Catalyst Manufacture Recovery and Use 1972

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FOREWORD

The detailed, descriptive information in this book is based on U.S. patents since 1962 relating to the manufacture of catalysts, their recovery and use.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legalistic phraseology, this book presents an advanced, technically oriented review of manufacturing techniques for making, using and recovering catalysts on an industrial scale.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic, commercially useful information. This information is overlooked by those who rely primarily on the periodical literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. One should have to go no further than this condensed information to establish a sound background before launching into research in this field.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor, and patent number help in providing easy access to the information contained in this book.

CONTENTS AND SUBJECT INDEX

INTRODUCTION

The factors that determine the effectiveness of a particular catalyst in a particular situation are still obscured despite the expenditure of enormous amounts of R & D dollars. Development of a new catalyst tends to be frustrating, time consuming, and expensive. Attempts to apply available catalysts to systems other than those in which they have been proved effective might well be as difficult and as expensive as the development of completely new catalysts.

There is general agreement that the key to catalyst activity lies in the catalyst structure, both microscopic and macroscopic. The activity of a given catalyst frequently depends on the precise method of preparation and activation, which may greatly influence the physical and chemical properties. The history of a solid material is important since the material may be exposed to chemical poisons, or may be rendered unusable as in the flaking caused by a highly exothermic reaction.

There is presently no generalized theoretical framework for systematic selection of catalysts. Hence, simple practical knowledge must dominate any process of choosing catalyst candidates for further testing. The existing knowledge of past catalyst types serves as a guide. Once the reaction type has been established, certain classes of catalysts can be chosen immediately on the basis of past successful applications to similar type reactions.

	Catalyst	
Reaction	Type	Examples
Oxidation	metal oxide	V_2O_5, WO_3, Ag_2O, Fe_2O_3, NiO
Hydrogenation	metals	Ni, Pt, Pd, Fe, Cu, Ag
Dehydration	metal oxides	Al_2O_3, SiO_2, MgO, ThO_2
Cracking	acidic	SiO_2-Al_2O_3 (molecular sieves)

Thus, in this review, an attempt will be made to cite numerous pertinent examples of current industrial operating practice as a guide to present applications and as a help to future selection of catalytic materials for the same or similar processes.

Many general practices are encountered over and over in the use of catalysts, whether in acrylonitrile manufacture, petroleum cracking or a variety of other processes.

> The physical form of catalysts must be prepared to suit the process. This may involve the preparation of pellets or spheres of particular composition, size, shape and porosity.
>
> The contaminants which decrease catalyst activity must be controlled when present in the feed stream and removed from the catalyst when accumulated or produced there in the course of the reaction. This frequently involves controlled combustion of carbonaceous deposits.
>
> The active ingredients in the catalytic body must be recovered in many cases, both because of the value of the material and also because of pollution which may be involved in their escape to the atmosphere.

Since these are problems common to many processes, a review of specific solutions should be of common interest in industry.

The general arrangement used in this book is to discuss classes of catalysts starting with the alkali-metal catalysts in Group Ia of the Periodic Table and going progressively through to the platinum catalysts in Groups VIII of the Periodic

Table. Then under each type of basic catalyst component, a variety of specific reactions are discussed with specific examples of catalyst manufacture, recovery or use for the process in question. Thus, a panoramic view of practical industrial examples of catalyst preparation, handling and utilization is presented which it is hoped, will be useful to the student and the practicing industrial technologist alike.

Of supplemental interest to the reader will be a "Survey of Commercially Available Catalyst and Sorbent Materials" by R.H. Cherry et al of Battelle Memorial Institute in Natl. Air Pollution Control Admin. Report APTD-0685 (July 17, 1969). Also of interest will be books dealing with catalytic applications in specific industrial fields such as "Catalytic Conversion of Automobile Exhaust" by J. McDermott, Noyes Data Corp., Park Ridge, New Jersey (July 1971).

ALKALI METAL-CONTAINING CATALYSTS

Metallic sodium with or without various supports has been proposed as a catalyst for a number of chemical processes. For example, metallic sodium has been proposed as a catalyst for the polymerization of monoolefins, diolefins (dienes) and skeletal isomerization of chemical compounds wherein a change in the physical conformation of a carbon chain is obtained.

For other information on the use of metallic sodium as a catalyst, the reader is referred to "Sodium, Its Manufacture, Properties and Uses", American Chemical Society Monograph 133, Reinhold Publishing Corp., New York, (1956) by Marshall Sittig.

For broader information on catalytic uses of the alkali metals in general, the reader is referred to "Handling and Uses of the Alkali Metals", Advances in Chemistry Series 19, American Chemical Society, Washington, D.C., (1957).

OLEFIN ISOMERIZATION

Standard Oil (Indiana)

A process developed by T.M. O'Grady and A.N. Wennerberg; U.S. Patent 3,260,679; July 12, 1966; assigned to Standard Oil Company (Indiana) pertains to a catalyst containing metallic sodium on a gamma-type alumina support wherein metallic sodium is promoted with at least a transition metal compound.

In research leading to this process there has been developed a nonpyrophoric active and selective supported promoted sodium catalyst which can be readily prepared and is safe to handle in chemical processing equipment. This catalyst comprises 1 to 25 weight percent metallic sodium and 0.1 to 10 weight percent transition metal compound, preferably a compound of iron on a metal oxide support, such as activated aluminas, silica, magnesia and the like as well as naturally occurring materials, such as bauxite, kieselguhr and boehmite among others. Desirably the supports contain mainly alumina converted or convertible to gamma-type aluminas.

One preferred method of catalyst preparation is as follows: A weighed amount of the calcined support is charged to a suitable 3-neck round-bottom flask provided with a stirrer, inert gas inlet and outlet tubes, and a thermocouple directly contacting the mixing materials. The flask is heated, while stirring the support, to the temperature at which the alkali metal is to be dispersed on the support. Temperatures above the melting point of the alkali metal are usually and preferably used so that it is dispersed as a molten liquid for better contacting. Other methods of dispersing the alkali metal, such as a physical admixture of it and the support, can be used, but they are not as effective. The support and liquid alkali metal are mixed at the preparation temperature for 5 minutes to 3 hours, usually 5 to 30 minutes. Predried promoters are added, and the mixing is continued at the preparation temperature for a specified time which is discussed later. The catalyst, cooled quickly to room temperature or below while mixing, is ready for use.

Preparation of optimum catalysts may be controlled colorimetrically. Where sodium and promoter are dispersed on alumina, a series of color changes occur. Initially, the color progresses from white to darkening shades of blue and sometimes, depending on preparation conditions and concentrations, to black. It then regresses to lighter shades of blue, to gray and finally to an off-white. During the latter color sequence a shade of blue is obtained at which catalyst activity is a maximum. These color changes undoubtedly relate to the reactions of the sodium and promoter on the support.

A process developed by W.F. Wolff; U.S. Patent 3,405,196; October 8, 1968; assigned to Standard Oil Co. (Indiana) involves a catalyst preparation method in a process for the isomerization of terminal olefins wherein a catalyst comprising an alkali metal dispersed upon a high-surface, substantially inert, solid support is contacted with an activating gas at a temperature between 5° and 50°C. in sufficient quantity to provide an oxygen-to-alkali metal ratio between 0.01 and

2.0 atoms of oxygen per atom of alkali metal. The activating gas is selected from a molecular oxygen-containing gas, nitrous oxide, mixtures thereof, and mixtures thereof with inert gases. The catalyst used in this process contains an alkali metal dispersed on a high-surface, substantially inert support. The alkali metal may be selected from a group comprising sodium, potassium, rubidium and cesium. Sodium is particularly desirable. The supporting material should possess a high surface area, large pores, and be only slightly acidic. The supporting material should be calcined to drive out the water. This calcination may be carried out at temperatures of from 150° to 650°C., 450° to 600°C. being particularly desirable, and a pressure of from 0.1 mm. of mercury to 1.0 atmosphere for 0.1 to 50 hours. The supporting material is desirable in a granular or powdered form. Activated alumina is a particularly desirable supporting material.

This alumina generally has a surface area ranging from 50 to 1,000 square meters per gram. The alumina used in the preparation of the catalyst has a surface area of 200 to 210 square meters per gram, a packed bulk density of 68 pounds per cubic feet and a particle size of 80 to 200 mesh. This granular alumina has an ignition loss of 6.8% at 1100°F. and is composed of 92.0% Al_2O_3, 0.8% Na_2O, approximately 0.1% SiO_2 and approximately 0.1% Fe_2O_3.

The supported alkali metal catalyst is prepared by contacting the high surface area supporting material with the alkali metal while the latter is in the molten state. This contacting is done in the presence of agitation under an inert atmosphere, such as argon, nitrogen or helium. This so-called inert atmosphere must be such that it will not react with the alkali metal to transform the alkali metal into a derivative that will not catalyze isomerization. The alkali metal may be added to the calcined support at a temperature of from 10° to 35°C. under an inert atmosphere. The resulting mixture is then heated to a temperature of from 150° to 500°C., 300° to 400°C. being particularly desirable. The mixture is continuously agitated at the elevated temperature until the alkali metal appears to be evenly distributed upon the surface of the supporting material. Even distribution usually will be attained within a period of from approximately 10 minutes to 2 hours.

If sodium is being distributed on activated alumina, a uniform layer of sodium is indicated by a blue-black color which occurs over the entire surface of the alumina. The catalyst may contain between 1 and 40% by weight of the alkali metal, depending upon the particular alkali metal and the particular supporting material employed. Generally, that amount of alkali metal which is sufficient to form a monomolecular layer on the support is desired. When sodium is to be on activated alumina, the resulting catalyst will usually contain from 2 to 15% by weight of sodium.

The improvement of this process comprises the pretreating of the supported alkali metal catalyst with an activating gas at a temperature within the range of 5° to 50°C., 20° to 35°C. being particularly desirable. Preferably a positive flow of the activating gas through the catalyst bed is maintained. Care should be taken during the pretreatment to avoid general or localized overheating of the catalyst. The activating gas is selected from the group consisting essentially of a molecular oxygen-containing gas, nitrous oxide (N_2O), mixtures thereof and mixtures thereof with inert gases. These inert gases are gases which will not chemically react with the sodium, e.g., nitrogen, argon, neon and helium.

It is desirable that the activating gas be used in an amount which is sufficient to provide a quantity of oxygen which will furnish an oxygen-to-alkali metal ratio within the range between 0.01 and 2.0 atoms of oxygen per atom of alkali metal. Of course, the atoms of oxygen would be the atoms of oxygen in the activating gas and the atoms of sodium are the atoms of sodium present in the catalyst that is being used to isomerize the terminal olefins. Preferably, the quantity of activating gas should be maintained at a level which will provide an oxygen-to-alkali metal ratio within the range between 0.1 and 0.4 atom of oxygen per atom of alkali metal. The rate of flow of the activating gas should be maintained at a level which will not result in the creation of excessive temperatures.

Figure 1 shows a suitable form of apparatus for the conduct of this process. The desired supported alkali metal catalyst, a sodium-on-alumina catalyst, is charged under an inert atmosphere to cylindrical vessel 1. Vessel 1 is insulated and contains coil 2 through which steam or a standard coolant can be circulated, depending upon whether heating or cooling of the contents of vessel 1 is desired. The inert atmosphere may be nitrogen. The catalyst exists in vessel 1 as a fluid bed 3. The particle size distribution of the catalyst is such that it will permit adequate fluidization so that efficient and uniform contacting of the catalyst particles with either a pretreating gas or the hydrocarbon being converted can be maintained.

At the lower end of vessel 1 is a support for the catalyst bed. This support is made up of a grid 4, a fine screen 5 and several layers 6 and 7 of different sized Alundum beads. The catalyst must be maintained under an inert atmosphere, which can be nitrogen. The inert gas is introduced into vessel 1 through lines 8 and 9 and drier 10. Such gas not only acts as an inert atmosphere, but also operates to keep the catalyst bed 3 fluidized. As the inert gas need not be at an elevated temperature at this time, heater 11 is not needed. Therefore, valves 12 and 13 remain closed while valves 14, 15 and 16 remain open. Drier 10 contains molecular sieves or some other suitable desiccant, and is used to remove moisture from the various gases which pass through it prior to their introduction into vessel 1.

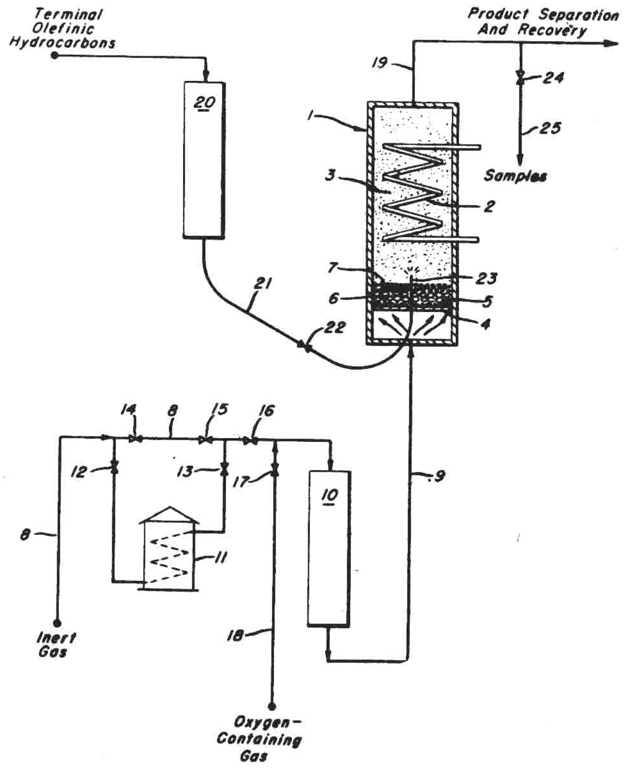
Before the catalyst is used to convert hydrocarbons, it receives a pretreatment with an activating atmosphere. The activating atmosphere comprises an oxygen-containing gas. The flow of inert gas to vessel 1 is stopped by closing valve 16.

Valve 17 is opened and the oxygen-containing gas is passed through lines 18 and 9 and drier 10 into vessel 1. The design of the vessel and the selection of the flow rate of gas should be such as to maintain a suitable fluidized catalyst bed. The fluidized bed will permit the most efficient and uniform treatment of the catalyst.

The oxygen that is passed through the bed 3 should be held to an amount that is slightly less than that which is required to convert half of the available alkali metal to its oxide. Tests have indicated that excessive treatments in oxygen will not produce optimum catalyst activity, but it should be noted that even the excessive oxygen treatments do result in activity improvement. The exhaust gas will exit from vessel 1 through line 19. When the pretreatment has been completed, valve 17 is closed. This prevents the introduction of additional oxygen-containing gas into vessel 1. Valves 14, 15 and 16 are open while valves 12 and 13 remain closed. This permits inert gas to flow through lines 8 and 9 and drier 10 into vessel 1.

Since in this specific embodiment the hydrocarbon feed will be such that an elevated temperature of the catalyst bed 3 is not desired, heater 11 will not be used. The hydrocarbon feed will be a refinery B—B stream. If heavier hydrocarbons were used, the heater 11 would be needed. The catalyst bed should be cooled to a temperature of approximately 20° to 25°F. When the catalyst bed is at the desired temperature, the hydrocarbon feed stock is introduced into vessel 1 through drier 20, line 21, valve 22 and inlet 23. The inlet 23 is so designed as to introduce the hydrocarbon without impinging it upon the sides of vessel 1. In this embodiment, a B—B stream is used as a hydrocarbon feed. The products from the reaction are withdrawn from vessel 1 through line 19 into a separation zone and appropriate recovery equipment. Samples of product are removed periodically from line 19 through valve 24 and outlet 25 so that the conversion can be monitored. When the results of appropriate tests performed on these samples indicate that the conversion has been reduced as a result of catalyst deactivation, the run may be halted, vessel 1 opened, used catalyst withdrawn and new catalyst installed. On the other hand, if a second vessel is present in the installation and is hooked in parallel with vessel 1, and if this second vessel contains pretreated catalyst, the hydrocarbon conversion can be switched to this second vessel while the catalyst in vessel 1 is changed. The parallel vessels may be operated alternately to furnish continuous operation.

FIGURE 1: APPARATUS FOR THE ISOMERIZATION OF TERMINAL OLEFINS USING ALKALI METAL CATALYST



Source: W.F. Wolff; U.S. Patent 3,405,196; October 8, 1968

OLEFIN DIMERIZATION

Shell Oil

A process developed by C.W. Bittner and G. Holzman; U.S. Patent 3,075,027; January 22, 1963; assigned to Shell Oil Company involves the regeneration of unsupported alkali metal catalysts utilized in condensation reactions which comprises heating the catalyst in the absence of modifying gases such as free hydrogen but in the presence of a substantially inert normally liquid carrier (in other words, in an inert medium) at a temperature between 200° and 400°C. for a period of time between 15 minutes and 24 hours. It has been found that this heat treatment unexpectedly and greatly improves the selectivity of an alkali metal containing catalyst with moderate regeneration of total activity of the catalyst. When the total activity of the catalyst has decreased to an undesirable extent, at least part thereof may be regenerated under more severe conditions comprising vaporizing the alkali metal from the residue with which it is usually associated after its use in condensation reactions.

A preferred cyclic process therefore comprises utilizing an unsupported alkali metal catalyst in the condensation of organic molecules containing an active hydrogen atom and an organic molecule having a double bond (in some cases the same type of molecule) by contacting the two organic molecules at a temperature between 100° and 350°C. and at a pressure from 5 to 200 atmospheres with a catalytic amount of at least 1 alkali metal catalyst, separating the catalyst from the condensation product so formed, regenerating the separated catalyst by heating at a temperature between 200° and 400°C. for a period between 1/4 and 24 hours in the absence of hydrogen and in the presence of a liquid carrier and contacting the regenerated catalyst with further quantities of the condensable organic compounds under the condensation conditions. In a further aspect of the process at least one of the less desired types of by-products from the condensation zone is recycled to the reactor thereto together with regenerated catalyst and additional quantities of fresh feed material for effecting a condensation reaction and at the same time minimizing further production of the undesired side reaction product. The regeneration step appears to result in freeing the catalyst from tarry residue.

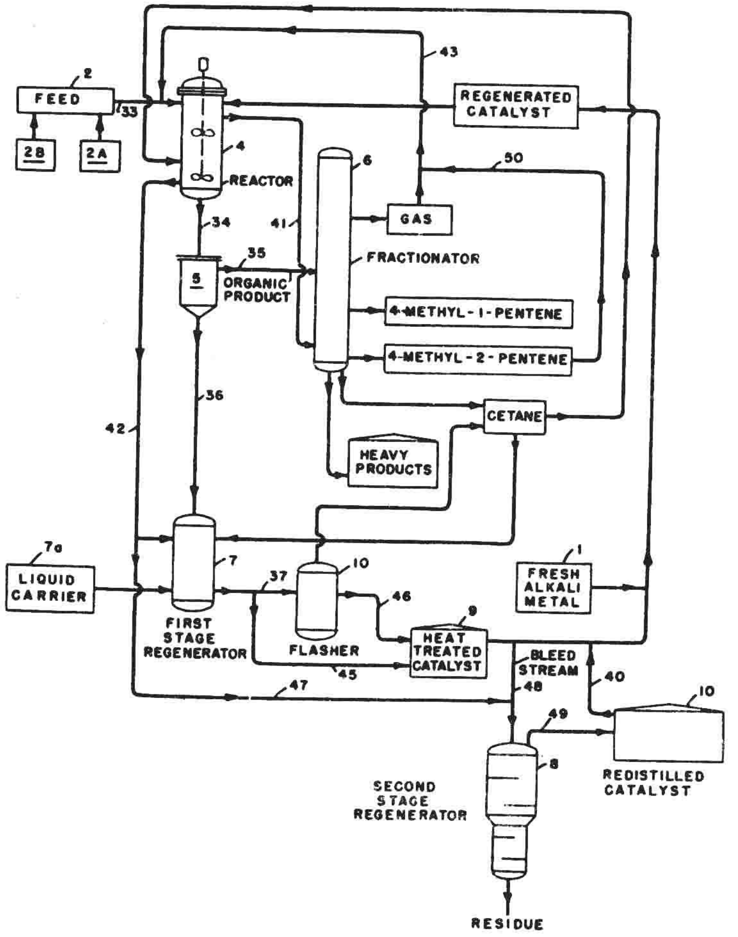
In the process under consideration, unsupported alkali metal catalysts, when contacted with olefinic condensable organic compounds, produce a mixture of condensation products predominating in terminal olefin dimers, in contrast to internal olefins which are produced by alkali metal catalyst supported on activated carbon. Out of this mixture usually one or several components are desired while the remainder of the product comprises either unreacted feed materials or undesirable or less desirable condensation products. As the reaction progresses, both the activity of the catalyst and its selectivity for terminal olefin production diminish. Consequently, it is important to regenerate the catalyst and to so regenerate it that the production of the desired condensation product is increased while the ratio of undesired or unreacted components is minimized.

Taking as an illustration the condensation of propylene in the presence of an unsupported alkali metal catalyst, a typical condensation product will contain C_1 to C_5 hydrocarbons, propane, C_9 olefins, heavier residues, C_6 olefins and particularly 4-methyl-1-pentene and 4-methyl-2-pentene. The former of these last two products is highly desirable since it can be utilized to great advantage in the preparation of the so-called Ziegler polymers. As the unsupported alkali metal catalyst is recycled for the condensation of further quantities of propylene, the ratio of 4-methyl-1-pentene to the corresponding -2-pentene rapidly decreases and shortly reaches an uneconomic level wherein undesirably high quantities of -2-pentene are being produced at the expense of the production of -1-pentene. Regeneration according to the process comprising heating of this used catalyst at a temperature of from 200° to 400°C. for a time from 15 minutes to 24 hours in the absence of hydrogen but in the presence of a normally liquid inert carrier substantially completely regenerates the catalyst with respect to this ratio of desired to undesired components.

In some cases, however, regeneration of total activity (i.e., total amount of conversion products formed under a given set of conditions) is not fully accomplished by this relatively mild treatment. Under some circumstances, therefore, it is economic and desirable to subject at least a portion of the catalyst periodically to harsher conditions whereby the alkali metal is vaporized from the carbonaceous residue with which it is associated prior to recombining with fresh alkali metal or alkali metal regenerated under milder conditions before recycling for the treatment of further portions of the feed organic compounds.

Figure 2 shows the type and arrangement of equipment which may be employed in the conduct of the process. Fresh alkali metal from source 1 may be introduced, if necessary together with regenerated alkali metal catalyst, and a feed hydrocarbon such as propylene from source 2 into the reactor 4, a stirred autoclave or pipeline reactor. The autoclave is preferably fitted with an agitator or stirrer or is vibrated in order to mix the contents thoroughly. Supersonic vibration may be employed for this purpose. The propylene and alkali metal catalyst (approximately 1 part by weight of catalyst for about 40 or more parts by weight of propylene) are heated with agitation in the autoclave at a temperature in the order of 200°C. for a period of 0.3 to 5 hours, the maximum pressure rising in this time to 900 to 3,000 lbs. per sq. in. Completion of the condensation between pairs of propylene molecules is indicated by a decrease in the pressure at the maximum reaction temperature to approximately half of the maximum pressure previously attained. One means of separating the catalyst so utilized comprises vaporizing the volatile components of the condensation product through line 41 to the base of a

FIGURE 2: FLOW DIAGRAM OF PROCESS FOR DIMERIZATION OF PROPYLENE TO 4-METHYL-1-PENTENE IN THE PRESENCE OF ALKALI METAL CATALYST



Source: C.W. Bittner and G. Holzman; U.S. Patent 3,075,027; January 22, 1963

fractionating column 6. The catalyst may then be regenerated in the reactor zone. The organic product is treated by fractional distillation in fractionator 6 to obtain predetermined products including gas, heavy products, carrier hydrocarbons, such as cetane, and the principal product, namely, 4-methyl-1-pentene. Gases including unreacted propylene taken from the top of the fractionating column 6 also may be recycled by means of line 43 to the reactor. Cetane or other substantially inert carrier hydrocarbon which is recovered during the fractionation from tower 6 may be recycled to the reactor or may be utilized also as a carrier during catalyst regeneration, being conveyed to the first stage regenerator by means of line 44.

The catalyst, sent by means of line 36 to the first stage regenerator, is heated in the presence of an inert liquid carrier from source 7a by a heater not shown to a temperature between 200° and 400°C., preferferably 225° to 350°C., for a period between 30 minutes and 24 hours, preferably 1/2 to 2 hours. This may be conducted under pressure such as in an autoclave or in a vessel through which a substantially inert gas such as nitrogen is passing to provide an inert atmosphere for the regeneration. The heat treated catalyst is then passed either directly by means of line 45 to a heat treated catalyst storage zone 9 or by way of a flasher 10 for the partial or complete removal of carrier fluids such as cetane and thence by line 46 to the heat treated catalyst storage zone 9.

If the total activity of the alkali metal catalyst has degenerated to such an extent that its use is unsatisfactory even after the mild heat treatment, it may be subjected to distillation, portions at least of the catalyst being taken either by means of line 47 or from the bleed stream line 48 to the second stage regenerator zone 8 wherein it is subjected to heating sufficient to vaporize the catalyst and convey it by means of line 49 to a redistilled catalyst storage zone 10. This redistilled catalyst is then recycled by means of line 40 for use in the condensation of further quantities of the feed propylene, combining it if necessary with make-up quantities of fresh alkali metal and/or further proportions of heat treated catalyst from the storage zone 10 or the first stage regenerator 7. If the catalyst is to be modified with promoters such as iron or the like this must be done prior to recycling to the reactor zone 4.

DIOLEFIN POLYMERIZATION

The polymerization of diolefins using sodium catalysts is old in the art, the World War I German Buna synthetic rubber having its name derived from the first letters of the German words butadiene and natrium (for sodium). Later emulsion polymerization proved a more practical process but interest has continued in the development of catalysts based on the low cost alkali metal, sodium.

Thus, Morton and coworkers in a series of papers in the Journal of the American Chemical Society, starting in 1947, described an organoalkali metal catalyst for the polymerization of olefins and particularly dienes which they term an alfin catalyst, Journal of the American Chemical Society 69, 161; 167; 950; 1675; 2224 (1947). The name "alfin" is taken from the use of an alcohol and an olefin in their preparation. The alcohol, a methyl n-alkyl carbinol, usually isopropanol, in the form of the sodium salt, the olefin, also in the form of the sodium salt, and an alkali metal halide, form a complex that constitutes the catalyst.

These catalysts were reported by Morten et al to cause the polymerization of butadiene, isoprene and other dienes, alone and together with other copolymerizable organic compounds, in most cases olefinic in nature. The catalyst was discovered in the course of a study of the addition of organosodium compounds to dienes. Later on, Morton summarized the work done up until 1950 in Industrial and Engineering Chemistry, 42, 1488 through 1496 (1950).

National Distillers and Chemical

A process developed by T.B. Baba; U.S. Patent 3,640,980; February 8, 1972; assigned to National Distillers and Chemical Corp. involves the preparation of alfin polymers by polymerization of the monomer by an alfin catalyst in the presence of a molecular weight moderator, treating the alfin polymer reaction mixture with a small amount of carbon dioxide to convert organometallic compounds to organic acid salts, extracting the acid salts with water and separating unreacted monomer, volatile low polymer and solvent, and thereafter purifying solvent and recycling it and optionally the monomer for reuse, and washing and drying the alfin polymer.

In accordance with the process, a continuous process for the preparation of alfin polymers is provided, comprising continuously blending monomer, alfin catalyst, molecular weight moderator and solvent, continuously effecting the polymerization of the monomer at a temperature at which the reaction proceeds by an alfin catalyst in the presence of the molecular weight moderator, treating reaction mixture with carbon dioxide to convert organometallic compounds such as acetylides and alkali metal cyclopentadiene compounds to the acid salts, continuously separating unreacted monomer, volatile low polymer and solvent from the alfin polymer reaction mixture and dissolving and extracting such acid salts in water, and steam distilling volatile materials from the resulting dispersion, and thereafter recovering solvent and optionally the monomer and recycling them for reuse, and washing and drying the alfin polymer.

The carbon dioxide treatment by converting acetylides and cyclopentadiene metal compounds into acid salts makes it possible to separate these from the solvent, and prevent acetylene and cyclopentadiene which otherwise would be regenerated when their organometal derivatives are brought in contact with water, from being distilled off with the solvent. If this occurs, they can be recycled with the solvent, and can react with and destroy alfin catalyst by being converted again into their alkali metal derivatives. Moreover, with each recycling, and each fresh portion of monomer, the content thereof will be increased, until a substantial loss of catalyst can occur. This is prevented by the carbon dioxide treatment.

Figure 3 is a flow diagram of the process. The synthesis of the alfin catalyst in this system takes place in Zone A. The process shown employs sodium, which is prepared as a dispersion in a liquid diluent at a 25 to 50 weight percent sodium concentration. The sodium dispersion is fed via pump 1 to the storage tank 2 where it is stored under nitrogen. Diluent enters via line 3 and sodium (molten) via line 3 into the mixing tank 5, where it is circulated via line 7 to a Gaulin mill 8 to reduce the particle size of the sodium, and then back via line 9 to the mixing tank, to provide an intimate dispersion of sodium of a particle size of less than 10 microns average diameter in the diluent. The finished dispersion is bled off continuously via line 10 to one of two storage tanks 11, 12, equipped with agitators to maintain uniformity.

To prepare the alfin catalyst, a batch technique is used. Diluent from storage 14 is charged via line 15 to the catalyst synthesis reactor 16, an agitated vessel equipped with cooling facilities. Sodium dispersion is added via line 15 from tanks 11 or 12, and isopropyl alcohol is gradually added from storage 17, via line 18 with agitation and cooling at a temperature of approximately 0° to 80°C. Since the reaction is exothermic, the alcohol addition is slow. In this way, 1/3 of the sodium is converted to sodium isopropoxide. The addition of butyl chloride from storage 19 via line 18 then converts most