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COMPLETE SPECIFICATION

Phosphoric Acid Catalyst and a process for the Conversion of Organic Compounds therewith

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a catalyst and process for converting organic compounds and more particularly for condensing unsaturated organic compounds. More specifically this invention is concerned with a process for converting unsaturated hydrocarbons into more valuable products by reaction with alkylatable aromatic compounds or by polymerization in the presence of a solid phosphoric acid catalyst.

The recent increase in automobile engines of high compression ratio and the increasing consumption of aviation gasoline has led to the need for the utilization of improved processes in the petroleum refining industry for the production of extremely high anti-knock hydrocarbons suitable for use in fuels for airplane and automobile engines having high compression ratios. The present invention permits the production of such hydrocarbons of high anti-knock values by the catalytic alkylation of aromatic hydrocarbons with olefins and also by way of polymerization of normally gaseous olefins. The isoparaffins and particularly isooctanes which are readily obtained by way of the catalytic condensation of butenes and hydrogenation of the resultant isooctenes constitute a very desirable component in fuels for aviation and high compression automobile engines.

Various polymers obtainable from olefinic monomers, particularly propylene are increasingly required as intermediates in the manu-
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facture of detergents and other chemical products. Moreover, numerous alkylated aromatic compounds which may be prepared by catalytic alkylation are useful per se or as intermediates in the production of plastics, resins and other organic materials. Ethylbenzene, which results from the alkylation of benzene with ethylene, is in large demand for dehydrogenation to styrene, one starting material for the production of some synthetic rubber. As another example, an aromatic compound such as benzene may be alkylated with an olefinic hydrocarbon such as propylene to form cumene which may then be oxidized to form cumene hydroperoxide. The latter compound may then be decomposed to form phenol and acetone, both of which are industrially important chemical compounds. Furthermore, an aromatic compound such as *p*-cresol may be alkylated with isobutylene to form 2,6-di-*t*-butyl-4-methylphenol, a very effective antioxidant for preventing the deterioration of organic substances due to oxygen.

Numerous catalysts have been proposed for effecting the condensation reactions and particularly a solid phosphoric acid catalyst has found extensive use in industrial applications of these reactions. However, each of the prior art catalysts has suffered from at least one inherent disadvantage. It is therefore an object of this invention to provide a solid phosphoric acid catalyst which can be used in condensation systems such as the aforementioned polymerization and alkylation reactions with avoidance of the disadvantages of the prior art catalysts.

Heretofore solid phosphoric acid catalysts which have been used in industrial practice for promoting condensation reactions have been produced by mixing a siliceous adsorbent with a phosphoric acid in such proportions that the weight ratio of P₂O₅ to siliceous

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adsorbent of the resultant composite would be about 2. Such a composite was then transformed into shaped particles and calcined at a temperature of from 260° to 430° C., the calcined catalyst then generally containing about 60 to about 65% by weight of total phosphorus determined as P_2O_5 . The catalysts so formed are active condensation catalysts and have an acceptable peripheral crushing strength (generally of from 4.5 to 10 kg) when freshly prepared but have a tendency to deteriorate during use by softening or losing activity too rapidly. In order to maintain a high activity of these catalysts, it has been necessary to add a small proportion of water vapor or steam to the reactant charge in order to decrease the loss of moisture from the catalyst during use and to thereby counteract an excessive dehydration of the catalyst which results in a lowering of catalyst activity and the deposition on the catalyst of heavy hydrocarbonaceous materials having the appearance of tar.

It is a well-known fact that commercial solid phosphoric acid catalysts had very good activities when calcined at a temperature in the neighbourhood of 370° C.; however, these catalysts suffered a very undesirable loss of crushing strength during use. In addition it is also a well-known fact that substantially higher calcination temperatures, for example 460° C., improved the crushing strengths to a certain extent but also had a serious drawback in that this calcination temperature seriously impaired the activities of the catalyst. Numerous proposals have been made for obtaining more satisfactory solid phosphoric acid catalysts by deviating in various ways from the method of manufacture of the hitherto commercially available and widely used solid phosphoric acid catalyst. It has been suggested, for example, to subject a composite of a phosphoric acid and siliceous material of the kind exemplified by the commercial solid phosphoric acid catalyst to calcination at high temperatures of the order of 485—595° C., thereby forming a nearly inactive calcined material. Impregnate this calcined material with a phosphoric acid, and then calcine at a temperature below 485° C. It has also been suggested to produce a solid phosphoric acid catalyst by starting from particles of a siliceous material obtained by calcining at temperatures of 650—1100° C. or more, impregnating these hard, porous particles with a phosphoric acid, and calcining the impregnated particles, preferably at 300—400° C., with the formation of a catalyst having improved structural stability and about the same activity as the previously available commercial solid phosphoric acid catalyst. None of the many suggested variations and modifications, however, has brought sufficient improvement to replace the widely used commercial solid phosphoric acid catalyst.

It has been stated in the German Patent publication (Auslegeschrift) No. 1010520 that phosphoric acid catalysts which would possess a sufficient activity, a satisfactory resistance to excessive hydration and at the same time an increased mechanical stability, relative to the commercial solid phosphoric acid catalyst, could not be produced by the previously known manner of manufacture from a paste-like means of a phosphoric acid and siliceous material such as for example kieselguhr. Nevertheless we have now discovered that a catalyst meeting these qualifications can be obtained from phosphoric acids and solid siliceous materials and that the catalyst thus provided by the present invention possesses a highly satisfactory structural stability and at the same time exhibits an exceptionally high activity in promoting condensation reactions, particularly the polymerization of unsaturated hydrocarbons and the alkylation of organic compounds having a replaceable hydrogen atom on a ring nucleus.

The catalyst according to the present invention is manufactured by preparing from a phosphoric acid and a solid siliceous material a mixture having a phosphorus content determined as P_2O_5 in the proportion of from 2.37 to 7.65 parts by weight per part by weight of the siliceous material, heating this mixture until it has assumed a semisolid moldable state then transforming the mixture into shaped particles and completing the catalyst preparation by calcining these particles at a temperature in the range of from 460° to 760° C. According to the present invention, moreover, the catalyst thus manufactured is used in the conversion of organic compounds by condensation reactions such as the polymerization of unsaturated hydrocarbons and the alkylation of organic compounds having a replaceable hydrogen atom on a ring nucleus with an unsaturated hydrocarbon or an alkyl chloride, alkyl bromide or alkyl iodide.

In a more specific embodiment of this invention, the conversion reactions are effected in the presence of catalyst particles which have been prepared from a mixture of from 25 to 10% by weight of organic compounds material and from 75 to 90% by weight of a phosphoric acid having a P_2O_5 content of from 79 to 85% by weight with heating of this mixture at a temperature in the range of from 95° to 232° C. and preferably at approximately 170—180° C. prior to its transformation into shaped particles. Particularly advantageous are catalyst particles which have been prepared from a mixture of the solid siliceous material and a polyphosphoric acid and having a phosphorus content calculated as P_2O_5 in the proportion of from 3.0 to 7.5 parts by weight per part by weight of the siliceous material.

It is preferred, moreover, according to the present invention that the catalyst particles,

upon their having been shaped from the heated moldable mixture, are finished by calcining at a temperature in the range of from 530° to 675° C., and that the calcination is effected in an inert gas for a time period of from 0.5 to 2 hours. As illustrated hereinafter by specific examples, the catalyst particles produced in accordance with the present invention are applied to the effecting of the condensation reactions without any change of composition intervening between their calcination and use. Thus, for example, the present invention avoids the rehydration treatment which has been required, prior to their use, by the solid phosphoric acid catalyst produced by one of the known procedures of shaping particles from a mixture of a phosphoric acid and solid siliceous material and calcining these particles at temperatures above 400° C. and up to 500° or 510° C.

The condensation reactions with the catalyst of this invention are readily performed at conditions of temperature and pressure which are within the ranges which are known per se in the art for use with solid phosphoric acid catalysts and which comprise temperatures upwardly from room temperature to 400° C. and pressures from atmospheric to 100 atmospheres.

Many different classes of organic compounds may be alkylated by the process of this invention. Among such classes of compounds are aromatic compounds including aromatic hydrocarbons, phenols, salts of phenols, aromatic amines, aromatic halides, aromatic ketones and the salts of aromatic carboxylic acids. The preferred aromatic compounds are aromatic hydrocarbons, and particularly monocyclic aromatic hydrocarbons, that is, benzene hydrocarbons. Suitable aromatic hydrocarbons include benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, ethylbenzene, *o*-diethylbenzene, *m*-diethylbenzene, *p*-diethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene (mesitylene), *o*-ethyltoluene, *p*-ethyltoluene, *n*-propylbenzene, and isopropylbenzene (cumene).

Higher molecular weight alkyl hydrocarbons are also suitable such as those produced by the alkylation of aromatic hydrocarbons with olefinic polymers. Such products are referred to in the art as alkylate, and include hexylbenzene, hexyltoluene, heptylbenzene, heptyltoluene, octylbenzene, nonylbenzene, nonyltoluene, decylbenzene, and dodecylbenzene. Very often such alkylate is obtained as a high boiling fraction in which the alkyl group attached to the aromatic hydrocarbon varies in size from C₆ to C₁₄. Other suitable alkylatable aromatic hydrocarbons include those containing an unsaturated side chain such as styrene, vinyltoluene, and allylbenzene. Still other suitable utilizable aromatic hydrocarbons include those with two or more aryl

groups such as diphenylmethane, triphenylmethane, fluorene and stilbene. Examples of suitable alkylatable aromatic compounds which contain condensed benzene rings include naphthalene, anthracene, phenanthrene, chrysene, rubrene, and indene. The term "alkylatable aromatic compound" includes generally the aromatic compounds containing a stable ring or nucleus such as is present in benzene, and which possess unsaturation in the sense that benzene does. Consequently, the term "aromatic compound" in the sense in which it is used in this specification, includes not only carbocyclic compounds but also heterocyclic compounds having a stable nucleus such as the pyridine, furan, thiophene, pyrrole, and pyrazole nucleus. In addition, the aromatic compounds contemplated for use in the present process may contain both a carbocyclic and a heterocyclic ring such as is found in indole and carbazole. Also, the aromatic compounds may contain both a benzene nucleus and a saturated ring such as is found in tetralin and in indan. The aromatic compounds containing non-hydrocarbon substituents which may be alkylated in the process of this invention include phenol, catechol, resorcinol, pyrogallol, aniline, *o*-toluidine, *m*-toluidine, *p*-toluidine, chlorobenzene, and bromobenzene. Among the aforementioned classes of alkylatable compounds the aromatic hydrocarbons constitute the preferred classes. The remaining alkylatable organic compounds are further not necessarily equivalent so that different reaction conditions may be necessary to involve them in reaction with the alkylating agents hereinafter set forth in the presence of the catalysts of this invention.

Suitable unsaturated organic compounds which may be utilized as alkylating agent and as polymerization charge, respectively, in the present condensation process are unsaturated hydrocarbons including monoolefins, diolefins and polyolefins. The preferred unsaturated organic compounds are olefinic hydrocarbons which comprise monoolefins having one double bond per molecule and polyolefins which have more than one double bond per molecule. These compounds are exemplified by the normally gaseous and normally liquid monoolefins including ethylene, propylene, 1-butene, 2-butene, isobutylene, the pentenes, hexenes and higher normally liquid olefins, the latter including various olefin polymers having from about 6 to about 18 carbon atoms per molecule. Typical diolefins are 1,3-butadiene, 1,3-pentadiene, and 1,3-hexadiene. Typical cycloolefins are cyclopentene, cyclohexene, various alkylcycloolefins such as methylcyclopentene and methylcyclohexene, and polycyclic olefins such as bicyclo [2.2.1]-2-heptene.

It is also contemplated within the scope of this invention that the alkylation of the aforesaid alkylatable compounds containing a re-



placeable hydrogen atom may be effected by utilizing olefin-acting compounds which are intended herein to be included by the term "unsaturated organic compounds" since they are capable of producing olefinic hydrocarbons, or of furnishing the alkyl group under the conditions of operation chosen for the alkylation reaction. Typical olefin producing substances capable of use include alkyl chlorides, alkyl bromides, and alkyl iodides capable of undergoing dehydrohalogenation to form olefinic hydrocarbons and thus containing at least 2 carbon atoms per molecule. Examples of such alkyl halides include ethyl chloride, n-propyl chloride, isopropyl chloride, n-butyl chloride, isobutyl chloride, t-butyl chloride, the amyl chlorides, hexyl chlorides, and corresponding bromides and iodides.

As stated hereinabove olefinic hydrocarbons and especially normally gaseous olefinic hydrocarbons, are particularly preferred for use as alkylating agents and as polymerization charge, respectively, in the condensation process according to this invention. This process, using the particular catalyst herein provided can be successfully applied to and utilized for the conversion of olefinic hydrocarbons when said hydrocarbons are present in minor quantities in gas streams. Thus, in contrast to other processes, the normally gaseous olefinic hydrocarbons need not be purified or concentrated. Such normally gaseous olefinic hydrocarbons appear in minor concentrations in various refinery gas streams, usually diluted with various unreactive gases such as for example hydrogen, nitrogen, methane, ethane and propane. These gas streams containing minor quantities of olefinic hydrocarbons are obtained in petroleum refineries from various refinery installations including thermal cracking units, catalytic cracking units, thermal reforming units, coking units, and polymerization units. Such refinery gas streams have in the past often been burned for fuel value since an economical process for their utilization as alkylating agents or olefin acting compounds has not been available except where an operation for concentrating the olefin hydrocarbons has been carried out concurrently therewith. This is particularly true for refinery gas streams containing relatively minor quantities of olefinic hydrocarbons such as ethylene. Thus, it has been possible catalytically to polymerize propylene and/or various butenes in refinery gas streams; however, the off-gases from such processes still contain ethylene. These refinery gas streams containing minor quantities of olefinic hydrocarbons are known as off-gases. In addition to containing minor quantities of olefinic hydrocarbons such as ethylene, propylene and the various butenes, depending upon their source, they contain varying quantities of nitrogen, hydrogen and various normally gaseous paraffinic hydrocarbons hereinbefore

mentioned. Thus, a refinery off-gas ethylene stream may contain varying quantities of hydrogen, nitrogen, methane and ethane with the ethylene in minor proportion, while a refinery off-gas propylene stream is normally diluted with propane and contains the propylene in minor quantities. Likewise, an off-gas butene stream is normally diluted with butanes and contains butylene in minor quantities. A typical analysis in mole percent for a utilizable refinery off-gas from a catalytic cracking unit is as follows: nitrogen, 4.0%; carbon monoxide, 0.2%; hydrogen, 5.4%; methane, 37.8%; ethylene, 10.3%; ethane, 24.7%; propylene, 6.4%; propane, 10.7%; and C₄ hydrocarbons, 0.5%. As readily observable the total olefin content of this gas stream is only 16.7 mole percent. Such gas streams containing olefinic hydrocarbons in minor or dilute quantities may be used as the alkylating agents or olefin-acting compounds in the present condensation process in which the olefin content of such gas streams undergoes reaction while the remaining components of the gas streams are vented from the process. Thus, by using the particular catalyst herein provided as the condensation catalyst it is apparent that an alkylating process for the preparation of such compounds as ethylbenzene, cumene, cymene, and diisopropylbenzene, may be carried out in a more economical manner than was possible heretofore with solid phosphoric acid catalysts.

The catalyst which is provided by the present invention is produced with a higher proportion of phosphoric acid to siliceous material in the mixture prior to calcination as well as with higher calcination temperatures, than the proportion and calcination temperatures heretofore employed together in producing commercial solid phosphoric acid catalysts from mixtures which are later transformed into particles and thereafter calcined. Calcination temperatures used heretofore in producing finished commercial solid phosphoric acid catalysts generally did not exceed 425° C. except in instances where the calcined composite was given a further steam treatment in which instance the calcination temperature reached a maximum of 455° to 510° C. after which the calcined composite was treated with steam at a temperature of from 230° to 290° C. In the catalyst manufacture of this invention a calcination temperature of from 460° to 760° C. and preferably a calcination temperature of from 530° to 675° C. is utilized. The calcination treatment is also carried out in much shorter time than that employed heretofore, namely, a time of from 0.25 to 8 hours whereas in the previous catalyst preparation the particles obtained from a mixture having a weight ratio of P₂O₅ to siliceous adsorbent of about 2 needed an appreciably longer calcination treatment in the range of from 1 to 60

hours at a temperature up to 425° C. The unusually high activities and the great mechanical stability exhibited by the present catalyst during use in this process will be shown in more detail in the examples given hereinafter.

The phosphoric acids used in the production of the present catalyst are those in which the phosphorus has a valence of 5 and include orthophosphoric acid, pyrophosphoric acid, triphosphoric acid, tetraphosphoric acid, hexametaphosphoric acid as well as mixtures of these phosphoric acids. However because of greater convenience in the mixing and calcining operations, it is generally preferable to employ the higher phosphoric acids, that is, those having a relatively high ratio of P_2O_5 to combined water. It is not intended to imply however that the different acids, which may be employed in this process, will produce catalysts having identical effects upon any given organic reaction mixture as each of the catalysts produced from different acids and by slightly varied procedure will have its own characteristic action.

In using orthophosphoric acid as a primary ingredient, one may start from different concentrations of the aqueous solution, for example, acid containing from 75 to 100% H_3PO_4 or orthophosphoric acid containing some free phosphorus pentoxide may be used. Thus the ortho acid may contain a definite percentage of the pyro acid which corresponds to the primary phase of dehydration of orthophosphoric acid. Within these concentration ranges the acids will be liquids of varying viscosities and these liquids are readily mixed with adsorbent materials. In practice it has been found that pyrophosphoric acid corresponding to the formula $H_4P_2O_7$ can be incorporated with siliceous adsorbents at a temperature somewhat above the melting point (namely 61° C.) and that the period of heating which is given to the pyro acid-adsorbent mixtures may be different from that used when the ortho acid is so employed.

Triphosphoric acid which may be represented by the formula $H_5P_3O_{10}$ may also be used as a starting material for preparation of these catalysts. The mixtures required in the manufacture of the present catalyst may also be prepared from the siliceous materials mentioned herein and a phosphoric acid mixture containing orthophosphoric, pyrophosphoric, triphosphoric, and other polyphosphoric acids.

Another acid of phosphorus which may be employed in the manufacture of the present catalyst is tetraphosphoric acid. It has the general formula $H_6P_4O_{13}$ which corresponds to the double oxide formula $3H_2O \cdot 2P_2O_5$ which in turn may be considered as the acid resulting when three molecules of water are lost by four molecules of orthophosphoric acid H_3PO_4 . The tetraphosphoric acid may be

manufactured by the gradual and controlled dehydration by heating of orthophosphoric acid or pyrophosphoric acid or by adding phosphorus pentoxide to these acids in proper amounts. When the latter procedure is followed, phosphoric anhydride is added gradually until it amounts to 520% by weight of the total water present. After a considerable period of standing at ordinary temperature, the crystals of the tetraphosphoric acid separate from the viscous liquid and it is found that these crystals melt at approximately 34° C. and have a specific gravity of 1.1886 at a temperature of 15° C. However, it is unnecessary to crystallize the tetraphosphoric acid before employing it in the preparation of the present solid catalyst inasmuch as the crude tetraphosphoric acid mixture may be incorporated directly with the siliceous material.

A phosphoric acid mixture which is generally referred to as polyphosphoric acid may also be employed and has been found to be particularly desirable. Polyphosphoric acid is formed by heating orthophosphoric acid or pyrophosphoric acid or mixtures thereof in suitable equipment such as carbon lined trays heated by flue gases or other suitable means to produce a phosphoric acid mixture generally analyzing from 79 to 85% by weight of P_2O_5 . Such a liquid mixture of phosphoric acids with 79.5% P_2O_5 content was found by analysis to contain 24.5% of orthophosphoric acid (H_3PO_4), 45.2% of pyrophosphoric acid ($H_4P_2O_7$), 26.0% of triphosphoric acid ($H_5P_3O_{10}$), and 4.3% by weight of unidentified phosphoric acids. Another polyphosphoric acid mixture somewhat more concentrated than the one just referred to and having a phosphorus content determined as P_2O_5 of 84% by weight was found by analysis to contain 57% by weight of triphosphoric acid ($H_5P_3O_{10}$), 17% by weight of hexametaphosphoric acid ($H_6P_6O_{19}$), 11% of pyrophosphoric acid ($H_4P_2O_7$), 5% by weight of orthophosphoric acid (H_3PO_4), and 10% by weight of unidentified phosphoric acids.

The solid siliceous materials which may be employed as adsorbents or carriers for phosphoric acids in preparing the mixture subsequently to be transformed into calcined particles are divided roughly into two classes. The first class comprises materials of predominantly siliceous character and includes diatomaceous earths, kieselguhr, and artificially prepared porous silica. Typical of these siliceous materials are the diatomites, such as those known as "Celite", "Dicalite 1" and "Dicalite 2" (the words "Celite" and "Dicalite" being Registered Trade Marks), which are naturally occurring kieselguhrs which have been dried by heating at a temperature in the range of from 205° to 370° C. and comprise 90% silica, the remainder being accounted for by various metal oxides and by approximately 3.7% ignition loss. The second class

of materials which may be employed either alone or in conjunction with the first class comprises generally certain members of the class of aluminum silicates and includes such naturally occurring substances as various fuller's earths and clays such as bentonite, montmorillonite and acid treated clays. Each adsorbent or supporting material which may be used will exert its own specific influence upon the net effectiveness of the catalyst composite which will not necessarily be identical with that of other members of the class.

In producing the catalyst composites which are utilized in the present invention, the phosphoric acid and siliceous solid are mixed at a temperature of from 10° to 232° C. and preferably at a temperature of from 95° to 180° C. to form an intermediate composite containing the acid in intimate admixture with finely divided siliceous material. Thus satisfactory results have been obtained by heating polyphosphoric acid (84% P₂O₅ content) at a temperature of 170° C. and then mixing this hot acid with diatomaceous earth which has previously been at room temperature. The polyphosphoric acid and diatomaceous earth form a composite in which the weight ratio of phosphorus pentoxide to diatomaceous adsorbent is from 3.0 to 7.5. This composite is slightly moist to almost dry in appearance but becomes plastic when subjected to pressure in a hydraulic press-type or auger-type extruder by which the composite is subsequently formed into pieces that are cut into shaped particles. The resultant composite while it is still hot is thus extruded through a die preheated to a temperature of 170° C. The extruded particles are then calcined by heating in air, nitrogen, flue gas or some other inert gas at a temperature of from 460° to 760° C. and preferably at a temperature of from 530° to 675° C. for a time of from 0.25 to about 8 hours and preferably 0.5 to 2 hours to form the final substantially granular catalytic material.

The condensation process utilizing the particular catalyst provided by this invention may be effected in any suitable manner and may comprise either a batch or a continuous type operation. When a batch type alkylation operation is used a quantity of the starting materials, namely, the alkylatable organic compound such as an aromatic hydrocarbon and the alkylating agent are placed in a suitable condensation apparatus such as a rotating autoclave or an alkylation flask along with particles of the catalyst the manufacture of which has been completed by the calcining at a temperature in the range of from 460° to 760°. The apparatus is sealed and heated to the desired temperature which may be in a range of from atmospheric to 400° C. In addition the process may also be carried out at pressures ranging from atmospheric to 100 atmospheres or more. However, the pressure

does not appear to be a critical variable inasmuch as the process may be carried out in either a liquid or vapor phase. Thus, the pressure utilized may be selected so as to obtain greatest advantage based upon economic considerations and upon the stability of the particular reactants which are charged to the process under the necessary processing conditions. At the end of a predetermined residence time the apparatus and contents thereof are allowed to cool to room temperature, any excess pressure present is vented and the desired reaction product comprising the alkylated aromatic compound is separated from the catalyst by conventional means such as filtration, further separated from any unreacted starting materials and recovered by conventional means such as, for example, by fractional distillation or crystallization.

The process of this invention may also be effected in a continuous type operation. The solid phosphoric acid catalyst of the particular type provided by this invention is particularly suitable for use in a fixed bed type of operation. In this type of operation the catalyst is disposed as a fixed bed in a reaction zone which may comprise either an unpacked vessel or reaction tube or which may be lined with an adsorbent packing material such as dehydrated bauxite, fire brick or alumina. The reaction zone is maintained at the proper operating conditions of temperature and pressure while the reactants comprising in the case of an alkylation treatment the alkylatable organic compound and the alkylating agent are continuously charged thereto through separate lines or, if so desired, the reactants may be admixed prior to entry into the reaction zone and charged thereto in a single stream. In carrying out the process of this invention in a continuous type of operation liquid hourly space velocities (the volume of hydrocarbon, measured as liquid, charged to the reactor per volume of catalyst per hour) may be varied within a relatively wide range of from 0.1 to 20 or more, the preferred range being from 0.1 to 10. The desired reaction product is continuously withdrawn from the reaction zone, separated from the reactor effluent and purified by conventional means while the unreacted components of the effluent may be recharged to the reaction zone as a portion of the feed material.

Other continuous types of operation which may be used in this process include the compact moving bed type of operation in which the bed of catalyst and the reactants pass either concurrently or countercurrently to each other in the reaction zone, the slurry type process in which the catalyst is carried into the reaction zone as a slurry in one of the reactants and, if the alkylating agent or polymerization charge is in gaseous form, the fluidized type of operation in which the catalyst is maintained in a state of turbulence

or hindered settling conditions in the reaction zone.

The following examples are given to illustrate the process of the present invention and the advantages of the catalyst thereof relative to catalysts outside the scope of this invention.

EXAMPLE I

A quantity of the desired solid phosphoric acid catalyst (catalyst A) was prepared by stirring 43.2 g. of a diatomaceous earth known in the trade as "Celite FC" into 160 g. of polyphosphoric acid (83.5% P_2O_5) which had been preheated for 20 minutes at 170° C. After a 5 minute mixing the resultant composite was heated in an oven at 170° C. for a period of approximately 30 minutes. After the first 10 minutes of this 30 minute period had elapsed the composite was stirred every 5 minutes. Prior to being put in the oven the composite was a wet, plastic mass which remained practically unchanged in appearance and consistency for 25 of the 30 minute period in the oven. However, the last 5 minutes of the drying period changed the appearance to a hardened mass of composite. The hardened composite was then taken from the oven and was extruded in a hydraulic press through a die which had been preheated to a temperature of 170° C. The

extruded strands were cut into pill shape and were then heated for one hour at 170° C., after which they were calcined in a muffled furnace for one hour at 560° C.

The catalyst thus prepared was used for the alkylation of benzene with ethylene in the following manner:

A benzene feed and the feed gas comprising a synthetic blend consisting of ethylene, ethane and methane were charged to a jacketed reactor containing 193 g. of the catalyst (A) prepared in the above manner. The conditions under which the reaction took place were a pressure of 63 atmospheres, a liquid hourly space velocity of 0.75, a benzene/ethylene mole ratio of about 10, a temperature of 290° C., and 0.26 mole percent water on the combined feed. The runs were made for periods of 22, 22 and 48 hours, respectively. Mass spectrometer analysis of the feed and exit gases showed that the conversion of ethylene was virtually complete. The crude liquid products were fractionally distilled and the desired cuts were subjected to an infra-red analysis which showed that 85 to 88% of the converted ethylene, or 93 to 95% of the converted benzene were accounted for as ethylbenzene. The results of these runs appear in Table I below.

TABLE I

% Ethylene converted	99	99	97
% converted ethylene accounted for as:			
Ethylbenzene	85.1	88.1	87.9
Higher aromatics	14.9	11.9	12.1
Total	100.0	100.0	100.0
% Converted benzene accounted for as:			
Ethylbenzene	93.0	94.3	94.5
Higher aromatics	7.0	5.7	5.5
Total	100.0	100.0	100.0

Two additional runs were made using similar conditions with one exception, that is, the runs were made at a temperature of 315°

C.; the results of these two runs are shown in Table II.

TABLE II

% Ethylene converted	98	98
% Converted ethylene accounted for as:		
Ethylbenzene	85.6	86.1
Higher aromatics	14.4	13.9
Total	100.0	100.0
% Converted benzene accounted for as:		
Ethylbenzene	93.0	93.2
Higher aromatics	7.0	6.8
Total	100.0	100.0

The catalyst after having been used for a total period of 123 hours, was analyzed and was found to have an increase of free P_2O_5 from 12.2% to 16.7% while the total titratable P_2O_5 decreased from 58.0% to 56.9%.

To illustrate the advantage of using the catalyst A the above experiment was repeated using a solid phosphoric acid catalyst (catalyst B) which contained 75% phosphoric acid and had been calcined at a lower temperature, namely at 310–360° C., and which thus was not in accordance with the present invention. The benzene feed was charged to the jacketed

reactor containing 185 g. of the catalyst B. The feed gas comprising the synthetic blend of ethylene, ethane and methane was also charged thereto. The conditions were similar to those abovementioned, that is, a pressure of 63 atmospheres, a liquid hourly space velocity of 0.75, a benzene/ethylene mole ratio of approximately 10.8, a moisture content of 0.26 mole percent on the combined feed, and a temperature of 290° C. The runs were made for periods of 12, 24, 24 and 23 hours. The results for these runs appear below in Table III.

TABLE III

% Ethylene Converted	86.6	86.7	86.7	87.2
% Converted ethylene accounted for as:				
Ethylbenzene	87.31	88.39	98.15	88.09
% Converted benzene accounted for as:				
Ethylbenzene	94.10	94.43	95.03	94.33

Therefore, it is readily apparent that the catalyst A which was in accordance with the present invention exhibited a greater ability to convert the ethylene than did the catalyst B.

EXAMPLE II

Another experiment was run in which the feed consisted of a simulated catalytic cracker off-gas. This gas was a synthetic blend of ethylene, nitrogen, hydrogen and methane, the ethylene content being 12 mol percent. The aromatic feed comprised a thiophene-free benzene and in a first part of the experiment this feed contained 0.4% by weight of iso-

propyl alcohol which furnished water of hydration for the catalyst. The conditions under which the experiment was run were a pressure of approximately 65 atmospheres, a temperature ranging from 290° C. at the beginning to 315° C. at the end of the run, a liquid hourly space velocity of 0.57 and a benzene to total olefin mol ratio of 8. The catalyst was prepared in the manner set forth above in Example I, (catalyst A) that is, a mixture was prepared which contained 80% polyphosphoric acid and 20% Celite FC, the mixture was dried and then extruded, the

extrudate was cut into particles and the particles were calcined for one hour at 560° C. The results of this experiment which consisted of a 580 hour life test of the catalyst

with respect to activity, stability, product distribution and quality of the catalyst are set forth in Table IV below.

Catalyst

Catalyst	Age in hours at: Start of period End of period	Mole % water (combining feed)	Catalyst temperature °C.	% Ethylene converted (average)	% Propylene converted	% Converted ethylene accounted for as:
	6 125	0.25	290	77.4	100.0	Ethylbenzene
	125	248	294	72.8	100.0	s-Butylbenzene
	243	268	72.8	82.6	100.0	Diethylbenzenes
						Bottoms calculated as diethylbenzenes
Total						
						% Converted propylene accounted for as:
						Cumene
						α-Methylstyrene
Total						
						% converted benzene accounted for as:
						Toluene
						Ethylbenzene
						Cumene
						α-Methylstyrene
						s-Butylbenzenes
						Diethylbenzenes
						Bottoms
Total						

The liquid feed for the period running from 372 hours to 580 hours comprised pure benzene with no isopropyl alcohol present in the feed. Prior to this period the isopropyl alcohol was dehydrated to provide 0.25 mole percent water on the combined feed. These results show that alkylation of the benzene feed under essentially anhydrous conditions, that is, after 364 hours of the test, and at a temperature of approximately 317° C. resulted in an improvement in the ethylene conversion as well as a substantial improvement in the efficiency of the conversion of ethylene and of benzene to ethylbenzene. During the last quarter of the test (the period running from 460 hours to 580 hours) less than 10% of the converted ethylene and only 5% of the converted benzene were tied up in material boiling above the ethylbenzene range.

The used catalyst, upon completion of the run, was removed from the reactor and was found to have a peripheral crushing strength of 5.27 kg. This used catalyst, however, was found to contain less than 1% carbon and to have increased in free P_2O_5 from 12.4% to 17% while there did not appear to have been any loss of total titratable P_2O_5 ; the fresh catalyst had a total titratable P_2O_5 content of 58.30% while the used catalyst had an average total titratable P_2O_5 content of 58.26%. (The total titratable P_2O_5 content represents a readily ascertainable analytical value which is convenient for comparisons but does not represent the total P_2O_5 content determinable by the more cumbersome gravimetric analysis). Therefore it can be readily seen that the

particular catalyst which is used in this reaction, that is, a catalyst produced from a mixture containing 80% polyphosphoric acid prior to the calcination and calcined at a relatively high temperature of over 530° C. may be used as an alkylation or condensation catalyst at a relatively low temperature and without the need of any additional moisture to maintain the activity of the catalyst.

To further illustrate the effectiveness of the above catalyst (A) another life test run was performed using a solid phosphoric acid catalyst (catalyst C) which contained less than 80% pyrophosphoric acid prior to calcination and like the catalyst B had been calcined at temperatures in the range of from 310° to 360° C. The simulated catalytic cracker off-gas feed again consisted essentially of ethylene, nitrogen, hydrogen and methane, the ethylene content being 12 mole percent. The benzene feed consisted of 98% benzene, thiophene-free, and 2% isopropyl alcohol. The conditions under which the test was run were: a temperature of 350° C., a pressure of 65 atmospheres, a liquid hourly space velocity ranging from 2 to 0.6, a benzene to total olefin mol ratio ranging from 15 to 7 and a moisture content of 1.4 mol percent calculated on the combined feed. The recovered product was subjected to fractional distillation and the desired fractions were subjected to infra-red analysis to determine the percentage of each component in the product which was recovered. The results of this test appear in Table V.

TABLE V

Temperature °C.	348	350	351	350	351	350	348
Catalyst							
Age in hours used at							
Start of period	6	132	149	245	266	290	518
End of period	125	149	245	261	290	386	583
Moisture, mole percent on combined feed	1.40	1.38	1.39	1.39	1.40	1.39	1.39
% Ethylene converted (average)	29	60	55	53	52	56	73
% converted ethylene accounted for as:							
Ethylbenzene	89.6		88.1			88.1	88.5
Higher aromatics	10.4		11.9			11.9	11.5
Total	100.0		100.0			100.0	100.0
% converted propylene accounted for as:							
Paraffins plus olefins boiling at 80.5–136° C.							
Cumene	94.4		91.5			91.3	2.0
Higher aromatics	5.6		8.5			8.7	84.8
Total	100.0		100.0			100.0	100.0
% Benzene accounted for as:							
Toluene	1.1		0.4			0.4	0.1
Ethylbenzene	38.3		60.4			58.2	53.7
Cumene	56.7		33.5			35.8	39.6
Higher aromatics	3.9		5.7			5.6	6.6
Total	100.0		100.0			100.0	100.0

The catalyst was removed at the end of the total period of 583 hours and was found to be carbonized, there being approximately 7% carbon on the extracted sample. In addition the total titratable P₂O₅ content was reduced

10³ creased to 3.16 kg.

It is to be noted that the catalyst A prepared in accordance with the present invention retained its activity after a life test of about 580 hours, showed an increase in titratable

crease in activity over the life of the test, contained a considerably larger portion of carbon with a corresponding decrease in the total titratable amount of P₂O₅ and free P₂O₅ and, in addition, did not give satisfactory conver-

or moisture in order to effect the condensation of the aromatic feed with the olefin whereas former catalyst A required a considerably lower temperature and also performed better under virtually anhydrous conditions, the ethylene conversion being increased in the absence of moisture rather than being decreased.

EXAMPLE III

Diatomaceous earth (32.5 g.) containing 7.8% of volatile matter was added all at one time to 120 g. of polyphosphoric acid (84.8% P_2O_5 content) at a temperature of 170° C. The initially very soft plastic mass so produced hardened to a material with an extrudable consistency after being maintained at a temperature of 170° C. for a time of 30 minutes. This plastic material was extruded through a 5mm. die at a temperature of 170° C. by means of a hydraulic press extruder by the application of initial and working loads of 3170 kg. and 2265 kg., respectively. The extrudate was cut into pieces of 5 mm. lengths by means of a stainless steel spatula. The resultant pills or pellets were first dried at a temperature of 170° C. for 1 hour and samples thereof then were calcined in a muffle

furnace at various temperatures in the range of from 360° to 660° C., for a time of 1 hour to produce finished catalysts having the activities, apparent bulk densities and peripheral crushing strengths given in Table VI. The activity of each of these catalysts was determined by placing 10 grams of the catalyst pills and 100 grams of a propane-propylene mixture containing 49.2 mole percent of propylene in a rotatable steel autoclave of 840 cc. capacity which was then operated for 2 hours, at a temperature of 232° C. after which the autoclave and contents were cooled and the percentage of propylene converted was determined. As the apparatus employed in measuring the peripheral crushing strength of the pills did not measure crushing strengths greater than 12.2 kg., the numerical values of averaging crushing strengths given in the table are followed by a plus sign in cases in which some or all of the pills had crushing strengths above 12.2 kg. Three intermediate composites each containing a different sample of diatomaceous earth were prepared and results obtained on the catalysts obtained from these composites are shown in Table VI.

TABLE VI

Diatomaceous Earth-Polyphosphoric Acid Catalysts

Catalyst No.	Catalyst Starting Materials	Calc. Temp. °C.	% Conv. of C_3H_6 (a)	A.B.D.* g./cc.	Average Crushing Strengths, Kg.	
					Before Test	After Test
1	80% PPA (b) and	460	87.2	0.785	12.2+	12.2+
2	20% diatomaceous	560	92.2	0.765	12.2+	12.2+
3	earth (c) (Celite)	660	89.5	0.723	11.55+	11.95+
4	80% PPA (b) and	510	66.1	0.824	12.15+	12.0+
5	20% diatomaceous	560	67.7	0.812	12.2+	11.9+
6	earth (c)	610	72.0	0.809	11.7+	12.2+
7	(Dicalite 1)	660	69.1	0.836	11.35+	11.85
8	80% PPA (b)	360	61.4	0.867	11.7+	9.7
9	20% diatomaceous	460	84.0	0.837	12.0+	12.15+
10	earth (c)	510	87.9	0.792	12.2+	12.2+
11	(Dicalite 2)	560	89.0	0.801	12.2+	12.2+

a) On 5 × 5 mm. cylindrical pills extruded on a laboratory hydraulic press.

b) Polyphosphoric acid with 84.8% P_2O_5 analysis.

c) Volatile matter-free basis.

* Apparent bulk density.

The particles formed from the composites were calcined at the indicated temperatures from 360° to 660° C. in 50° and 100° C. steps, as shown. The limited quantity of each catalyst sample and the desirability of determining the highest temperature which each

composite could tolerate before its activity would start to decline did not permit calculation of all composites at all the temperatures.

Table VI shows the unexpected high activities and high after-use crushing strengths obtained with these groups of catalysts when calcined at temperatures from 460° to 660° C. Thus the propylene polymerizing activities reached the unusually high values of 89 and 92%, and high after-use crushing strengths of 12.2+ kg. were obtained on catalysts calcined at 560° and 660° C. Maximum activities were attained at calcination temperatures in the neighbourhood of 560° to 610° C., the optimum temperature being dependent upon the particular diatomaceous earth employed. Different calcination temperatures had only a small effect on the after-use crushing strengths over the calcination temperature range of 460° to 660° C. There was an unmistakable tendency for both the polymerizing activities and the used-pill strengths to drop on catalysts calcined at temperatures below 460° C.

EXAMPLE IV

25 An intermediate composite was prepared by mixing 120 g. of polyphosphoric acid (84.8% P_2O_5 content) and 33.5 g. of diatomaceous earth (9.6% volatile matter content)

according to the procedure described in Example III. The resultant composite was then heated for 30 minutes at a temperature of 170° C. prior to extrusion at that temperature. The extrusion by means of a hydraulic press extruder was initiated with a load of 3620 kg. and was continued with a load of 3170 kg. The extrudate was cut into 5 × 5 mm. pellets by a stainless steel die. It was then dried for one hour at a temperature of 170° C. and divided into four portions which were calcined in a muffle furnace at 560° C. for times of 1, 2, 4 and 8 hours.

A similar intermediate composite was prepared in the same manner and extruded into particles which were also dried for one hour at a temperature of 170° C. after which the pellets were divided into four portions and calcined at a temperature of 360° C. for different lengths of time. The polymerizing activities and crushing strengths of these groups of catalysts finished by calcining at 560° C. and 360° C., respectively, for different lengths of time are shown in Table VII. The activities of these catalysts were determined on a propane-propylene mixture containing 49.2 mol percent of propylene by the procedure outlined in Example III.

TABLE VII

Effect of Time of Calcination on Activities and Crushing Strengths of Catalysts Produced from Polyphosphoric Acid and Diatomaceous Earth

Catalyst No.	Catalyst Starting Materials	Calcination Temp., °C.	Time Hrs.	% Conv. of C_3H_6 (a)	A.B.D. g./cc.	Average Crushing Strength, Kg.	
						Before Test	After Test
12	80% PPA (b)	560	1	75.1	0.765	12.2	10.45
13	20% diatomaceous earth (c)	560	2	78.8	0.757	12.2	11.55
14	(Dicalite 2)	560	4	78.0	0.762	12.05	10.5
15		560	8	80.3	0.737	11.55	9.2
16	80% PPS (b)	360	1	59.6	0.812	17.9	6.54
17	20% diatomaceous earth (c)	360	2	61.3	0.781	10.9	10.2
18	(Dicalite 2)	360	4	61.4	0.772	10.2	6.16
19		360	8	58.6	0.788	11.55	7.98
20		360	1	81.5	0.738	12.2	9.0
		560	1	(d)			
21	70.2% PPA (b)	360	1	62.8	0.738	12.18	4.0
22	29.8% diatomaceous earth (c)	460	1	66.1	0.729	12.18	3.36
23	(Dicalite 2)	510	1	64.6	0.746	12.05	2.5
24		560	1	42.2	0.710	11.9	12.2

a) On 5 × 5 mm. cylindrical pills extruded on a laboratory hydraulic press.

b) Polyphosphoric acid with 84.8% P_2O_5 analysis.

c) Volatile matter free basis.

d) First calcined one hour at 360° C. followed by one hour calcination at 560° C.

As shown in Table VII, calcination at either 360°, 460° or 510° C. of an experimental composite (Catalysts 21—23) prepared from polyphosphoric acid and diatomaceous earth in the proportions commonly employed heretofore in producing commercial solid phosphoric acid catalysts caused hardly any variation in activity or used-pill peripheral crushing strength. The activities ranged from 62 to 66%, while the used-pill crushing strengths varied from 2.5 to 4 kg. On the other hand, the calcination of the same composite at 560° C. (catalyst 24) seriously lowered the activity (42%) which offset the value of the improved used-pill strength (12.2 kg.).

From the above indicated results it is obvious that the catalysts produced from composites containing 80% of polyphosphoric acid and hereinafter referred to as the 80% acid catalyst are definitely superior to the 70% acid catalysts (conventional commercial solid phosphoric acid catalysts). The activities of both the 80% acid catalysts and the 70% acid catalysts start at about the same value (approximately 60%) at 360° C. but the activities of the former catalysts continue to rise to 89% at 560° C. calcination (Table VI), whereas those of the 70% acid catalysts remain about the same (62 to 66%) over the 360°—510° range and then drop abruptly at higher temperature, namely to 42% to 560° C. (Table VII, catalysts 21—24). Moreover, throughout the same temperature range, the used pill strengths of the 80% acid catalysts rise from 10 to 12.2 kg. while those of the 70% acid catalysts remain low (2.7 to 4.1 kg.) between 360° and 510° C. and only rise to the value of the considerably more active 80% acid catalyst at the 560° C. calcination temperature, at which the activity of the 70% catalyst drops to below the useful range.

The particles formed from the polyphosphoric acid-diatomaceous earth composite having an 80% acid content showed remarkably constant activities after calcinations for various lengths of time (1, 2, 4, and 8 hours) at either 360° or 560° C. The activities in the 360° C. series, however, were only 59 to 61%, whereas in the 560° C. series the activities were 75 to 80%. In the 560° C. series the peripheral crushing strengths after use

decreased almost linearly from 11.5 to 9.2 kg. as the calcination time was increased from two to eight hours. In the 360° C. series the crushing strengths after use did not line up on any simple curve. Some of the used pill strengths were good (8 and 10 kg.) and some rather mediocre (6.5 kg.). Evidently a prolonged low temperature calcination of composites with a very high acid content is not a substitute for a short time-high temperature calcination.

When the activities and crushing strengths after use of the 80% acid catalysts were plotted against calcination time, the activity values were on practically a straight, almost horizontal line. There was no diminution in the excellent activities even after an 8 hour calcination. In fact, the activities actually appeared to improve somewhat (from 75 to 80%) as the calcination time was raised from 1 to 8 hours. The used-pill strengths of these catalysts likewise were on practically a straight line. Though these crushing strengths after use were all good (above 9 kg.) they seemed to decrease very slowly and almost linearly as the length of the calcination time was increased. It is also interesting to note that a one hour calcination at 560° C. after an initial calcination of one hour at 360° C. (catalyst 21) improved considerably both the activity and used-pill strength.

EXAMPLE V

Intermediate composites similar to those produced in Examples III and IV were formed by mixing 82.5% of orthophosphoric acid (H_3PO_4) and 17.6% by weight of diatomaceous earth so as to form a phosphoric acid-diatomaceous earth composite having the same P_2O_5 to siliceous adsorbent ratio as contained in the catalysts of Examples III and IV which were prepared from 80% by weight of polyphosphoric acid. These composites were then heated at a temperature of 170° C. to produce a plastic mass suitable for extrusion and cutting to form pill or pelleted catalyst particles. The resultant particles were then calcined at temperatures of 360°, 460°, 510°, 560° C. for one hour each. Activity test results and crushing strengths of these catalysts were obtained as shown in Table VIII.

TABLE VIII

Phosphoric Acid-Diatomaceous Earth Catalysts

Catalyst No.	Catalyst Starting Materials	Calcination Temp., °C.	Time Hrs.	% Conv. of C_3H_6 (a)	A.B.D. g./cc.	Average Crushing Strengths, Kg.	
						Before Test	After Test
25	82.4% H_3PO_4	360	1	33.3	0.809	9.8+	9.85+
26	and 17.6% dia-	460	1	47.7	0.734	12.2+	12.2+
27	tomaceous earth (b)	510	1	59.1	0.743	12.2+	12.2+
28	(Dicalite 2)	560	1	70.9	0.705	12.2+	12.2+

a) On 5 × 5 mm. cylindrical pills extruded on a laboratory hydraulic press.

b) Volatile matter free basis.

Comparison of the activities and crushing strengths of the catalysts referred to in Table VIII with similar catalysts prepared from polyphosphoric acid and diatomaceous earth (Catalysts 8—11 of Table VI) indicates that when using a calcination time of one hour, the orthophosphoric acid yielded structurally strong catalysts which, however, had lower activities than those produced in analogous manner from polyphosphoric acid. The data of Table VIII, moreover, indicate that the use of a calcination temperature of 360° C. resulted in an activity which was too low for practical use. Some correlation seems to exist between the differences in the activities of any corresponding pair of catalysts in the two series (namely pairs of catalysts produced from the different acids with calcination at the same temperature) and the differences in their residual amounts of water (that is the water contained in the catalyst composition after final calcination).

WHAT WE CLAIM IS:—

1. A process for the conversion of organic compounds wherein an unsaturated organic compound is subjected to a condensation reaction in the presence of a solid phosphoric acid catalyst at a temperature up to 400° C. and a pressure of from atmospheric to 100 atmospheres, characterized by the use of a catalyst which has been manufactured by preparing from a phosphoric acid and a solid siliceous material a mixture having a phosphorus content determined as P_2O_5 in the proportion of from 2.37 to 7.65 parts by weight per part by weight of the siliceous material, heating said mixture until it has assumed a semi-solid moldable state, then transforming the mixture into shaped particles and completing the catalyst preparation by calcining said particles at a temperature in the range of from 460° to 760° C.
2. Process as claimed in claim 1, characterized by the use of catalyst particles prepared from a mixture of from 25 to 10% by

weight of the solid siliceous material and from 75 to 90% by weight of a phosphoric acid having a P_2O_5 content of from 79 to 85 weight percent with heating of said mixture at a temperature in the range of from 95° to 232° C. prior to its transformation into shaped particles.

3. Process as claimed in claim 1 or 2, characterized by the use of catalyst particles prepared from a mixture of the solid siliceous material and a polyphosphoric acid and having a phosphorus content determined as P_2O_5 in the proportion of from 3.0 to 7.5 parts by weight per part by weight of the siliceous material.

4. Process as claimed in any of the claims 1 to 3, characterized by the use of catalyst particles which upon their having been shaped from the heated moldable mixture have been finished by calcining at a temperature in the range of from 530° to 675° C.

5. Process as claimed in claim 4, characterized by the use of catalyst particles which have been finished by effecting the calcination in an inert gas for a time of from 0.5 to 2 hours.

6. Process as claimed in any of the claims 1 to 5, characterized thereby that the catalyst particles upon their calcination at a temperature in the range of from 460° to 760° C. are used, without any intervening change of composition, in the alkylation of an aromatic compound having a replaceable hydrogen atom on a ring nucleus by reaction with an unsaturated organic compound of the group consisting of the hydrocarbons having olefinic unsaturation and the alkyl chlorides, alkyl bromides and alkyl iodides.

7. Process as claimed in claim 6, characterized thereby that the calcined catalyst particles are used in the alkylation of a benzene hydrocarbon with a monoolefinic hydrocarbon.

8. Process as claimed in any of the claims 1 to 5, characterized thereby that the catalyst particles upon their calcination at a tempera-



TABLE VIII

Phosphoric Acid-Diatomaceous Earth Catalysts

Catalyst No.	Catalyst Starting Materials	Calcination Temp., °C.	Time Hrs.	% Conv. of C_3H_6 (a)	A.B.D. g. cc.	Average Crushing Strengths, Kg.	
						Before Test	After Test
25	82.4% H_3PO_4	360	1	33.3	0.809	9.8+	9.85+
26	and 17.6% dia-	460	1	47.7	0.734	12.2+	12.2+
27	tomaceous earth (b)	510	1	59.1	0.743	12.2+	12.2+
28	(Dicalite 2)	560	1	70.9	0.705	12.2+	12.2+

a) On 5 × 5 mm. cylindrical pills extruded on a laboratory hydraulic press.

b) Volatile matter free basis.

Comparison of the activities and crushing strengths of the catalysts referred to in Table VIII with similar catalysts prepared from polyphosphoric acid and diatomaceous earth (Catalysts 8—11 of Table VI) indicates that when using a calcination time of one hour, the orthophosphoric acid yielded structurally strong catalysts which, however, had lower activities than those produced in analogous manner from polyphosphoric acid. The data of Table VIII, moreover, indicate that the use of a calcination temperature of 360° C. resulted in an activity which was too low for practical use. Some correlation seems to exist between the differences in the activities of any corresponding pair of catalysts in the two series (namely pairs of catalysts produced from the different acids with calcination at the same temperature) and the differences in their residual amounts of water (that is the water contained in the catalyst composition after final calcination).

WHAT WE CLAIM IS:—

1. A process for the conversion of organic compounds wherein an unsaturated organic compound is subjected to a condensation reaction in the presence of a solid phosphoric acid catalyst at a temperature up to 400° C. and a pressure of from atmospheric to 100 atmospheres, characterized by the use of a catalyst which has been manufactured by preparing from a phosphoric acid and a solid siliceous material a mixture having a phosphorus content determined as P_2O_5 in the proportion of from 2.37 to 7.65 parts by weight per part by weight of the siliceous material, heating said mixture until it has assumed a semi-solid moldable state, then transforming the mixture into shaped particles and completing the catalyst preparation by calcining said particles at a temperature in the range of from 460° to 760° C.

2. Process as claimed in claim 1, characterized by the use of catalyst particles prepared from a mixture of from 25 to 10% by

weight of the solid siliceous material and from 75 to 90% by weight of a phosphoric acid having a P_2O_5 content of from 79 to 85 weight percent with heating of said mixture at a temperature in the range of from 95° to 232° C. prior to its transformation into shaped particles.

3. Process as claimed in claim 1 or 2, characterized by the use of catalyst particles prepared from a mixture of the solid siliceous material and a polyphosphoric acid and having a phosphorus content determined as P_2O_5 in the proportion of from 3.0 to 7.5 parts by weight per part by weight of the siliceous material.

4. Process as claimed in any of the claims 1 to 3, characterized by the use of catalyst particles which upon their having been shaped from the heated moldable mixture have been finished by calcining at a temperature in the range of from 530° to 675° C.

5. Process as claimed in claim 4, characterized by the use of catalyst particles which have been finished by effecting the calcination in an inert gas for a time of from 0.5 to 2 hours.

6. Process as claimed in any of the claims 1 to 5, characterized thereby that the catalyst particles upon their calcination at a temperature in the range of from 460° to 760° C. are used, without any intervening change of composition, in the alkylation of an aromatic compound having a replaceable hydrogen atom on a ring nucleus by reaction with an unsaturated organic compound of the group consisting of the hydrocarbons having olefinic unsaturation and the alkyl chlorides, alkyl bromides and alkyl iodides.

7. Process as claimed in claim 6, characterized thereby that the calcined catalyst particles are used in the alkylation of a benzene hydrocarbon with a monoolefinic hydrocarbon.

8. Process as claimed in any of the claims 1 to 5, characterized thereby that the catalyst particles upon their calcination at a tempera-

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ture in the range of from 460° to 760° C. are used, without any intervening change of composition, in the polymerisation of olefinic hydrocarbons.

5 9. Process as claimed in claim 8, characterized thereby that the calcined catalyst particles are used in the polymerisation of normally gaseous monoolefinic hydrocarbons.

10 10. Process for producing a solid phosphoric acid catalyst suitable for use in the conversion of organic compounds and particularly in the process of any of the claims 1 to 9, characterized thereby that a composite containing a phosphoric acid in intimate admixture with a finely divided solid siliceous material and having a phosphorus content determined as P_2O_5 in the proportion of from 2.37 to 7.65 parts by weight per part by weight of the siliceous material is heated until the composite has assumed a semi-solid moldable state, said composite is then transformed into shaped particles and the catalyst preparation is completed by calcining said particles at a temperature in the range of from 460° to 760° C.

15 11. Process as claimed in claim 10, characterized thereby that a composite of from 25 to 10% by weight of a diatomaceous earth and from 75 to 90% by weight of a phosphoric acid having a phosphorus content determined as P_2O_5 of from 79 to 85 weight percent is heated at a temperature in the

range of from 95° to 232° C. prior to its transformation into shaped particles.

12. Process as claimed in claim 10 or 11, characterized thereby that a composite prepared by intimately mixing the solid siliceous material and a polyphosphoric acid and having a phosphorus content determined as P_2O_5 in the proportion of from 3.0 to 7.5 parts by weight per part by weight of the siliceous material is subjected to the heating and then to the transformation into shaped particles.

13. Process as claimed in any of the claims 10 to 12, characterized thereby that the heating of the composite prior to its transformation into shaped particles is effected at a temperature of 170—180° C.

14. Process as claimed in any of the claims 10 to 13, characterized thereby that the preparation of the catalyst is completed by calcining the shaped particles at a temperature in the range of from 530 to 675° C.

15. Process as claimed in claim 14, characterized thereby that the calcination of the shaped particles is effected in an inert gas for a time period of from 0.5 to 2 hours.

16. Solid phosphoric acid catalyst particles suitable for use in the conversion of organic compounds whenever produced by the process of any of the claims 10 to 15.

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ERRATA

SPECIFICATION NO. 863,539

Page 3, line 46, after "o-ethyl" insert "hyphen"

Page 4, line 79, for "37.8;" read "37.8%"

Page 4, line 123, after "in" insert "a"

Page 11, line 23, for "however" read "moreover"

Page 16, line 58, delete "in"

THE PATENT OFFICE,
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