NICKEL CATALYSTS

A NEW SERIES OF CATALYSTS FOR HYDROGENATION PURPOSES

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One of the most common concepts of catalysts is that the catalyst must be prepared in a finely divided state, thus exposing a large amount of catalytic surface. This trend of thought in the oil hardening industry has led to the use of carriers, such as kieselguhr, to support the metallic nickel, and to the use of relatively large quantities of filter aid to prevent the presence of finely divided nickel in the finished product. Both of these conditions necessitate the handling of a much larger bulk of catalytic material, cause a slower rate of oil filtration, and create numerous disadvantages which are not encountered by the use of a catalyst of a particle size sufficiently large to permit ready filtration.

The author, while working in other catalytic fields, found that the subdivision, or particle size, was of minor importance, and that the most important consideration was the nature of the surface exposed to the reaction. This thought has been taken into the field of hydrogenation and a relatively coarse and uniform particle size catalyst has resulted which requires no filter aid nor catalytic support for its use.

The Foraminate Structure

The term "Foraminate" has been given to the catalysts prepared by a selective corrosion and etching action on a carefully prepared aggregate which contains the catalytic material and one or more other constituents. This selective corrosion and etching action is usually performed by means of a solvent which attacks the non-catalytic portion of the aggregate and which has little or no action on the catalytic portion. The strength of the solvent selected, and the time and temperature of treatment, are adjusted to permit a good surface corrosion wihout any material disintegration of the particle. The particle size of the final catalytic material is, therefore, determined by the particle size of the aggregate selected for the corrosion treatment, and this particle size can be controlled by a careful grinding and sizing of the starting material.

The preparation of this starting material is of primary importance. A nickel catalyst, for example, will differ very materially in its properties in accordance with the ratio of nickel to soluble material in the starting aggregate, yet the catalyst will possess the crystal lattice dimensions of pure nickel in all cases. The change in the properties of the catalyst is, therefore, attributed to the atomic arrangement on the surface of the catalytic particles and to the degree of freedom of these nickel atoms. By controlling the composition of the starting aggregate the catalyst can be made to possess definite properties over a wide range, and these properties can be accurately reproduced. Both of these factors are of great value in securing and maintaining the desired hydrogenated product.

Selectivity and Activity of Catalysts

Selective hydrogenation is usually referred to as the hydrogenation of the more unsaturated glycerides in preference to those of less unsaturation. A highly selective catalyst for cottonseed oil, according to this definition, is one which permits the conversion of a large portion of the linolin to olein with little or no formation of stearin. Of equal, or greater, importance, however, is the quantity of iso-olein which is formed during this period of hydrogenation.

There appears to be a difference of opinion among various experimenters as to the origin of the iso-olein, as well as to the exact conditions which favor or retard its formation. It is undoubtedly true that temperature, pressure, agitation, and quantity of catalyst employed are all important considerations, but it appears evident that the type of catalytic surface is of major importance.

In our development of catalysts for hydrogenation purposes we have found that a variation of the ratio of nickel to soluble material in the foraminate catalysts, all hydrogenation conditions remaining the same, will permit the production of hydrogenated products having a wide range of composition. This is due to the fact that the composition of the hydrogenated product depends upon controlling the rates of the reactions

1. Linolin → Olein,
2. Linolin → Iso-olein, and
3. Linolin → Stearin,

and that a modification in the catalytic surface alters the rates of these various reactions. It is possible, therefore, by altering the surface of these catalysts to accelerate one reaction and retard other reactions.

An interesting example of the great variation in the composition of hydrogenated cottonseed oil as the result of changes in the catalytic surface can be seen by examination of the results in Table 1. These results were obtained by the hydrogenation of 10,000 pound batches of cottonseed oil possessing an iodine number of 107. A temperature of 125°C. (257°F.) and a hydrogen pressure of 25 pounds per square inch were employed. The quantity of catalyst selected in all cases was such that five pounds of nickel were present in the 10,000 pounds of oil. The absorption time was approximately one hour for all runs and the hydrogenation was stopped when the product showed a Wiley melting point of 35°C. ± 0.2°C.

TABLE 1

Catalyst No.	*Per Cent of Total Fatty Acids Present*			
	Saturated	*Iso-Oleic*	*Oleic*	*Linolic*
Original Oil	23	2	30	45
1	19	42	30	9
2	29	21	42	8
3	44	13	31	12

These analyses are the result of the lead salt-ether method of separation, followed by iodine determinations to fix the amounts of linolic and oleic acids in the ether soluble lead salts and the amount of iso-oleic acid in the insoluble salts. The amount of iso-oleic acid found in the original oil indicates the degree of accuracy which this method permits.

If we assume that the three reactions above are the only ones taking place, and the results indicate that this is substantially true, then it is evident that:

1. Practically all of the linolin hydrogenated is converted to iso-olein in the presence of catalyst No. 1.
2. The amount of linolin hydrogenated to iso-olein is greatly reduced by catalyst No. 2, a very substantial amount is converted to olein, and a perceptible amount to stearin, and
3. The conversion of linolin to iso-olein is further reduced by catalyst No. 3, practically no linolin is converted to olein, and a large amount of linolin is hydrogenated to stearin.

A consideration of this data shows that the relative rates of these three reactions have been varied over extremely wide limits. Two of the three reactions have been retarded to the extent of practical elimination and the third reaction has nearly approached this condition. Various intermediate results have been obtained during these studies and it now becomes evident that these three reactions can be controlled as desired.

Since these results have been obtained at a temperature of 125°C. (257°F.) it should be stated that the nature of the catalytic surface is of equal importance at other temperatures. A change in the temperature will alter the relative rates of the various reactions and the nature and extent of these alterations will be determined by the nature of the catalytic surface. Usually the predominating reaction is accelerated to a greater degree by increased temperatures.

The above examples have not been given for the purpose of showing what composition may be desired for any particular purpose. The primary object is to show that these reactions can be controlled, and it should be evident to those interested in the development of a product of some definite composition that intermediate or more extensive alterations can be made.

It has been contended by some experimenters that the more active catalysts are the more selective, the term active being used here to denote the rate of hydrogenation. We have found that one catalyst may permit a much faster rate of hydrogen consumption by cocoanut oil than another, yet the first catalyst may be much less selective and active when used on cottonseed oil. Or, a catalyst may even possess a greater activity when used on cottonseed oil than a second and still be much less selective. The selectivity, within reasonable limits, is independent of the activity. The fact that a catalyst may lose its selectivity and activity simultaneously by use is no argument against the above conclusion, since it is only natural to expect that the gradual poisoning may also be selective in nature.

The reason that the activity of a given catalyst may be greater for one oil than for another is because of the difference in the composition of the two oils. A catalyst which is highly selective for cottonseed oil has its surface developed to accelerate a reaction which may not take place during the hydrogenation of some other oil, and also to retard the rate of a second reaction which may be the desired reaction when hydrogenating some other oil. Whenever economically feasible, therefore, the catalyst should be adjusted to suit the conditions of hydrogenation.

Other Properties of Foraminate Catalysts

The nickel foraminate catalysts are produced in a highly active form and tests in several plants have shown that 0.05 to 0.075% nickel will permit hydrogenation under conditions comparable with the use of 0.2 to 1.0% of nickel in the form of other catalysts.

The surface nature of these catalysts is such that an especially good color reduction in the oil is obtained during the hydrogenation period. This characteristic has been observed when contrasted with various catalysts in several different refineries and a particularly good color reduction has been obtained on palm oil, certain fish oils, and other oils which are considered difficult to bleach.

A further outstanding characteristic is the property of retarding the formation of free fatty acids during hydrogenation, and it has been found that this characteristic many times eliminates the necessity of rewashing the oil. A few examples of this case are given in Table 2 to show the change in free fatty acids as compared with the effect simultaneously observed with catalysts employed in five different refineries.

These analyses are given in the form submitted by the laboratories connected with the refineries where these tests were made.

TABLE 2

Temperature °F. Employed	*Oil Used*	*F.F.A. In*	*F. F. A. Out*	
			Foraminate Catalyst	*Comparative Catalyst*
260	Cottonseed	.044	.032	.065
260	“	.064	.050	.080
300	“	.05	.05	.07
300	“	.064	.060	.12
300	“	.04	.03	.07
325	Cocoanut	.042	.036	.100
325	“	.04	.03	.07

Acknowledgment

The author is indebted to the Intermetal Corporation for permission to discuss these results and it is expected that a more extensive discussion of the various phases of this work will be published at a later time.

ANNUAL GOLF TOURNAMENT

The Annual Golf Tournament of the A.O.C.S. was held at the Metarie Golf Club on Thursday afternoon, May 31. The entry list was larger this tournament than ever before, as was the prize list. Even the new President of the Society, Mr. Hutchins, won a prize—for the most freakish game.

Mr. C. S. Williamson, for the third successive time, won the Nuchar Cup and thus becomes its permanent possessor. Messrs. J. J. Trunzler and L. B. Forbes tied for second low gross.

A list of the prize winners together with the donors is given below.

PRIZE DONORS AND WINNERS

1934 Golf Tournament American Oil Chemists' Society

LOW GROSS

Winner **Prize** **Donor**

First—C. S. Williamson, Jr., Golf Medal and Fob, Industrial Chem. Sales Co.

Second—J. J. Trunzler, Cocktail Set, The Filtrol Co. of Calif.

Third—L. B. Forbes, Silver Tray, John P. Harris.

LOW NET

First—E. R. Barrow, Water Pitcher, Wilson & Bennett Mfg. Co.

Second—E. B. Freyer, Bon Bon Dish, F. B. Arbeiter.

Third—N. C. Hamner, Ice Bowl, L. C. Haskell.

Fourth—W. H. Irwin, Set Clubs, The Sharples Specialty Co.

Fifth—R. C. Hatter, Cocktail Shaker, The Peerless Clay & Min. Co.

1ST 9 HOLES

First—R. W. Bartlet, Pr. Golf Shoes, The Roosevelt Hotel.

Second—E. J. Bennett, Leather Golf Bag, The Sharples Specialty Co.

Third—Jack Harris, Set Irons, Bennett-Clark Co., Inc.

2ND 9 HOLES

First—H. C. Dormitzer, Smoking Set, H. Reeve Angel & Co.

Second—J. J. Ganucheau, Golf Bag, The French Oil Mill Mchy. Co.

Third—J. J. Vollertsen, Electric Clock, The Peerless Clay & Min. Co.

LOW PUTTS

First—J. N. Pless, Golf Sweater, The Filtrol Co. of Calif.

Second—R. D. Irwin, Swim Suit, General Reduction Co.

MOST HONEST GOLFER

Wm. N. Kesler, Jr., Cigarette Lighter, Skelly Oil Co.

POKER HAND—LONG HOLES

First—A. S. Richardson, ½ doz. Golf Balls, E. H. Sargent & Co.

Second—G. M. Partee, Ash Tray, Wilson & Bennett Mfg. Co.

POKER HAND—SHORT HOLES

First—A. F. Sanchez, ½ doz. Golf Balls, E. H. Sargent & Co.

Second—John R. Shipner, Ash Tray, General Reduction Co.

MOST FREAKISH GAME

W. D. Hutchins, Zipper Bag, Wachtel's Physician Supply Co.