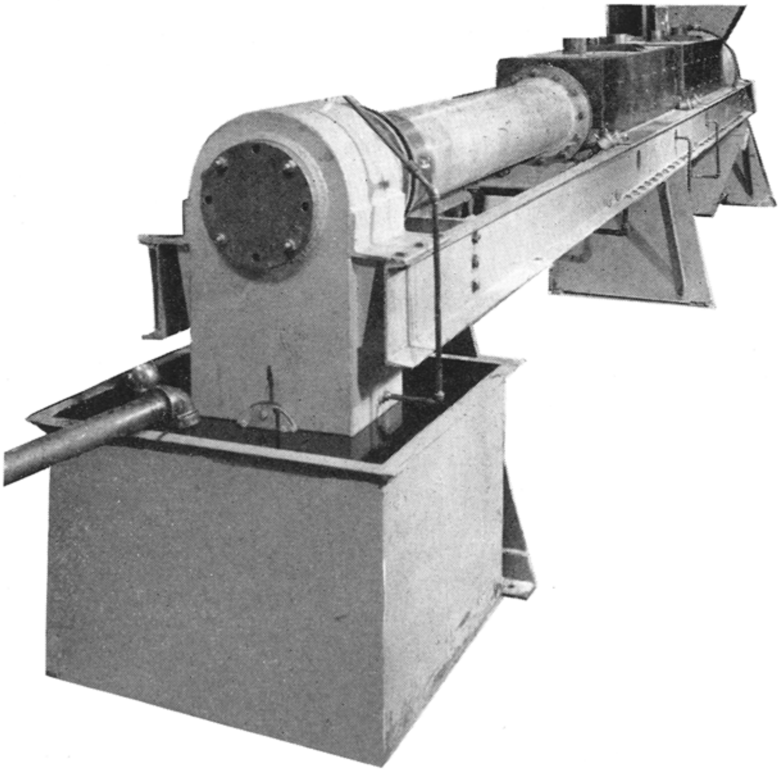
Steam and excess hydrogen leave the tube through the hollow shaft of the feed screw. The agitator or paddle wheel at the discharge end continuously works the finished catalyzer into the oil, preventing an accumulation with the possibility of blocking at this end.

When a sufficient quantity of finished catalyzer has been accumulated in the oil in the catalyzer tank the auxiliary oil seal is raised to the position shown in dotted lines and the oil and catalyst pumped out. Fresh oil is added and the auxiliary oil tank dropped. There is therefore no necessity for stopping the reducing operation while the tank is being emptied.

The time of transit of the catalyzer through the reducing tube can be varied by changing the speed of rotation of the tube. The amount of green catalyst fed in and consequently the depth of the catalyzer in the tube can be regulated by changing the speed of rotation of the feed screw. Temperature control is, of course, obtained by the regulating valves on the gas burners.



Discharge End of Furnace

Inasmuch as the reducing tube is rotating continuously while the burners are lighted there is no overheating of any part of the tube to cause warping or misalignment. An automatic valve shuts off the gas to the burners in case of power failure and consequent stopping of the motor which drives the tube. As the conveyor flights rotate with the tube the sticking or binding which was common with the older type furnaces, in which the conveyor turned inside of a stationary tube, has been entirely eliminated.

This furnace produces a very uniform catalyst with lower consumption of labor, heating gas and hydrogen than would be required in an intermittent or batch furnace of the same capacity.

Catalysts for Hydrogenation

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Abstract

Heterogeneous catalysts are differentiated with respect to sulphur poisoning, viz. sulphur sensitive, e.g. Ni, and sulphur immune, e.g. MoS_2.

Immunity to poisoning is related to temperature, and inversely to catalyst activity. It is stated that nickel catalyst for the selective hydrogenation of cottonseed and like oils should be pure and preferably derived from an unusually active and readily reducible compound of nickel. Three sources of impurities, and the possible relation to promoters of one source in particular, are described. Catalysts are differentiated with respect to the form of the support, viz. powder, impregnate, superficial. The superficial catalyst in stationary form appears best adapted for continuous hydrogenating equipment in the industry.

INTRODUCTION

THE heterogeneous catalytic art emerged from a totally unscientific aspect about 1834, apparently dating back to Faraday's[8] catalytic oxidation work on platinum surfaces. Faraday drew a remarkably simple conclusion from his work, which is underlying to this paper and which is discussed later herein. About a century ago, and shortly after Faraday's work, Berzelius[9] gave catalysis its present nomenclature.

About forty years ago, the art entered a new phase of development with Sabatier's[10] well-known work and the discovery of nickel as a heterogeneous catalyst for hydrogenation. Despite wide industrial development, and recent intensive application by the motor fuel industry, the art still appears to be only in a semi-scientific stage, from which it is not likely to emerge for years to come.

Until that time, any attempt to treat the subject broadly must be rather qualitative and subjective. Because of the many variables involved, some of which are not even generally recognized, the perfection of a catalysis requires much detailed work and careful judgment, with specific attention to the catalyst. The apparent lack of scientific development is probably no fault of those in the art, for the subject is nearly as broad as chemistry itself, and also extends into the science of physics.

There is evidence too that hydrogenation is the elementary chemical reaction. The extensive nature of organic hydrogenations and a general bibliography of the subject is given by Ellis[1]. However, inorganic substances may also be hydrogenated. For example, the hydrogenation of atmospheric N_2 to NH_3 uses more H_2 than the sum total of all other hydrogenations in this country. On the other hand, nickel is a catalyst for a variety of reactions other than hydrogenation, some of which may furnish the clues to the mechanism of catalytic hydrogenation. More than 400 references to nickel catalysts and catalyses have recently been compiled by Fraser[2].

Differentiation of Catalysts with respect to Poison Sensitivity and Immunity

A catalyst is sulphur sensitive if it permanently reacts with or adsorbs to sulphur during the catalysis of sulphur bearing reactants. If a catalyst does not so react or adsorb, it is sulphur immune. Sulphur apparently is the typical chemical poison.

Nickel comprises a preferred sulphur sensitive catalyst. Cobalt and copper and the noble metals in a diffuse state are also sulphur sensitive catalysts. MoS_2 comprises a preferred sulphur immune catalyst, in catalysis for example at 400° C. to 600° C. and at 200 to 300 atmospheres pressure. Coal may be hydrogenated without added catalyst under those conditions. In general, sulphur sensitive catalysts are much more active, being effective at much lower temperatures. Comparing two catalysts, that one is the more active which can be used at lower temperatures under otherwise similar conditions. Catalyst activity generally decreases with use. Increases of pressure and catalyst concentration do not increase catalyst activity.

Sensitivity or immunity depends upon the temperature, as well as upon the specific nature of the catalyst. Sensitivity is the low temperature form, immunity the high temperature form. For example, a nickel catalyst is markedly inhibited by carbon monoxide for the selective hydrogenation of cottonseed and similar oils at temperatures below 150° C. Yet the same catalyst is relatively immune to the effects of carbon monoxide when hydrogenating at temperatures above 200° C.

In general, heterogeneous catalysts appear to degrade both physically and chemically, the degradation being predominantly physical and slow with sulphur immune catalysts; the degradation being predominantly chemical and rapid with sulphur sensitive catalysts.

The domestic petroleum industry has now had opportunity to compare the two general catalyses, and the present trend appears to be toward the sulphur sensitive or nickel type of catalysis, as exemplified in the hydrogenation of isooctene to isooctane. Isooctane is a 100 octane rating motor fuel component, now extensively used in aviation. The alkali promoted iron catalyst for the NH_3 synthesis is sulphur sensitive.

Increasing Catalyst Efficiency, Purity and Activity

Nickel catalyst is usually discarded when used to only a small fraction of its total sulphur sensitive capacity, particularly in the low temperature and selective hydrogenation of cottonseed and like oils. Apparently this catalysis uses only the extreme upper range of the catalyst activity of the nickel.

There are two distinct means of increasing this catalyst efficiency:

1. the use of the catalyst, spent with respect to the selective hydrogenation, subsequently in a higher temperature operation, e.g. in complete hardening, or in the hydrogenation of a low grade oil such as a marine oil;
2. by increasing the initial activity of the catalyst, which appears also to increase potential selectivity.

As used herein, selectivity refers to that partial hydrogenation in which the formation of isooleic and like comprising components is depressed. Not considered herein is that partial hydrogenation in which isooleic components are not depressed, and which is characteristically obtained with lesser activity catalysts, and at temperatures substantially above 150° C.

Catalyst activity may be increased in two ways, the first of which is an application of Faraday's qualitative criterion, viz. that the catalyst should be CLEAN and PURE. Purity as a criterion for selective type nickel catalyst is receiving renewed attention in the endeavor to prepare more active catalysts for selective hydrogenation. A catalyst may be contaminated with impurities from three distinct sources:

1. The raw material of the major catalytic component, e.g. iron or arsenic in the raw bulk nickel.
2. Residual chemicals in the preparation of the catalyst, e.g. alkali in the precipitate from a nickel salt.
3. The reactants, e.g. the non-glyceride portions of the oil, or carbon oxysulphide in the hydrogen.

The detrimental effects of impurities from the first source are not well known, principally because of confusion in the knowledge of catalyst promoters. The functions of promoters seem to be stabilizing rather than activating, and to be generally indirect, multiple and various, e.g. a copper compound addition to a nickel compound may lower the reduction temperature of the latter, or alumina additions to nickel salts may give mechanical support and inhibit sintering of the reduced nickel, or chromous oxide in reacted additions to copper oxide may prevent reduction of the copper oxide. The various forms of a catalytic component may mutually promote each other. But apparently the added foreign promoter seldom if ever directly and substantially increases the activity of a more active major component. More likely the foreign material directly decreases the catalyst activity. The added promoter, however, may more than compensate its possible inherent direct detriment by means of indirect or stabilizing effects. The more common promoters are closely related chemically to the major component, which perhaps minimizes any direct inherent detriment. For example, nickel has often been promoted with cobalt, which is closely related both chemically and physically to nickel. Cobalt appears in all commercial forms of nickel other than those derived from the Mond process and to the extent of more than one part cobalt to 300 parts nickel. Iron and copper are well recognized impurities of nickel. Metallic impurities tend to accumulate in catalysts made from acid recovered spent nickel catalyst.

Impurities from the second source, e.g. residual alkali or sulphate in the precipitation of nickel hydroxide and/or carbonate from nickel sulphate solution, have been recognized as usually detrimental and difficult to remove. The difficulties involved in washing out these impurities are greatly enhanced when the precipitate is relatively fine or colloidal. Taylor[3] claims improved washing using a common anion salt solution such as aqueous ammonium carbonate for washing precipitated nickel carbonate. The method is expensive.

Subsequent to a recent patent[4] expiration, the domestic use of nickel formate has increased. Nickel formate may be prepared by dissolving nickel carbonate and/or hydroxide in formic acid, and then crystallizing out the nickel formate. The purity of such nickel formate should therefore exceed that of the nickel carbonate and/or hydroxide.

Precipitation of nickel solutions with sodium carbonate yields a combined nickel carbonate and hydroxide, because of the partial hydrolysis of sodium carbonate to sodium hydroxide. The nickel carbonate type of precipitate is of low apparent density when dried and unsupported. In the low apparent density type of precipitate, the ratio of catalytic to inert metal appears greater than usual.

Impurities from the third source involve the application of Faraday's criterion of cleanliness, a variation of the criterion of purity. Cleaning is essential to the reactivation of stationary catalyst, and is discussed later.

The second means of increasing the activity of nickel and like catalysts appears to be the preparation of a readily reducible compound which is specifically more active, e.g. a peroxide. Such compounds may be reduced at lower temperatures. Readily reducible nickel compounds apparently more active than the formate or carbonate or hydroxide in a corresponding state of purity may be electrolytically prepared in either the powder or stationary forms. Certain other catalysts, e.g. those prepared by alkali dissolution by the methods of Raney[6] and of Jenness[7] may be prepared in unusually active states.

Powder and Stationary Catalysts

Nickel catalytic surfaces are generally supported by an underlying, uniform sized, non-catalytic surface, which may increase or stabilize the ratio of catalytic to inert nickel. A heterogeneous catalyst may be prepared in one of three general forms, depending upon the mechanical form of the support. In order of industrial development, these are listed in the table below with typical supports for nickel catalytic surfaces:

Order of Development	General Form	Typical Form	Typical Support
1	Powder	sediment	kiesulguhr
2	Impregnate	granule	alumina
3	Superficial	elongate	bulk nickel

All three forms may be used for batch hydrogenation. All three forms may use bulk non-catalytic metal as the support for the catalytic surface. The impregnate or superficial forms are preferably assembled as in cages, and preferably used for either liquid or vapor phase catalysis in continuous operation and without agitation.

The powder form, generally used only for liquid phase catalysis with agitation, is at present almost the only form utilized by the domestic glyceride industry.

Impregnate catalysts are made in the form of small, porous pellets, cylinders, reduced cinders and other foraminous granules. The impregnate appears to be the form generally used in other domestic industries, e.g. for the synthesis of ammonia and methanol, for the Standard-I.G. sulphur immune hydrogenation, and for the hydrogenation of isooctene to isooctane.

Superficial catalysts are perhaps the most difficult form to prepare, but are the most readily reactivatable without disturbance to the catalyst and support. In the elongate form, such as nickel turnings or screens, the free space is large. Resistance to flow is thereby small, facilitating reactivation. The best known catalyst of this type is the anodically prepared stationary nickel catalyst of Bolton and Lush[5], which has received world-wide use. A number of attempts have been made to prepare superficial nickel catalysts, most of which have failed because of an insufficient catalyst concentration, excluding inert components. The practical impregnate catalyst possesses a large catalyst concentration by virtue of the large surface area within the foraminous support. But the superficial type of catalyst with much less surface area must rely on depth of surface layer rather than superficial area in order to gain a practical catalyst concentration. The true catalyst portion, i.e. the catalyst excluding the inerts or the support, must be diffuse in order to contact the reactants directly, regardless of the form or other property of the catalyst. A surface resistant to turbulent flow and reactivation chemicals, yet deep and diffuse, is a severe specification. Such a surface should be substantially integral with the support, and may be said to be semi-adherent. But once prepared, this catalyst appears to be more accessible to reactivating agents and reduces more readily than the impregnated catalyst.

Catalyst reactivation generally comprises two steps:

1. a physical cleaning or removal of residual reactants or products;
2. a chemical activation, generally oxidizing in nature.

The chemically activated surfaces, particularly for the selective hydrogenation of cottonseed and like oils, should be free of traces of organic matter. Usually the chemical activation must be relied upon to remove these last traces. The CLEAN portion of Faraday's catalyst criterion may be appreciated.

Catalyst reduction may be considered as a third reactivation step. Aside from the use of more active catalyst metal compounds, reduction temperatures may also be lowered by reducing in oil, or by means of a heat conducting type of catalyst support.

Continuous Hydrogenation

The urge toward a continuous hydrogenation process formerly came from outside the industry, but now also comes from within. Practically all of the domestic hydrogenation in industries other than the glyceride industry is of the continuous type. Recently continuous alkali refining has become established in the refining of natural glycerides, while continuous deodorizing is under intensive development. Hence the need for an intermediate continuous hydrogenation process, particularly one which is simple and compact and adapted to selective hydrogenation.

The powder catalyst continuous unit lacks compactness, and may be said to be transitional in type. A compact hydrogenation unit apparently requires a stationary catalyst, which may be either the impregnate or superficial type. However, the impregnate catalyst is not only difficult to reactivate, but the support generally gives rise to secondary reaction products such as free fatty acids. A simple and compact continuous unit may be constructed with a stationary superficial catalyst, which on a corresponding scale of operation eventually may save approximately one-half of the operating or hydrogenating costs, which exclude oil and hydrogen costs. Most of the catalyst and filtration costs, and most of the floor space is saved. The contact time of the oil and powder catalyst is usually a matter of hours; that of the oil and stationary catalyst is a fraction of an hour, resulting in better keeping quality by the continuous method, other things being equal. The superficial nickel surface can be reduced at unusually low temperatures and can otherwise be obtained in unusually active forms.

Superpressure continuous units with superficial catalysts have been domestically built and operated.

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The Heats Of Hydrogenation Of Unsaturated Hydrocarbons

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Abstract

Recent precise experimental work on the heats of hydrogenation of hydrocarbon compounds containing one or more double bonds shows a variation from compound to compound which can be correlated with the structure of the molecule. For compounds containing one double bond or several non-conjugated bonds, the heat of hydrogenation per double bond is nearly constant. However, in compounds containing conjugated double bonds the average heat of hydrogenation per bond is less than in non-conjugated systems due to the interaction energy between the double bonds tending to stabilize the system. This effect is most pronounced in aromatice compounds. Although the hydrogenation of benzene to form cyclohexane (addition of three molecules of hydrogen per molecule of benzene) is an exothermic reaction, the hydrogenation of benzene to form cyclohexadiene -1,3 (addition of one hydrogen molecule per molecule of benzene) is an endothermic reaction. This signifies that the energy associated with the aromatic character of benzene is greater than the energy of hydrogenation of a double bond, so that the resultant of these two effects is an endothermic reaction.

TO a first approximation, the energy of a gaseous molecule containing electron-pair bonds may be considered to be the sum of the energies due to the various bonds. It therefore follows that the heat of hydrogenation of any unsaturated hydrocarbon (per mole of hydrogen) should be approximately constant, inasmuch as the hydrogenation involves in each case the formation of a carbon-carbon single bond and two carbon-hydrogen single bonds and the destruction of a carbon-carbon double bond (and a hydrogen-hydrogen single bond).

The recent accurate experimental work of Kistiakowsky and his co-workers* roughly substantiates the foregoing conclusions for unsaturated hydrocarbons not containing conjugated double bonds. For these latter systems, the heats of hydrogenation vary widely.

Table I shows some of the results of Kistiakowsky.

Table I. Heats of Hydrogenation

Compound	▲H at 83° C.
Ethylene	—32.8 kcal per mole
Propylene	—30.1
Butene-2 (cis)	—28.6
Butene-2 (trans)	—27.6
Trimethylethylene	—26.9
Tetramethylethylene	—26.6
Cyclohexene	—28.6
Cyclohexadiene 1, 3 (to form Cyclohexene)	—28.8
Benzene (to form Cyclohexadiene, 1, 3)	+5.6

In comparing the values for the series ethylene, propylene, butene-2 (*cis* and *trans*), trimethylethylene, and tetramethylethylene, the heats of hydrogenation are observed to decrease in the order given, corresponding to a decrease in affinity for hydrogen in the same order. In other words, the affinity of a carbon atom for hydrogen depends upon the number of hydrogens already attached to it. This conclusion is in accord with other known chemical properties of these compounds.

When we come to the aromatic hydrocarbons, we see that the addition of one mole of hydrogen is actually an endothermic reaction. The addition of another mole of hydrogen to the product of the first addition, cyclohexadiene — 1, 3, proceeds normally.

The free energy of the first reaction at 25° C. is calculated to be +13.6 kcal. whereas the free energy of the second reaction is —17.7 kcal. Thus, the equilibrium does not favor the addition of one mole of hydrogen to benzene. The equilibrium involving the simultaneous addition of three hydrogens to benzene favors the addition. However, this reaction is too difficult to occur kinetically. We therefore have a comprehensive understanding of the chemical behavior of aromatic compounds toward addition reactions.

If benzene could be simply regarded as cyclohexatriene with no interaction between the double bonds, the heat of hydrogenation to form cyclohexane should be just three times the heat of hydrogenation of cyclohexene to form cyclohexane. From Table I, this is 3 × -28.6=-85.8 kcal. The experimental value is -49.8 kcal. Hence benzene is more stable by an amount -49.8 -(-85.8)=36.0 kcal. than it would be if it were completely unsaturated in character (with no interaction between the double bonds). From the theoretical viewpoint, this extra stability of benzene (and other aromatic compounds) is shown to be a consequence of the fact that the normal state of the molecule is not that corresponding to either Kekulé structure but is a sort of combination of the two.

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* J. B. Conant and G. B. Kistiakowsky, Chem. Rev. 20, 181 (1937).