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Hydrogenation of Fats and Oils. Isomerization During Hydrogenation[1]

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Abstract

This presentation includes a survey of the development of the presently accepted theory for the formation of isomers based on a half hydrogenation-dehydrogenation mechanism with atomic hydrogen, an appraisal of the relevant work of recent years for its significance when applied to the problem of isomerization, and certain experimental evidence from other fields of heterogeneous catalysis of interest in the hydrogenation of fats and oils. Effects of temperature, pressure, catalyst concentration, and degree of agitation used in commercial plants on the degree of isomerization are discussed. In addition the conditions necessary for the proper application of the term "selective" to a hydrogenation are examined. An interpretation of recent work to reduce isomerization while retaining selectivity by extending the normal range of the variables and by the use of solvents is covered. Selected works on catalysis from related fields are used to indicate possible modifications of the isomerization mechanism and, perhaps, to reveal fruitful avenues of research.

Introduction

HYDROGENATION is the oldest and most important of the commercial processes used in the chemical modification of fats and oils. Sabatier in France as early as 1897 and Normann in Britain in 1903 were responsible for the basic development of the process as it is known today. By 1911, the first commercial product containing hydrogenated fat was on the market in this country. Today, the importance of the process is difficult to overemphasize. Currently, in excess of three billion pounds of vegetable oils are hydrogenated annually. The process has contributed more than any other technique to the great increase in the diversity of use of various fats and oils.

Discussion

Essentially the process involves bringing together an unsaturated fat or oil, a nickel catalyst, and hydrogen under such conditions that the hydrogen combines with the oil. The product is usually a semisolid, or plastic fat. The original purpose of this process was to permit the use of cheaper vagetable oils in the place of more expensive animal shortenings. The first commercial products were crude and, sometimes, unsatisfactory. They consisted of blends of a solid (completely hydrogenated) fat with a liquid (refined and bleached) oil. It was not unusual for the consumer of the early products to find that the two phases had separated into their original unblended state. There was some "consumer resistance." Gradual improvements in the process and the products led to today's all-hydrogenated shortenings and related products, that are not only accepted, but are preferred by many consumers.

Yet, even today, hydrogenation must be regarded as an enigma of the fat and oil industry. Fundamentally, it is not well understood. Certain problems, which have plagued the industry from the beginning, are growing in importance. Much can be done toward modifying and improving the hydrogenation of vegetable oils. An increasingly recognized problem is that these hydrogenated oils differ chemically from natural oils to a large extent. An excellent review of the changes in the nutritive value of fats and oils after hydrogenation is available (10). Hydrogenated oils contain glycerides that may consist partially of positional and geometric isomers of normal linoleic acid. Hydrogenated oils may contain large amounts of positional and geometric isomers of oleic acid, *cis*-9-octadecenoic acid. It is generally agreed that glycerides of these isomers of oleic acid are utilized by the animal body as readily as are those of oleic acid itself, provided the fat product in which they occur does not have too high a melting point. Further work may be needed to assess fully the importance of isomeric products in human diets.

While no solution to the problem of eliminating the formation of geometrical or positional isomers during hydrogenation will be presented, it is hoped that various sections of this discussion will be of value to those interested in this field. The objectives of this paper will be to survey the development of the presently accepted theory for the formation of isomers, to appraise some of the more relevant work of recent years for its significance, to stress the paucity of the means of solution with the present theory, and to engender interest in more fruitful avenues of research by reviewing certain work from other fields of heterogeneous catalysis.

Development of Theory

The historical evolution of present-day theory of

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the hydrogenation of fats and oils, while interesting, is not necessary for an understanding of the subject. An orderly development of the process will be sufficient and is all that is intended. This development will necessarily be brief and may be said to be oversimplified. References are included for those who desire more information. What is true of the development of the theory may, in all probability, be scored against the interpretation put on some of the results and the choice of articles from related fields of catalysis.

Though the preparation of the oil, gas, and catalyst may affect the formation of isomers during hydrogenation, the details of their proper preparation are beyond the scope of this presentation. These details have been described by Bailey (6), who gives a thorough discussion of all phases of the hydrogenation process as it was understood prior to 1951. His discussion is valid today. However, the customary variables of the hydrogenation process and the usual ranges of these variables in commercial practice are basic to a discussion of isomer formation. Temperature, catalyst concentration, pressure, and degree of agitation are the customary variables. Today, as for many years past, temperatures range from 150 to 200C; catalyst concentrations from 0.01 to 0.50%; pressures from slightly above atmospheric to about 100 psi. At least enough agitation is prescribed to uniformly and intimately mix the oil, catalyst, and gas. Generally, this is all the agitation that is supplied. Temperature and catalyst concentration are the more important variables because pressure and degree of agitation are dictated by the design of the equipment and are not easily changed.

The effects of the four variables have always been determined by measuring the physical and chemical properties of the products. Hydrogenation is usually continued until the lowest iodine value (I.V.) suitable to the desired physical consistency, or plastic range, of the product is obtained. Melting and congeal points along with other physical tests are used to gauge the consistency of the fat. After a consideration of the melting points of the component fatty acids and their triglycerides together with the required physical consistency and mouthing qualities of the products, it is obvious that the hydrogenation of a linoleic to an oleic acid instead of an oleic to a stearic is required to achieve the desired physical characteristics in the products. Thus, the concept of a ''selective'' hydrogenation as being one in which the polyunsaturated component is preferentially hydrogenated to a monounsaturated component became accepted. The original formulation of this definition of selectivity is attributed to Richardson (23). Moore et al. (21) showed early that linoleic acid is hydrogenated much more readily than the oleic.

In early attempts to achieve more selective hydrogenation, the individual effect of the variables on the products was investigated. Representative of this type of inquiry is the work of Bailey, Feuge, and Smith (7) as well as that of Richardson and of Moore, cited above. Such studies revealed that an increase in temperature will increase the selectivity as long as the other variables are held constant. In like manner, an increase in catalyst concentration was found to increase selectivity, whereas increasing either the pressure or the agitation decreased selectivity.

Those conditions which produce high selectivity are also the conditions that gave, at room temperature, larger amounts of a solid acid fraction that is not saturated, known as ''iso-oleic acids'' (7,16,17). Such acids are now known as the geometrical and positional isomers of oleic acid and, because of better analytical techniques, are known to be formed in greater quantities than originally suspected. However, processors learned by a proper adjustment of the variables, principally temperature and catalyst concentration, to maintain a careful balance between selectivity and isomer formation, thus preparing highly acceptable products with a wide range of physical properties. Generally, high selectivity is desired; only when a greater plastic range is wanted will the processor deliberately hydrogenate nonselectively and then only when preparing an unblended product. In spite of the success achieved, there was, and is, a desire to have more definite control over the process, to have some means of improving selectivity at will without the concomitant increase in isomer formation.

The formation of isomers as it is understood today will be clearer if one considers what effect changes in the variables have on the concentration, or availability, of hydrogen on the catalyst surface. A highly significant result is obtained by such a consideration. This result may be summarized as follows: any change that tends to decrease the availability of hydrogen at the catalyst surface tends to increase the selectivity. A few examples may help clarify this statement. Consider the effect of an increase in temperature. Because an increase in temperature increases the rate of reaction, hydrogen on the surface of the catalyst is consumed more rapidly; if all other factors, including rate of supply of hydrogen to the surface, remain constant, then the availability of hydrogen on the catalyst surface will decrease and the reaction will be more selective. Similarly, if more catalyst is added to the reaction, all other factors being constant, the supply of hydrogen to the catalyst as a whole decreases and the reaction becomes more selective. Increasing the pressure or the degree of agitation obviously makes more hydrogen available to the catalyst surface and the process becomes less selective. Through this idea of hydrogen availability on the catalyst surface it is possible to be more specific in a description of ''selective'' conditions: a run is considered to be more selective only if there is a comparative shortage of hydrogen at the catalyst surface. It should be emphasized that these considerations of selectivity are general and apply only under the normal commercial conditions described earlier.

Finally, all of the previous knowledge was augmented and synthesized into a theory to account for both selectivity and isomer formation during the hydrogenation of a variety of vegetable oils. A number of investigations, (2,4,9,11,14,27,28) have been concerned with this further development of theory. The principle has also been expanded to cover conjugated systems of double bonds (3,5). The theory is based on a half hydrogenation-dehydrogenation of the double bond with atomic hydrogen. The theory postulates that hydrogen gas is chemisorbed in the form of atomic hydrogen in and on the nickel catalyst. With large excesses of hydrogen, some molecular hydrogen may be present on the surface. The oil or fat is also adsorbed on the catalyst surface. The reaction takes place on or near certain ''active centers'' on the nickel and is visualized as consisting of the addition of one hydrogen atom to one of the carbons of the double bond to form a free radical. This free radical may then either react with another hydrogen atom to complete the reaction, or lose a hydrogen atom to the catalyst to reform the double bond. Selec-

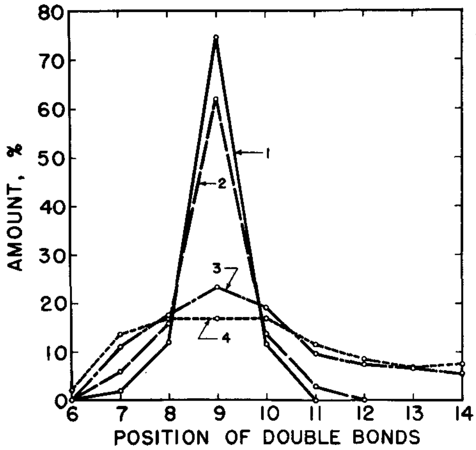

FIG. 1. Effect of temperature on the formation of positional isomers during the hydrogenation of methyl oleate with 0.2% electrolytic nickel catalyst and good dispersion of hydrogen. Curve 1, 90C; 2, 110C; 3, 170C; 4, 200C (15).

tive conditions increase the chance that the fat will lose a hydrogen atom (dehydrogenate); non-selective conditions favor the transfer of another hydrogen atom to the bond (saturation). The reaction may be thought of as a competition between the gas and the fat to supply hydrogen atoms to the active centers of the nickel.

The half-dehydrogenation process results in the formation of both positional and geometrical isomers. Positional isomers form if the hydrogen atom removed during the dehydrogenation step is not the same as that which originally added to the fat. Such a process of a half-hydrogenation and a half-dehydrogenation involving different hydrogen atoms is capable of moving the double bond one carbon atom up or down the chain. By repetition of the process, double bonds may migrate along the entire carbon chain. The theory explains the formation of geometrical isomers by assuming free rotation of the half-hydrogenated bond of the radical. Under such conditions, each time the fat loses a hydrogen atom the resultant double bond that forms has two chances out of three of being *trans*. The formation of both types of isomers proceeds simultaneously. Some idea of the magnitude of the effects involved and the degree of control presently being exercised over the isomerization of the double bonds in methyl oleate and linoleate is given by Figures 1, 2, and 3.

Recent Work

Much of the relevant research in recent years has been concerned with studying the effect of extending the range of the variables beyond that normally encountered in commercial work. The use of solvents has also been reported. All of the studies are not concerned particularly with the isomerization problem but the results may be validly interpreted for our purposes.

The effect of pressures up to 1800 psi has been studied by Sims (25) during the hydrogenation of soybean oil. At a pressure of 400 psi, or higher, temperature increases from 125 to 200C had little effect on selectivity. Also at these higher pressures the usual effects of agitation and catalyst concentration were reversed. These results are unusual unless it is assumed that truly selective conditions, that is, a scarcity of hydrogen on the catalyst surface, were never attained. At such high pressures, and particularly with good agitation, comparatively minor successive changes in the catalyst concentration, the degree of agitation, and the temperature may do little to decrease availability of hydrogen.

Eldib and Albright (14) investigated the effect of very high rates of agitation. Cottonseed oil was hydrogenated at temperatures, pressures, and catalyst concentrations within the normal range of commercial operation. The rates of agitation were such that mass transfer resistances were eliminated. Here again, all of the gas that was needed could have been always present regardless of how the other variables were modified, making it impossible to have truly selective conditions on the catalyst surface.

Although the conclusions of a comparative analysis of such different series of hydrogenations are debatable, the results of both these reports seem to verify the above conclusions. Selectivity between runs in either group may be compared, but both groups, overall, must be considered non-selective when compared with the results of a normal operation. Simultaneously increasing the catalyst concentration or otherwise attempting to adjust further the conditions in either series of hydrogenations would generally only return the system to its original condition except for tremendously increased reaction rates. To determine whether or not any particular group of experiments is truly selective would require a more quantitative specification of selectivity. Perhaps such an attempt should be made. As applied to cottonseed oil under normal operation, such a specification would require a reduction in the concentration of the linoleic acid groups to less than 5% at an I.V. of sixty.

In other work (13,15), it has been shown that lowering the temperature results in the formation of less positional and geometrical isomers. During the hydrogenation of methyl linoleate (Fig. 3) at 110C more than 50% of the total double bonds were found in the original 9 and 12 positions and about 30% were in the 10 and 11 positions, the rest being distributed rather uniformly in the remaining positions from 7 through 14. More selective conditions (higher temperatures) increased the concentration of bonds found at the 10 position and the distribution of the bonds all along the chain. When methyl oleate was hydrogenated at 90C, about 74% of the unhydrogenated bonds remained in the 9 position, Figure 1. Again more selective conditions increased the migration of the bonds. The formation of *trans* isomers during the hydrogenation of both methyl linoleate and oleate conformed with earlier observations; that is, more selective conditions increased the rate of formation of *trans* as shown in Figure 2. However, no attempt was made to determine the effect of these conditions on selectivity. It is highly probable that the general selectivity would decrease because of an increase in hydrogen on the catalyst surface due to the slower reaction rate.

The results of all work, then, on the extension of the range of the variables does not seem a likely method for obtaining high selectivity with low concentration of isomers.

The use of solvents in hydrogenation may afford a more promising approach to the selectivity-isomerization problem. A study (12) of the hydrogenation of methyl oleate with Raney nickel catalyst has indicated that hexane is capable of, and is superior to other solvents in, causing a reduction in *trans* and positional isomers. Hydrogenation products obtained with Raney nickel and solvents contained as little as 20.7% *trans* bonds at an I.V. of about 50. Large proportions of double bonds were found in the original 9 position. Kaufmann (19), also using a Raney catalyst, succeeded in hydrogenating various crude oils in hexane at 35C. A continuous system employing counterflow between the oil:hexane and hydrogen was used. A very low concentration of *trans* isomers was found in the product. Similar results, though not as outstanding, were obtained by Sanders (24). The hydrogenation of cottonseed oil with and without various solvents at high rates of agitation (1) resulted in both low selectivity and isomerization; the results were essentially identical for solvent and nonsolvent runs. Apparently extremely high rates of agitation cancel any beneficial action of the solvent. This is correct if one assumes selective hydrogenation was obtained in the other solvent work. A solvent may not significantly affect the concentration of hydrogen on the catalyst surface and therefore would not affect selectivity. In fact, because of an increased reaction rate, the solvent may actually decrease the availability of hydrogen at the catalyst surface, thus making the reaction more selective. Adsorption of the solvent on the catalyst may be partly responsible for these results but more work of a fundamental nature is needed for a better understanding of the mechanism.

Possible Modifications

The work to date on the isomerization problem has not been very successful and the "hydrogenation-dehydrogenation" concept of isomer formation as it is now understood does not offer much help in suggesting methods of attack on the problem. The theory indicates that the problem is insolvable. The present concept presents a dilemma in which the same condition of catalyst surface produces both high selectivity and high isomerization; one result cannot be obtained without the other. Since the same nickel "active centers" are responsible for all reactions, a *trans* forming center cannot be blocked while leaving a selective center free to operate.

However, the effect of solvents, at least, on isomer formation warrants some doubt in this matter. It may be argued that solvents are capable of blocking the efficiency of a *trans* center while permitting the selective center to operate as usual. Since theories are seldom perfect, a discussion of some of the more obvious modifications of the present one may be apropos. To form a groundwork for the discussion of these modifications, the results of a few investigations in the fields of heterogeneous catalysis not related to fats and oils will be reviewed. Such investigations show that hydrocarbons, oxygen, hydroxyl groups, and water may be adsorbed on, or react with, the same materials found in regular commercial catalysts used in hydrogenation of fats and oils. These adsorbed materials are very difficult to remove completely and may reasonably be expected to be present during a typical hydrogenation of a fat or oil.

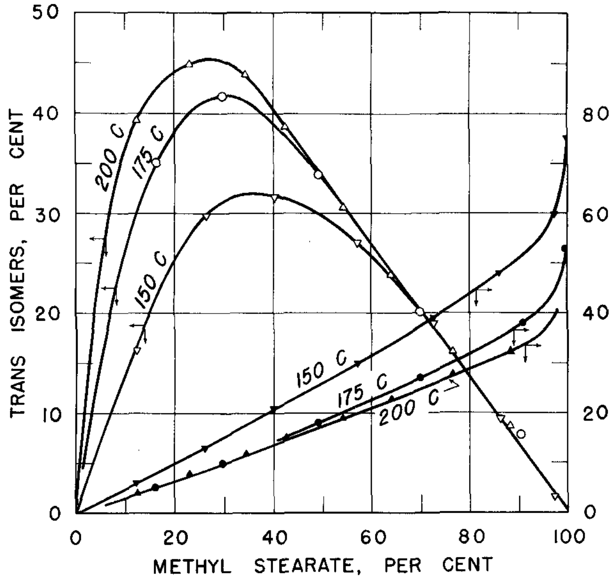

Fig. 2. Effect of temperature on the formation of *trans* isomers during hydrogenation of methyl oleate with 0.25% electrolytic nickel catalyst and good dispersion of hydrogen (17).

Galwey and Kimball (18) studied the dissociative adsorption of hydrocarbons on a supported nickel catalyst. The catalyst was prepared from nickel nitrate supported on silica in a ratio of Ni/SiO_2 of 1/6.3. The hydrocarbons studied were n-pentane, 2-methylbutane, 2,3-dimethylbutane, and cyclohexane. The extent to which dissociative adsorption occurred was directly measured by the exchange of the adsorbed hydrogen atoms with gaseous deuterium. The mixtures were analyzed by means of a thermal conductivity gauge. Results indicate that cyclohexane exchanged four hydrogen atoms from each chemisorbed molecule; n-pentane and isopentane exchanged five each; and 2,3-dimethylbutane only four. These results were used in an attempt to assign configurations to the multiply-adsorbed species. Temperature has a pronounced effect on the results. There was some activity between 0 and 75C, almost complete inactivity from 90 to 150C, and normal activity between 160 and 200C. The decrease in activity between 90 and 150C was attributed to a build-up of strongly adsorbed and multiply-bonded species of hydrocarbon. These species were stable only up to around 150C and their removal at that temperature permitted the reaction to continue. This work indicates that the dissociative adsorption of hydrocarbons is thermodynamically possible and lends support to the dehydrogenation concept in fat chemistry. The experimental technique is not limited to hydrocarbons but may be used with a wide range of molecules containing hydrogen atoms.

Sinfelt, Hurwitz, and Rohrer (26) investigated the isomerization of n-pentane over a $Pt\text{-}Al_2O_3$ catalyst. A reaction mechanism was proposed that is interesting because it involves migration of the reactant on the catalyst surface between two types of sites. In this

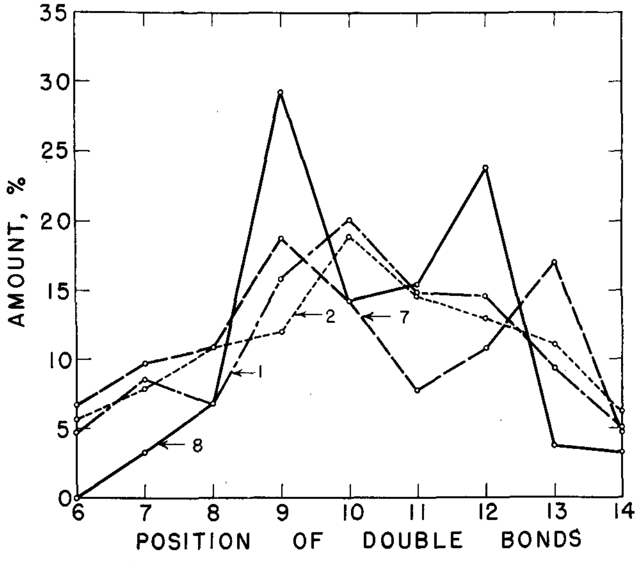

Fig. 3. Effect of temperature on the formation of positional isomers during the hydrogenation of methyl linoleate with 0.2% electrolytic nickel catalyst and good dispersion of hydrogen. Curve 8, 110C; 7, 140C; 1, 170C; 2, 200C (13).

mechanism the n-pentane was visualized as dehydrogenating on a Pt site to n-pentene. The n-pentene migrated to an acidic site (alumina or silica-alumina) and isomerized by a carbonium ion mechanism through the addition of a proton from the catalyst surface and the normal rearrangement of the ion on the surface according to the rules for these reactions. The isomerized carbonium ions then eliminated a proton, the isopentene migrated to a Pt site, and hydrogenated to corresponding isoparaffins to complete the reaction. Although the conditions for this reaction and the preceding one are not the same as those used with fats and oils, the proposed mode of action of the catalyst is of interest.

The complexity of the reactions on the surface of an amorphous silica carrier was investigated by Lowen and Broge (20). An "amorphous" surface is one that contains irregularities in the spacings of the surface Si atoms. This extent of departure from what might be called a "crystalline surface" increases with prolonged grinding. A silicon atom on the surface of such a carrier tended to maintain tetrahedral coordination with an oxygen atom by being covalently bound to an outwardly disposed hydroxyl group. Such hydroxyl groups constituted "bound water" in silica gels. In a humid atmosphere this layer of silanol groups became hydrogen bonded to additional water molecules thus causing the surface to become covered with physically adsorbed water. When heated, amorphous silica lost the physically adsorbed water. At approximately 200C, only the "bound water" remained. Above 200C, additional water was given off without appreciable sintering, or loss of area. Above 600C, water evolution continued, but with sintering. The experiments indicated that temperatures of about 1400C would be required to obtain a fully dehydrated amorphous silica by ignition in air.

These surface silanol groups may also be replaced by chemical means. Ballard et al. (8) found that the silanol groups could be esterified with alcohols, usually 1-butanol, under anhydrous conditions at 110 to 200C. The surface became partially covered with alkoxy groups. Alcohols from 1-propanol to 1-octadecanol were used.

Puri and co-workers (22) found a carbon carrier to be as complex as SiO_2 and Al_2O_3. Residual oxygen provided isolated active centers which adsorbed water in the form of clumps or clusters through a hydrogen bonding mechanism. Treatment of carbons at 400C for twelve hr with hydrogen left approximately 30% of the original water on the carbon.

Different carriers do not always behave in the same manner toward identical adsorbates. Alumina will strongly chemisorb acetylene at room temperature by holding the gas perpendicular to its surface through the acetylenic hydrogen. The acetylene may also be weakly adsorbed and held parallel to the surface. Different sites on the alumina are responsible for these two types of adsorption. Silica, on the other hand, does not strongly adsorb acetylene.

Thus, from this work, one modification of our present theory of catalysis would be to consider the catalyst as something more than elemental nickel. At the very least, a regular catalyst would contain, besides nickel, silicon and oxygen atoms contributed by the catalyst carrier. The effects of this carrier should be taken into consideration; the carrier may be surface active; it could contain other adsorbed atoms and molecules. Different carriers could have different effects. A surface active carrier would present new types of adsorption centers and the possibility of migration of the adsorbate on the catalyst surface. Migration of such weakly adsorbed species is not unreasonable.

All of these things—highly complex catalyst structures with catalyst carriers participating in the reaction, the presence of extraneous atoms and molecules on the surface, and migration of adsorbed molecules and atoms on the surface—are accepted ideas in the general field of heterogeneous catalysis. There is no reason why these ideas should not be applied to the hydrogenation of fats and oils. Certainly, all such possibilities should be considered in any future investigation of the isomerization problem. For example, in a low temperature hydrogenation in solvent it would be necessary for the entire system, particularly one that recycles the hydrogen, to be dry in order to avoid adsorption of water on the catalyst. The role of oxygen, either chemically-bound or adsorbed in some form, may also be important. It may be necessary for it to be present for hydrogenation to take place. It is known that the presence of oxygen (air) is necessary for hydrazine to effect the hydrogenation of fatty materials. Lack of oxygen may also explain why finely powdered nickel prepared either from the bulk metal under an inert atmosphere or from nickel hydride is supposedly not effective as a catalyst. Hydrogen may be strongly chemisorbed on oxygen-containing materials since there are enormous differences in diffusion rates (one thousand to one) between helium and hydrogen through certain glasses.

Some indication of the type of work being done in heterogeneous catalysis may be gleaned from these few references. Neither time nor space will permit an exhaustive cataloguing of such an extensive field. Perhaps these few references will be sufficient to foster an interest in more detailed studies of the role of the catalyst in the hydrogenation of fats and oils. The solution to the problem of isomerization, if such a thing exists, probably lies hidden in the function of the catalyst.

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