature. However, this reaction was very well agitated.

### 3.3.3 Effect of Agitation

The heterogeneous hydrogenation of oils involves not only several consecutive and simultaneous chemical reactions, but also physical steps of mass transfer of the gas and liquid to and from the solid catalyst surface. Therefore, the reaction mass must be agitated. The agitation must accomplish the distribution of heat or cooling for temperature control, and it must keep the solid catalyst suspended throughout the mass for uniformity of reaction.

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 increases but selectivity and isomerization 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 [17,21,25].



Industrial hydrogenators use the system of bubbling the hydrogen into the liquid at the bottom of the tank. The hydrogen available for reaction comes partly from the fraction of the hydrogen bubbles that are adsorbed during their passage through the oil and from the gas in the headspace that is stirred back into the oil. Agitation is provided by a central shaft with one or more blades that may be flat blades or of the turbine type. Also, the position of the blade on the shaft is important [27,28]. The speed of the agitators and the tendency to cavitate affect the amount of hydrogen in the oil. There may be flat plate baffles to break the flow. The configuration, the number, and the placement of the coils for heating and cooling are also important in agitation, as well as the size and the quantity of hydrogen bubbles going through the oil. Thus the "agitation" of the reaction mass is the sum of many factors that can be only estimated.

The main function of agitation is to supply dissolved hydrogen to the catalyst surface. Therefore, as shown in Figure 3.2, at low temperatures of hydrogenation the change of hydrogenation rate is less at higher agitation speeds. Thus at slow reaction rates the agitation of higher speeds is sufficient to provide almost enough hydrogen to the catalyst, and increased agitation does not change the hydrogen supply. However, at high hydrogenation temperatures there is a rapid change of hydrogenation rate with change in agitation, so the supply of hydrogen limits the rate of hydrogenation.

#### 3.3.4 Effect of Catalyst Concentration

The catalyst concentration may be varied over a wide range, but economic considerations dictate the use of minimum catalyst consistent with rapid reaction.

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 decreases [15]. However, since the hydrogen concentration at the catalyst surface decreases, consequently, selectivity and isomerization increase. When no diffusion steps are controlling, the concentration at the catalyst surface is unchanged. Consequently there are no changes [17,21,25] in selectivity, isomerization, or rate of hydrogenation per unit weight of catalyst (i.e., the overall rate is directly proportional to the amount of catalyst).

As shown in Figure 3.5, increasing the amount of nickel catalyst for hydrogenation of oils offers decreasing returns. At low level of catalyst, the increase of catalyst concentration causes a corresponding increase in the rate of hydrogenation. However, if more and more catalyst is used, a point is finally reached at which no further increase in rate is observed.

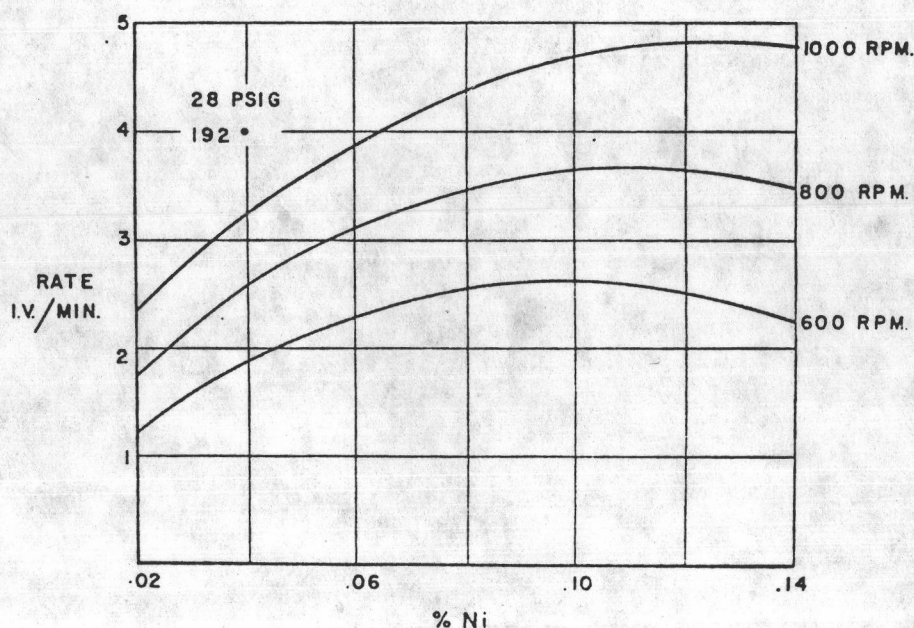


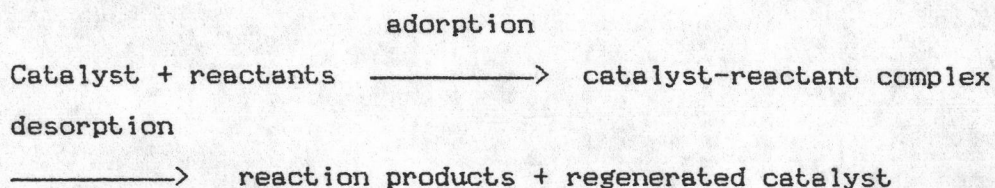
Figure 3.5 Effect of catalyst concentration on rate of hydrogenation of soybean oil [15].

### 3.4 Heterogeneous Catalysis

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 somewhat sharply distinguished from homogeneous catalysis, in which the catalyst and the reactants comprise a single phase. In homogeneous catalysis the catalyst functions in the form of individual molecules, which are uniformly distributed throughout the reacting system. Thus the question 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 submicroscopic character of its surface renders the study and the control of such catalysts very difficult. Apparently similar catalysts may differ enormously in their activity and specific action.

In heterogeneous catalysis it is now generally assumed that reaction proceeds through the formation of unstable intermediate compounds or adsorption complexes, in which the catalyst is temporarily combined with one or more of the

reactants. If such compounds exist, it is probable that in most cases they are not definite chemical combinations but consist merely of strongly bound molecules of the reactant that 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:



#### 3.4.1 Catalysis in Relation to Energy of Activation

Chemical reactions, catalyzed or uncatalyzed, do not occur instantaneously 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, is represented graphically in Figure 3.6 as the height of a potential barrier opposing the reaction.

Modern views relative to the energy factor in catalysis have been reviewed by Berkman et al. [29]. More recently, Grosse [30] has presented a simplified treatment of a catalytic action from the standpoint of energy relationships, from which the following is taken.

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

$$k = A \exp(-E_{\text{act}}/RT)$$

where  $T$  is the absolute temperature,  $A$  is a factor related to the concentration of the reactants, and  $E_{\text{act}}$  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. Thus, for example, if the activation energy at 300 K is 50,000 calories, a 10% lowering of this energy requirement will increase the reaction rate 4400 times; even a 1% lowering will increase it 2.3 times.

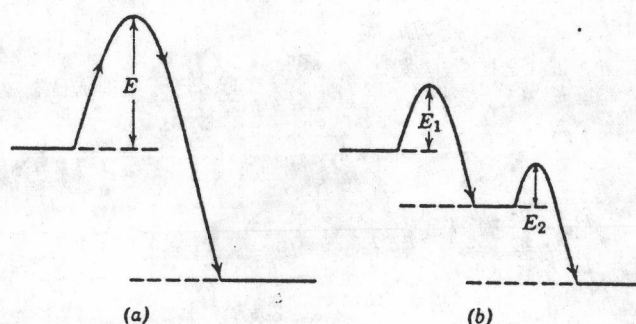


Figure 3.6 Graphical representation of the activation energy factor in (a) uncatalyzed and (b) catalyzed reactions. (After Grosse [30].)

Catalysts increase the reaction rate through their influence on the activation energy. A catalyst breaks the reaction up into two successive steps: the combination of catalyst and reactants to form an unstable intermediate compound and the breakdown of this compound to yield a new product and the free catalyst. This has the effect of permitting the energy barrier to be surmounted in two small steps, rather than one large one (Figure 3.6). In other words, two reactions with relatively low activation energies are substituted for a single reaction with a high activation energy. The alteration caused in the reaction rate is measured by the difference between the activation energy of the

uncatalyzed reaction and that of the slower of the two steps of the catalyzed reaction. In view of the 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.

### 3.4.2 Theory of Catalyst Structure

Since heterogeneous catalysis is a surface phenomenon, 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.

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 Taylor [31]. This theory assumes that the metal atoms on the surface of the catalyst possess 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 that are thus highly unsaturated are the ones capable of entering into temporary combination with the hydrogen and the unsaturated oil, thereby 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 (Figure 3.7).

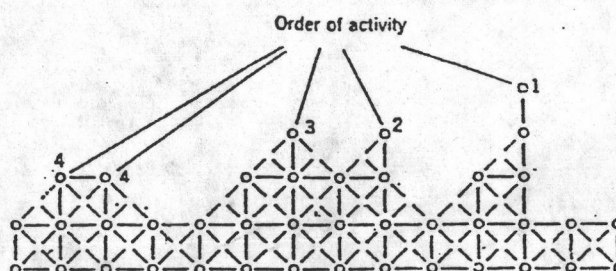


Figure 3.7 Schematic representation of a catalyst surface [15].

An alternative theory of catalyst structure envisions 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 normal interatomic spacing of  $2.47 \text{ \AA}$  is actually a little smaller than the theoretical optimum. Expansion may occur as metallic nickel is produced by the reduction of a nickel compound.

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, and nickel-aluminum alloy, and then reducing the resulting compound to regain the nickel 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 shown in Figure 3.8.

There is considerable evidence that the hydrogenation of an ethylenic compound must be preceded by two-point adsorption of the carbon atoms on either side of the double bond [32]. This requirement would impose certain dimensional limitations on the space lattice of any catalytically active metal. Actually, the metals that are at all effective in the hydrogenation of double bonds (nickel, cobalt, iron, copper, platinum, and palladium) all have interatomic spacings close to that ( $2.73 \text{ \AA}$ ) calculated as optimum for such two-point adsorption.

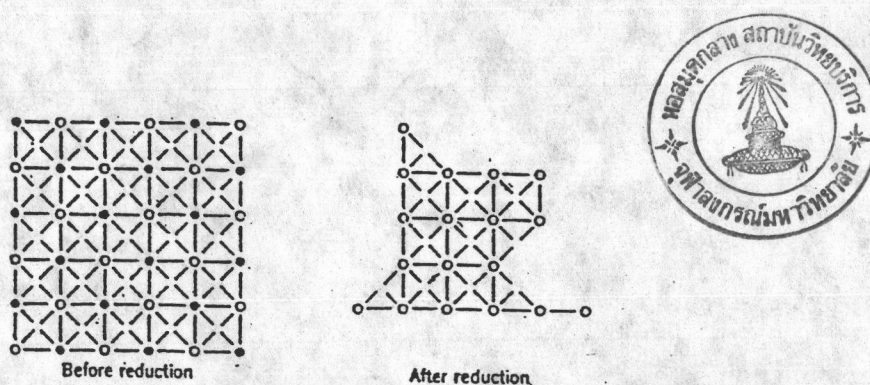


Figure 3.8 Schematic representation of effect reduction on a nickel catalyst. White circle, nickel atom; black circle, atom of oxygen. aluminum, and so on [15].

Twigg and Rideal [33] have correlated the catalytic activity of various metals with their interatomic distances. Using the distances  $2.47 \text{ \AA}$  for Ni-Ni,  $1.52 \text{ \AA}$  for C-C, and  $1.82 \text{ \AA}$  for C-Ni, they showed that for adsorption of the C-C group the valence angle for the bond would have to be  $105^{\circ} 4'$  (Figure 3.9), which is considerably less than the tetrahedral



angle  $109^{\circ} 28'$ . For the valence angle of the bond to equal the tetrahedral angle the interatomic distance for the metal would have to be  $2.73 \text{ \AA}$ . Significantly, the interatomic distances for platinum and palladium are  $2.76$  and  $2.74 \text{ \AA}$ , respectively. They should fit the C-C group without appreciable strain and probably are very good catalysts for that reason.

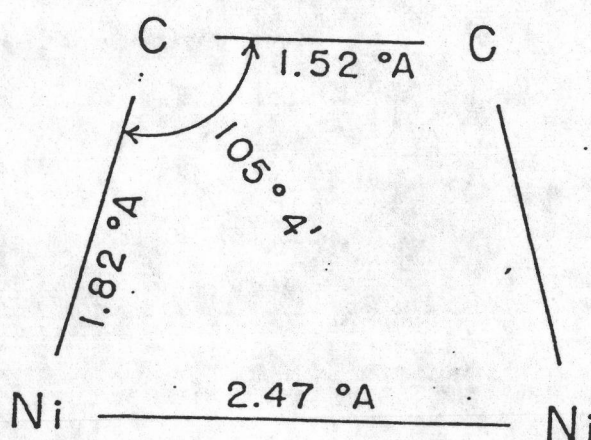


Figure 3.9 Interatomic distance and valence angle for C=C adsorbed on nickel surface [34].

### 3.4.3 Catalyst Preparation by Dry-reduction Method [34]

To prepare a catalyst by this method, a nickel salt solution is absorbed on some type of carrier such as clay, alumina, or diatomaceous earth; then the material is dried and ground. The ground material is heated in a closed furnace in the presence of  $\text{H}_2$  to about  $500^{\circ}\text{C}$ . The supported nickel salt is reduced to black metallic nickel during the reduction. After the reduction is complete, the catalyst is quite pyrophoric so usually an inert gas is substituted for the hydrogen on the catalyst before the catalyst is exposed to the air. Thus the catalyst is stabilized and may be shipped without danger.

There are many types of process such as, precipitation method, electrolytic precipitation method, and impregnation method are commonly used for making dry-reduced catalyst. The detail of the methods were discussed in the followings.

#### 3.4.3.1 Precipitation

The precipitation involves in its initial stages the mixing of two or more solution or suspensions of material, causing precipitation; this is followed by filtration, washing, drying, calcining and reducing.

The salts of nickel which can be used in the production of precipitated catalysts are the chloride, nitrate and sulfate. The latter is employed by far the most frequently, primarily because of its lower cost, and is one of the two main compounds used to prepare catalysts for the plant-scale hydrogenation of fats and oils. The other compound is nickel formate. The chloride and nitrate of nickel are used for precipitated catalysts when it is necessary to eliminate, insofar as possible, impurities which can poison the hydrogenation reaction. The nickel nitrate, in particular is desirable because on heating it decomposes into oxides of nitrogen and nickel oxide, NiO.

As precipitants for nickel salts, successful use has been made of sodium, potassium, and ammonium hydroxides, the corresponding carbonates and bicarbonates. Of these, sodium carbonate and sodium bicarbonate are the most generally suitable and are used predominantly. The use of ammonium hydroxide does have one advantage: Traces of ammonium salts which remain behind in the precipitated mass are easily volatilized during the

reduction process.

A procedure essentially as described by Bailey [35] yields a good, active catalyst. According to this procedure 70 parts of chemically pure nickel sulfate hexahydrate is dissolved in 2500 parts of water. The solution is heated to boiling; and 15 parts of a fine grade of diatomaceous earth is added. A second solution is prepared consisting of 42 parts of chemically pure sodium bicarbonate and 650 parts of cold, distilled water. The second solution, which must be used while fresh, is added to the first solution at a uniform rate over a period of 1.2 to 1.5 hours while the latter is kept boiling and is being agitated vigorously with a mechanical stirrer. The final solution containing the diatomaceous earth and nickel carbonates in suspension should be alkaline to phenolphthalein. At this point an additional 15 parts of diatomaceous earth is added, and boiling and agitation are continued for an additional 0.5 to 1.0 hour after which the mixture is filtered to remove the spent solution. The solid are resuspended in 2200 parts of distilled water, and the mixture is boiled for a short time and refiltered. The washing operation is repeated once or twice, care being taken not to prolong it unduly. Immediately after washing, the solid are dried at 105 to 110 °C and pulverized to a fine powder which is the unreduced catalyst. After pulverization the solids are of high specific volume and fluffy in nature. Nickel content is approximately 25%. Reduction is accomplished by heating in a stream of hydrogen for about 8 hours at 480 to 510 °C.

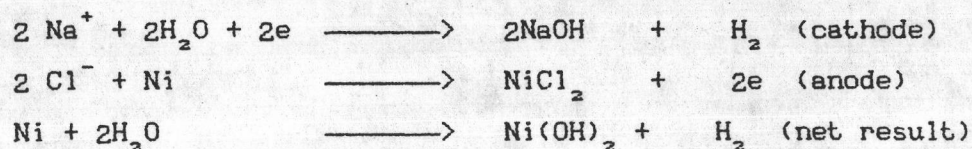
As is the reduction of all catalysts of this type, care must be exercised to remove entrapped air before the catalyst is heated in the presence of hydrogen; otherwise an explosion may result. The reduced catalyst is highly pyrophoric and must not come in contact with air. After reduction, the hydrogen over the

catalyst can be replaced with carbon dioxide and thus lessen the possibility of explosions. A general practice is to suspend the catalyst in oil in which form it is stable.

#### 3.4.3.2 Electrolytic Precipitation

A more recently introduced method of catalyst preparation, which yields a product of very high activity, good characteristics, and remarkable uniformity, is that of electrolytic precipitation [36,37]. This method involves the corrosion of sheets of metallic nickel in an electrolyte by the passage of a direct current. The nickel is precipitated in the form of nickel hydroxide on kieselguhr suspended in the electrolyte. The superiority of the electrolytic method over other methods of precipitation appears to be due to the fact that by this means the entire mass of catalyst can be precipitated at a constant and controllable pH, whereas in ordinary precipitation by the addition of one solution to another the pH of the precipitant solution continuously varies. Furthermore, the product is usually free of undesirable sulfur compounds.

A sheet of the metallic nickel to be converted to nickel hydroxide is made the anode of the electrolytic cell while another sheet of nickel or other corrosion resistant metal is employed as the cathode. On passing a direct current through the electrolyte (a dilute solution of sodium chloride) the following reactions occur:



In addition to the reactions indicated, a small amount of side reaction occurs: some basic nickel chloride is formed. This tends to increase the pH of the electrolyte as the reaction continues. In the original procedure, as described by Sieck [36], this tendency for the pH to increase was overcome to some extent by employing a mixture of sodium acetate and ammonium chloride as the electrolyte because of their buffering qualities. Current practice is to introduce an acidic material to control the pH.

The following is one of the proven procedures for preparing electrolytically precipitated nickel catalyst. The nickel sheet to be corroded (anode) is suspended in a vat made of wood or other inert material. Two cathodes (one on each side of the anode) are suspended to within 1 to 4 inches of the anode. The vat is almost filled with a 1% solution of chemically pure sodium chloride, and amount of fine diatomaceous earth equal in weight to the nickel to be corroded is added. The mixture of earth and electrolyte is heated to 50 °C; and while it is kept in uniform suspension by mechanical stirring, direct current is passed through the cell at a current density of 44 to 57 amperes per square foot, based on the total anode surface. To produce this current density, about 6 volts is required. The temperature of the electrolyte is maintained at 50 °C. The pH is maintained between 9.0 and 9.5 by introducing carbon dioxide at a slow, uniform rate. When the proper amount of nickel has been corroded, electrolysis is discontinued, and the suspended catalyst is separated from the electrolyte by filtration, washed, dried and ground to a fine powder. This unreduced catalyst should contain about 38.5% of nickel. Reduction is accomplished by heating it at 370 to 480 °C in a stream of hydrogen for 2 to 4 hours.

### 3.4.3.3 Impregnation

Impregnation is the easiest method of making a catalyst. A carrier, usually porous, is contacted with a solution, usually aqueous, of one or more suitable metallic compounds. The size and shape of the catalyst particles are that of the carrier. The impregnation technique requires less equipment since the filtering and forming steps are eliminated and washing may not be needed. It is the preferred process in preparing supported noble metal catalysts for which it is usually economically desirable to spread out the metal in as finely divided a form as possible.

There are two methods of contacting. The support is sometimes dipped into an excess quantity of solution, but the composition of a batch of solution will change as additional supports are impregnated. The release of debris into the treating solution can form a mud, which makes it difficult to completely utilize the treating solution. More precise control is achieved by a technique termed by dry impregnation, or impregnation to incipient wetness, which is commonly used industrially. The support is contacted, as by spraying, with a solution of appropriate concentration corresponding in quantity to the total known pore volume of slightly less. This allows accurate control of the amount of the active ingredient that will be incorporated into the catalyst. Good reproducibility from one particle to another may be achieved but the maximum loading obtainable in a single impregnation is limited by the solubility of the reagent. In any event, the resulting catalyst is then usually dried and calcined. In a few cases, in order to obtain more uniform dispersion, the active ingredient may be fixed inside the catalyst by immersing the impregnated catalyst in a reagent to cause precipitation occur.

Oxide supports such as alumina and silica are readily wet by aqueous solutions, as are most activated carbons, which have a layer of chemisorbed oxygen on them. Capillary forces then ensure that liquid will be sucked up into the entire porous structure. Because of capillary pressure, even pores closed at one end will be nearly filled, and the solution of gas in the liquid assists the process. If the support is not readily wetted, e.g., a carbon that is highly graphitized or without chemisorbed oxygen, an organic solvent may be used or the support may be impregnated under vacuum. These procedures are somewhat more costly to use in the plant than incipient impregnation.

The time required for liquid penetration into a pore may be calculated by equating the capillary force to the viscous drag. For a wetting liquid where the contact angle is zero, the time required for liquid to penetrate a distance  $x$  into a capillary is given by:  $t = 4\eta x^2 / \gamma d$ , where  $\eta$  is the liquid viscosity,  $\gamma$  is the surface tension, and  $d$  is the pore diameter.

#### 3,4,4 Catalyst Poisoning

They are four basic mechanisms of catalyst decay: poisoning, fouling, thermal degradation, and loss of catalyst material through formation and escape of vapors. Poisoning and vapor transport are basically chemical phenomena; fouling is mechanical; thermal degradation is, naturally, thermal.

Heterogeneous catalysts are typically small crystals (crystallites) of metal, metal oxide or metal sulfide attached to inert carriers. Poisoning is the strong chemisorption of reactants, products or impurities on these active catalytic-metal sites. A poison blocks the sites, and may also induce changes in the surface or result in formation of compounds.

This is an operational definition. A certain species may be a poison in some reactions, but not in others, depending on its adsorption strength relative to that of other species competing for catalytic sites. For example, oxygen is a reactant in the partial oxidation of methane to methanol, but a poison in ammonia synthesis.

Catalyst poisons can be classified according to chemical species, types of reactions poisoned, and selectivity for active catalyst sites [39].

Catalyst poisoning may be irreversible, leading to permanent inactivation of the catalyst, or it may be reversible if under certain conditions the poison can be removed and the original activity of the catalyst restored. Both reversible and irreversible catalyst poisoning are encountered in the hydrogenation of fats and oils.

**Gaseous Poisons.** Among the worst poisons for nickel catalysts are the gaseous sulfur compounds: hydrogen sulfide, carbon disulfide, sulfur dioxide, carbon oxysulfide, and so on. These compounds are of considerable concern in practical hydrogenation since they may occur as impurities in crude hydrogen prepared by the steam-iron, water gas-catalytic, or hydrocarbon reforming processes. They are rapidly adsorbed by nickel catalysts and poison the catalysts irreversibly.

Besides the sulfur compounds mentioned previously, the catalyst poison most likely to cause trouble in the hydrogenation of fats and oils is carbon monoxide, which is also present in small amounts in unpurified steam-iron and steam-hydrocarbon hydrogen. Carbon monoxide is adsorbed more slowly than are the sulfur compounds and poisons the catalyst



reversibly. It may be removed and the catalyst restored to its original activity by interrupting the hydrogenation and continuing to agitate the catalyst-oil mixture under a reasonably good vacuum (about 25 in Hg or better) for a short time.

Most other gases that may be present as impurities in hydrogen, including carbon dioxide, nitrogen, and methane, are not catalyst poisons, although in a hydrogenation apparatus of the "dead-end" type they will, of course, slow the reaction if allowed to accumulate in the headspace of the hydrogenator and will dilute the hydrogen. Small amounts of water vapor in the hydrogen appear to have no poisoning effect but cause the formation of free fatty acids.

**Poisons in the Oil.** The matter of catalyst poisoning through impurities in the oil has been discussed to some extent previously in connection with the effect of the catalyst concentration on the course of hydrogenation. Not a great deal is known about the natural oil and fat impurities that may function as catalyst poisons. Free fatty acids in small concentrations have little effect on the activity of the catalyst. The carotenoid pigments like-wise appear to be devoid of poisoning tendencies since there is no correlation between the color of an oil and the readiness with which it may be hydrogenated. There are catalyst poisons (probably phosphatides) in most crude oils, however, for these oils are more easily hydrogenated after refining. In the case of some oils, for example, crude fish oil, treatment of the crude oil with a liberal quantity of active bleaching clay is as effective in removing catalyst poisons as is alkali refining.

Sodium and other alkali soaps are very pronounced catalyst poisons. Soap sufficient to seriously poison the catalyst will seldom be found in vegetable oils that have been well bleached after alkali refining, but lard, edible tallow, or other light-colored animal fats that require little or no bleaching are often soapy enough after refining to cause trouble in hydrogenation. Soap is quite effectively adsorbed by used catalysts that have become largely inactivated; hence in hydrogenating alkali-refined lard and so on it is sometimes expedient to give the fat a pretreatment with old catalyst before fresh catalyst is added.

A wide variety of substances were tested for their effect on nickel catalyst by Ueno [40], who reported the following to be poisons: soaps of potassium, sodium, lithium, magnesium, barium, beryllium, iron, chromium, zinc, cadmium, lead, mercury, bismuth, tin, uranium, and gold; copper hydroxide; ammonium molybdate; boric, arsenious, and hydrochloric acids; glycolic, lactic, hydroxystearic, oxalic, succinic, fumaric, malic, citric, and tartaric acids; sodium taurocholate; iron, zinc, lead, mercury, sulfur, tellurium, selenium, and red phosphorus; proteins, blood albumin, blood fibrin, gelatin, glycerol, lecithin, sucrose, dextrose, mannitol, starch, morphine, strychnine, amygdalin, potassium cyanide, zinc oxide, and aluminum silicate.

The following were found to be without poisoning effect: soaps of calcium, strontium, aluminum, cerium, nickel, manganese, copper, silver, vanadium, thorium, and platinum; nickel acetate, butyrate, stearate, lactate, oxalate, and succinate; and

tungstic acid, fatty acids, nucleic acid, nickel, tin, zirconium, aluminum, copper, hemoglobin, cholesterol, squalene, and glycogen.

Molecules having an unsaturated electron structure (e.g., CO, NO, HCN, benzene) may chemisorb through multiple bonds [39].

The effective life of a catalyst probably depends on the extent to which it adsorbs poisons from the oil. Some slight content of poisonous substances appears to be unavoidable, even in the most carefully refined oils. Even if the latter consisted of absolutely pure glycerides, it is quite possible that some degree of catalyst poisoning might occur through the formation and the adsorption of oxidation products or other degradation products of the oil. The literature on catalyst poisoning - particularly with respect to poisons in the oil - has been reviewed in detail by Bodman et al. [41].

Drozdowski and Zajac [42] found that poisons or "inhibitors" increased the induction period of the hydrogenation as well as decreased the catalyst activity.

#### 3.4.5 Promotion of Nickel Catalysts

A "promoter" is a metal or other substance that enhances the activity of a catalyst without being a catalyst for the reaction in question. The promotion of catalysts is much practiced in fields of catalysis other than the hydrogenation of fats, and the employment of catalysts of two, three, four, or even more components is by no means unusual. In such complex systems

the action of some of the components may more properly be called "synergistic" than "promotive," since usually more than one component will possess catalytic activity alone. Promotion in its proper sense is, however, very common.

A number of mechanisms have been proposed to explain the phenomenon of promotion. It has been supposed that the promoter acts as a secondary catalyst, accelerating the formation or decomposition of intermediate compounds; assists in the adsorption of the reactants; or protects the catalyst from poisons. With catalysts for the hydrogenation of fats, however, it appears more reasonable to assume that the function of a promoter is simply structural and that it permits the development of larger numbers of active centers on the catalyst surface.

Promoters play a major role in the manufacture of fat hydrogenation catalysts, since catalysts of satisfactory selectivity can be prepared with their aid.

Metals referred to in the patent literature as useful promoters, either as such or in the form of oxides, are chromium, cobalt, thorium, zirconium, copper [42,43], titanium [44], and silver.