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CATALYSIS AND THE CHEMICAL INDUSTRY

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Before the advent of organized chemistry, alchemists were searching for a "philosopher's stone," a hypothetical substance which was reputed to be able to turn basic metals into the precious metal, gold. While their crusade was never rewarded with success, they laid the foundation for the chemical study of today. In this field a catalyst for a desirable chemical reaction has turned out to be a true "philosopher's stone." Catalysts have played an important part in the production of substitutes which are very useful in today's limited markets.

By way of definition, when a chemical reaction between one or more substances is influenced by the presence of a third substance which remains unchanged in the process, catalysis has taken place and the third substance is known as a catalyst. It does not have the ability to turn the substances involved in the reaction into gold, but it is able to produce on an economical basis substances which can be marketed and thereby turned into gold.

Berzelius¹ in 1836 surveyed a number of chemical changes, which were difficult to understand because they apparently proceeded in the presence of a specific agent

¹Jons Jakob Berzelius (1779-1848) was professor of chemistry at Chirurgico Medical Institute, Stockholm, Sweden. His work on atomic weights and the minute investigations of chemical proportions established chemistry as a science on a firm basis and he is credited with being the organizer of chemistry. An excellent teacher, he influenced some of the later leaders in this field, whom he had as students. Some of these were Heinrich, Mitscherlich, Wohler and Mosander, all of whom made unusual contributions to the chemical field.

but did not react in its absence, and he came to the conclusion that reaction was due to what he termed catalytic forces. He also called the specific agent that caused this force a catalyst.

Perhaps the first catalytic chemical reaction used by the alchemists was the oxidation of sulphur to sulphuric acid by heating with nitre. In 1740 Roebuck and others introduced the lead chamber process in which large amounts of sulphur dioxide were oxidized to the acid with comparatively small amounts of the oxides of nitrogen. About the beginning of the nineteenth century, Darg and Clements showed that the oxides of nitrogen had the function of what is now termed a catalyst. It is interesting to point out that at the beginning of the twentieth century another catalytic process was developed for the manufacture of this acid using finely divided platinum as a catalyst. Known as the contact process, it gives promise of replacing the chamber process now in use, since less costly catalysts have been developed to replace the expensive platinum.

In 1781, Parmentier discovered the hydrolysis of starches by acids and De Saussure's work in 1818 on the saccharification of gluten was the first to conceive the idea of acceleration of reaction. About 1796 the first investigations of surface catalysis was carried out when Van Morum observed the dehydration of alcohol by metals and Dermann, Lawrenburg, Bond and van Troostwijk studied the dehydration by clay.

Following the ideas advanced by Berzelius, a long epoch was filled with attempts to explain and interpret the "catalytic force." Powerful opposition was given by Leibig when he asserted that the idea of "catalytic force" was too hypothetical as an explanation. This controversy fostered many different theories of catalysis, the most outstanding of which assumed that a molecular field of force existed between the reactants and the catalyst and was broken when reaction took place. Toward the close of the nineteenth century Ostwald introduced the idea of the velocity of change as a measure of catalytic action. This idea led to the classical definition of a catalyst as "any substance which

alters the velocity of a chemical reaction without appearing in the end products of the reaction.”²

The idea of velocity of change has been a very fruitful one and a large number of catalyses have been investigated from this standpoint. Abundance of experimental work has lead not to a general theory of catalysis as one would expect, but the application of catalysis has not suffered from this lack of theory. The one big question still to be solved is why a substance catalyzes a reaction. This is as yet unanswered.

Catalytic reactions are usually classified by describing the state of matter of the reactants and that of the catalyst. If the state is the same in each case the reaction is said to be an example of homogenous catalysis. If the states are different, such as the reactants being liquids while the catalyst is a solid, then an example of heterogenous catalysis is shown.

Types of Catalytic Reactions

Polymerization reactions have found wide application in the chemical field in the past few years. These reactions involve the combining of several similar molecules to form a larger molecule. The number of molecules that may combine to form the larger one is not usually known. By carefully controlling the conditions under which the reaction takes place and by selecting the proper catalyst, molecules that have about the same properties may be obtained. Reactions of this type are known that do not require catalysts, but these are usually slow and not as easily controlled.

The catalysts usually employed are the mineral acids (often sulphuric or phosphoric); the anhydrous chlorides of aluminum, zinc and iron; porous materials such as activated carbon, silica gel, and activated earth (i e. clays. While not used in industry, metallic sodium, oxygen and peroxides are used in laboratory work. As this chemical reaction is affected by temperature, pressure and light, it is

²Wilhelm Ostwald (1853-1932) professor of physical chemistry at Leipsig, instituted the first laboratory for institutions in physical chemistry. An inspiring teacher, a prolific writer and an outstanding scientist Ostwald attracted students from all over the world.

sometimes necessary to adjust these to conditions under which the desired results can be obtained.

In the field of plastics, polymerization is of prime importance. Starting with a purified coal-tar distillate, a resin or synthetic plastic is produced by treating this distillate with sulphuric acid under carefully controlled conditions of temperature. Purification of the resultant mass by removal of the acid, drying and distilling gives a good quality resin, which varies in color from pale yellow to dark brown, depending upon the composition of the original material. These resins are known as the Coumar Resins or Nevidene and have been used extensively in the paint and protective coating industries.

Natural gasses can be made the basic material for a large number of synthetic resins which find innumerable uses in industry. The several reactions which must be produced before suitable substances are obtained are dehydrogenation, oxidation, or halogenation, followed by polymerization. Ethylene, propylene, and butylene, all of which can be produced by the action of certain catalysts on natural and refinery gases, are essential in the production of plastics.

Starting with ethylene and chlorine (a halogen), a compound known as vinylidene chloride is formed. By a slight change in the above reaction another compound known as vinyl chloride can be produced. If these two compounds are added together and made to join to one another a plastic called "Saran" is produced. This polymer is tasteless, odorless, nontoxic, non-flamable and a thermoplastic. At the present time commercial quantities of this plastic are being fabricated in the form of pipe and tubing. It can be threaded by the use of the regular pipe threading tools and threaded fittings of "Saran" are available. The chemical resistance of "Saran" towards chemicals and solvents is such that it is replacing copper tubing and may be used in place of iron pipe. "Saran" tubing, however, is not recommended for use above 170°F. When research removes this obstacle a very useful plastic will be at hand, especially for the building trade.

Another resin called "Vinylite V" can be made by using vinyl chloride (mentioned above) and vinyl acetate, which

may be made by treating acetylene with acetic acid. Several different types of these vinyl resins, all having different properties, are produced by changing the conditions under which the condensation is carried out. Plexiglas or lucite is another resin made from acetone, hydrocyanic acid and methanol. The material that undergoes polymerization is known as methyl methacrylate and the above material is sometimes called methacrylate resin. The acetone used in this preparation may be obtained from propylene.

A substance called ethyl benzene can be prepared by the reaction between ethylene and benzene. By careful control of the temperature this material when heated, can be converted to styrene. After boiling for a time in the presence of a catalyst, styrene undergoes polymerization to the plastic known as "Styron" or "Lustron."

The importance of plastics cannot be over emphasized at this time. Steel formerly used in many instances is being replaced by suitable plastics, which prove superior in certain uses. Where a transparent non-shatterable part is necessary in an airplane, plexiglas is employed. The new alloys now being used in airplanes together with plastics now being developed will appreciably affect the motor car of the post-war period, and also our future mode of living.

It should be mentioned in passing that any of the components necessary for the manufacture of plastics of all types can be prepared from catalytic treatment of natural gas. The Bakelite type of plastic requires formaldehyde which is usually made by one of two methods: by oxidation of wood alcohol, or by the oxidation of methanol produced from the catalyzed reaction between carbon monoxide and hydrogen. By using air and natural gas and a catalyst, formaldehyde and methyl alcohol may be produced. This latter reaction is expected to supply sufficient amounts of both products to meet the increased production of Bakelite.

Butane may be converted to butadiene by dehydrogenation of the butane. This butadiene is very useful today, as nearly every process for the manufacture of synthetic rubber uses this material. Several kinds of rubber may be made by varying the material that reacts with the

butadiene. If styrene is used and the resulting condensation product polymerized, a "styrene" rubber is produced. If acrylonitrile and butadiene is used, the resulting product is called Chemigum. If isobutylene and butadiene are used, butyl rubber is produced. Each of these synthetic rubbers has properties that differ from one another. The one big advantage of synthetic rubber is its unvarying constitution. The natural rubber, which contains a number of unknown components, is dependent upon several variable factors for its properties such as the life cycle of the rubber tree, the climate and soil conditions. While synthetic rubber has components of known characteristics and its composition may be controlled by conditions and catalysts to give it the desired properties. Tires will be manufactured that should have a life as long as the automobile to which they are attached.

A synthetic lubricating oil which has good viscosity curves, low pour-point, good color and stability towards oxidation, can be obtained from the viscous oil which results from the treatment of ethylene with anhydrous aluminum chloride. The viscous oil when treated with steam and fractionally distilled results in the above mentioned lubricating oil. A synthetic gasoline with an octane number of 96-100 has been prepared by the following method: either natural gas or refinery gases under pressures of approximately 200 pounds per square inch are heated from 200-300°F and pass over solid phosphoric acid which polymerizes the gasses to form a liquid. On refining, this liquid may be converted to gasoline.

The Fischer-Tropsch process, which utilizes carbon monoxide and hydrogen to produce oil, has been one of the outstanding catalytic developments of the past decade. At the beginning of World War II, about 15,000,000 barrels of oil per year were being produced by this method.

The mixture of gases under a pressure of 200 atmospheres pressure and a temperature of 400°F is passed over a catalyst composed of oxides of nickel, chromium and cobalt. Along with the oil, hydrocarbons are produced, some are gases, some liquids and some solids. The solids

are usually paraffin waxes while the liquids produce gasoline, gas oil and Diesel oil. The gases produced are usually the lower members of the saturated types of hydrocarbons. These can be converted to carbon monoxide and hydrogen by the use of steam and the gases used over again. Or the gases may be purified by removing the higher molecular weight material, and then converted to ethylene or ethyl alcohol from which the synthetic rubber may be produced. The gasoline from the above reaction is of low grade having an octane number of about 40. By catalytic cracking the octane number may be raised.

Research over a period of approximately eight years has shown a use for the above mentioned paraffin wax. A catalyst (any of a large number of substances such as oxides of metals, metallic soaps, or certain free fatty acids) added to the wax and air, at an elevated temperature, is passed through the mixture. Oxidation of the wax takes place to convert it to fatty acids. Blowing is continued for a period until the acid number of the mixture remains the same or starts to decrease slightly. Not all of the wax is converted to fatty acids so the wax must be separated by saponification of the acids to form soaps. The soaps are then extracted from the wax and the acids regenerated by treatment with a mineral acid. The fatty acids are then purified by fractional distillation under reduced pressure. By this means a source of fatty acids useful in the manufacture of soap and fats is obtained.

The propane that appears in the gases from the original reaction between carbon monoxide and hydrogen can be converted to propylene by dehydrogenation. Propylene is then chlorinated and the resulting product is hydrolyzed to produce glycerine. The glycerine may be nitrated to form nitro glycerine and used as an explosive, or it may be reacted with the fatty acids prepared from paraffin to produce fats. These fats are synthetic in the nature and differ slightly from fats produced by natural processes. By experiments on animals it has been proven that the synthetic fats are as useful to the body as the naturally oc-

curing fats. Of course there are no vitamins in the synthetic product.

Another catalytic reaction of a different type is the synthesis of ammonia. Nitrogen and hydrogen in the ratio of 1 to 3 are passed over a solid catalyst at pressures of 200-1000 atmospheres and at temperatures from 400°-600°C. The catalyst used is generally an alkali-iron material. The amount of ammonia produced by passing the gases over the catalyst once, is rather small so that the ammonia is scrubbed from the mixture of gases and then the gases recycled. If higher temperatures are employed to try to increase the yield it is found that less ammonia is obtained since its decomposition is an endothermic reaction and is favored by an increase in temperature. Large amounts of ammonia are being made by this method today.

Ammonia can be oxidized to nitric acid by mixing it with approximately twice the volume of oxygen and passing the mixture over platinum or platinum-rhodium alloy which is heated to about 700°C. Conversion of approximately 95% of the ammonia present is claimed. The oxides of nitrogen produced are reacted with water to form nitric acid. At present this method has considerable use in the manufacture of explosives.

The addition of hydrogen to an organic compound that is unsaturated with respect to hydrogen is a catalytic reaction that has proved very helpful. From an industrial standpoint the greatest application of this reaction has been in the hardening of fats for use in food, soaps, and candles, although several other applications give promise. The above mentioned uses of hard fats call for more than are usually produced. Liquid fats are more abundant in nature so that a method of converting them to solid fats is desirable. Roughly speaking, the glycerides of oleic, linoleic and linolenic acids are the more abundant liquid fats, while the glycerides of lauric, palmitic and stearic acids are the more abundant solid fats. A glyceride of one of the more liquid fats when treated with finely divided nickel in an atmosphere of hydrogen, may be converted to one of the more solid fats. Other metals which can accomplish this hydro-

genation are platinum, palladium, cobalt and copper; however, for industrial work nickel is nearly always employed.

Hydrogenation of cotton-seed oil is used today to produce a higher melting-point fat suitable for cooking and frying. This is accomplished by adding catalytic nickel to the oil and passing hydrogen through the mixture at a temperature of 400°F for a period of hours or until the desired degree of hardness is obtained. This hydrogenation reaction may be used for purification and bleaching of fats that are "of color" or are dark in color.

Another hydrogenation process that may be used in the future results from the reaction of hydrogen and coal. The product is a liquid which may be used as a good grade of fuel oil. The catalyst of this reaction is a sulphide of molybdenum. The coal is ground to a fine powder and molybdenum sulphide which acts as the catalyst is mixed into the coal. This mixture is suspended in an unreactive liquid solvent and agitated in the presence of hydrogen gas under a pressure of 250 atmospheres. The oil is obtained by distilling the reacted mass.

The discussions of these important reactions show that catalysis is playing a vital role in the chemical industries. The application of catalysis will undoubtedly expand to a considerable degree within the next decade. Truly these catalysts have proven to be "philosopher's stones" in many fields of industrial chemistry.