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2,447,599

METHYLATION OF AROMATIC
HYDROCARBONS

Louis Schmerling, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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This invention relates to the treatment of aromatic hydrocarbons to produce methylated and poly-methylated aromatic hydrocarbons. More specifically the process is concerned with the conversion of benzene into toluene and poly-methylated benzenes in the presence of a granular catalyst.

It is recognized that benzene has been converted into toluene and other methylated benzenes by treatment with methanol in the presence of a relatively large proportion of aluminum chloride. This reaction has certain disadvantages, particularly the fact that a complex addition compound is formed which involves the aluminum chloride, produces sludge-like material, and prevents continuous operation of the process.

Although it is known that composites of phosphoric acid and carriers catalyze the alkylation of benzene by olefins or alcohols containing 2 or more carbon atoms per molecule, it has hitherto been considered impossible to bring about the condensation of benzene and methanol in the presence of such catalysts. The present invention is different from the prior art on this subject in that methylation of an aromatic hydrocarbon as benzene by methanol or by another suitable methylating agent is effected in the presence of a relatively stable granular catalyst, namely a calcined composite of an acid of phosphorus and a generally siliceous adsorbent such as diatomaceous earth.

In one specific embodiment the present invention comprises a process for producing methylated aromatic hydrocarbons which comprises contacting an aromatic hydrocarbon with methanol under methylating conditions in the presence of a calcined composite of an acid of phosphorus and a generally siliceous adsorbent.

While the process of this invention is particularly applicable to the production of toluene from benzene, it may also be utilized for converting other aromatic hydrocarbons into methylated and poly-methylated aromatic hydrocarbons. Thus aromatic hydrocarbons which may be methylated under suitable operating conditions include benzene, toluene, other alkylated benzenes, naphthalene, alkylated naphthalenes, and other polynuclear aromatic hydrocarbons obtainable by the distillation of coal, by the dehydrogenation of naphthenes, by the dehydrogenation and cyclization of aliphatic hydrocarbons as well as of alkylated aromatic hydrocarbons, and by other means.

Besides methanol, which may be formed by destructive distillation of wood, by controlled ox-

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dation of hydrocarbons, and by catalytic conversion of a mixture of carbon monoxide and hydrogen, other suitable methylating agents include methyl halides, methyl ether, methyl esters, and other methoxy-containing organic compounds capable of reacting with aromatic hydrocarbons to yield a substantial proportion of methylated aromatic hydrocarbons in the presence of a catalyst as hereinafter set forth.

When employing methyl compounds as methanol, dimethyl ether, and methyl halides as methylating agents, hypothetical methylene is probably formed, which may be represented by the formula, $=CH_2$, and possibly serves as the active methylating agent. For convenience methylene may herein be considered as the first member of the olefin series which undergoes reaction, for example, with benzene to produce toluene and poly-methyl benzenes while other aromatic hydrocarbons may similarly yield other methylated aromatic hydrocarbons. The different methylating agents, however, are not necessarily equivalent in their action nor used under the same conditions of operation to form desired products.

The essential ingredient of a granular catalyst which is employed to methylate an aromatic hydrocarbon, according to the process of the present invention, is phosphoric acid which may constitute 80% or more of the catalyst mixture and in most cases is over 30% by weight thereof. Of the various acids of phosphorus, ortho- or pyrophosphoric acids are generally preferred on account of their methylating abilities, their cheapness, and the readiness with which they may be procured, although the invention is not restricted to their use but may employ any of the other acids of phosphorus insofar as they are adaptable. It is not intended to infer, however, that the different acids of phosphorus which may be employed will produce identical effects upon any given methylation reaction as each acid will exert its own characteristic action. The methylating activity of a given catalyst is also dependent upon the ratio of acid to siliceous adsorbent contained therein.

Solid phosphoric acid catalysts, which are particularly utilizable in the present methylation process, may be made by mixing an acid of phosphorus, such as ortho- or pyrophosphoric acid, with a finely divided, relatively inert and a generally siliceous carrier such as, for example, kieselguhr, to form a rather wet paste (the acid ordinarily being in major proportion by weight); calcining at temperatures in the order of 400° to 500° C. to produce a solid cake; grinding and siz-

ing to produce particles of usable mesh; and rehydrating the catalyst granules at temperatures of the order of 260° C. to produce an acid composition corresponding to the optimum methylating activity which usually corresponds approximately to the pyro-acid in composition.

This catalyst preparation procedure may be varied by forming particles from the original paste by extrusion or pelleting methods and following with the calcining and rehydrating steps. In the reactions taking place during calcination it is evident that some acid is "fixed" on the carrier and that some metaphosphoric acid, which is substantially without methylating activity is formed. The rehydrating step evidently produces an acid composition corresponding closely to the pyro-acid having a formula $H_4P_2O_7$. Unless rehydration is practiced the temperature of approximately 300° C. should not be exceeded in the calcination step. And if higher temperatures produce catalyst particles of greater structural strength, depending upon the character of the carrier and the composition of acid fixed therewith, the composition of the acid may be brought to the desired point by contact with superheated steam at approximately 260° C. at atmospheric pressure. This brief description of a solid phosphoric acid catalyst and of its preparation is not exhaustive, as both have been generally described already in U. S. Patents Nos. 1,993,512 and 1,993,513 and others.

Solid phosphoric acid catalysts are hygroscopic to a variable extent and are best ground, sized, and preserved for use out of contact with moist air.

Because of the possibility of varying both the active phosphoric acid ingredients and its proportions with the relatively inert adsorbent materials which go to form the solid phosphoric acid catalyst masses, a number of alternative catalysts exist each of which will have its own particular catalyzing character which will not be exactly equivalent to that of the masses of different composition.

In the methylation of aromatic hydrocarbons by methanol or by another methylating agent, substantially any of the acids of phosphorus which have been found to promote polymerization of olefins or the alkylation of aromatic hydrocarbons with olefins may be employed as catalyst either alone or supported by a suitable carrier. Calcined composites of an acid of phosphorus and a generally siliceous adsorbent which are usually referred to by the term "solid phosphoric acids" are preferable in that they permit continuous methylation with a fixed bed catalyst. Other suitable methylating catalysts include certain acid-acting salts of phosphorus such as cadmium phosphate, copper pyrophosphate, calcium acid phosphate, and others.

In effecting reaction between benzene or another aromatic hydrocarbon and a methylating agent as methanol according to the process of the present invention, the exact method of procedure varies with the nature of the reacting constituents as well as with the composition and activity of the catalyst employed. A simple procedure which is used in methylating benzene consists in contacting a mixture of benzene and methanol with a solid phosphoric acid catalyst at a temperature of from about 350° to about 500° C. and preferably from about 350° to about 425° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres or more. Intimate contact of the reacting components with

the catalyst is effected by passing the reaction mixture over a fixed bed of the solid phosphoric acid or the reactants may be mixed with finely divided or powdered catalyst in a substantially fluid type of operation. The reaction mixture undergoing treatment preferably contains between about 1 and about 20 molecular proportions of benzene, or other aromatic hydrocarbon per molecular proportion of methanol or other methylating agent in order to diminish production of poly-methylated hydrocarbons and to favor the production of toluene or of other monomethyl compounds when an aromatic hydrocarbon other than benzene is similarly treated.

Thus benzene and methanol are commingled and passed through a reactor containing the granular catalyst such as a calcined composite of an acid of phosphorus, or at least a portion of the benzene is charged to a reactor while the methanol as such or preferably diluted by another portion of the benzene being treated, is introduced at various points between the inlet and the outlet of the reaction zone in such a way that the reaction mixture being subjected to contact with the granular solid phosphoric acid catalyst contains at all times a relatively low proportion of methanol and thus favors production of toluene rather than the formation of more-highly methylated aromatic compounds.

While the method of passing a methylating agent, as methanol, and benzene or other aromatic hydrocarbon, either together or concurrently, through a suitable reactor containing a fixed bed of granular catalyst is generally customary procedure, the interaction of methanol and an aromatic hydrocarbon may also be effected in batch type operation utilizing a closed vessel in which some of the reacting constituents are in liquid phase and in which the catalyst is present preferably in finely divided form and is maintained in dispersion or suspension by some means of agitation. Reacting constituents may also be contacted with the catalyst in mixed phase to effect a similar type of reaction. The choice of operating procedure is dependent upon such circumstances as the temperature and pressure found to be most effective for producing the desired reaction between a particular aromatic hydrocarbon and a methylating agent as methanol.

In general the products formed by interaction of methanol with a molal excess of an aromatic hydrocarbon are separated from the unreacted aromatic hydrocarbon by suitable means as by distillation and the unreacted portion of the aromatic hydrocarbon originally charged and methyl ether which may be formed from methanol are returned to the process and commingled with additional quantities of the mixture of methanol and aromatic hydrocarbon being charged to contact with the catalyst. Thus the methylated aromatic hydrocarbons may be freed from the excess of the originally charged aromatic hydrocarbon and then be separated into desired fractions or individual compounds by distillation at ordinary or reduced pressure or by other suitable means.

Methylation of aromatic hydrocarbons of the types hereinabove set forth are also carried out in the presence of hydrogen or of a hydrogen-containing gas. There is less formation of carbon and heavy hydrocarbonaceous material upon the catalyst when these conversion reactions are carried out under hydrogen pressure but carbon

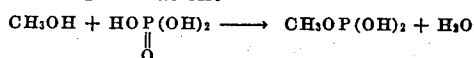
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formation does occur to a substantial extent in the absence of added hydrogen.

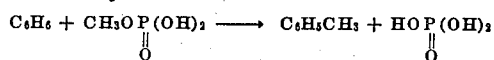
The process of this invention may also be applied to the alkylation of aromatic hydrocarbons with ethanol or with other primary alcohols which ordinarily are difficult to react with aromatic hydrocarbons.

Methyl ether generally appears as a by-product of the methylation of benzene with methanol in the presence of a solid phosphoric acid catalyst. Considerations relating to the mechanism of the methylation of benzene with methanol indicate that the reaction proceeds almost as readily with di-methyl ether as with methanol. The reaction mechanism appears to involve the formation of a rather stable intermediate methyl acid phosphate which may undergo reaction with benzene to produce toluene or with methanol to form dimethyl ether as illustrated in the following equations but this mechanistic concept should not be misconstrued as limiting the broad scope of the invention.

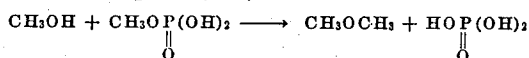
(1) Ester formation:



(2) Methylation:



(3) Ether formation:



Chemical decomposition of the methyl ester of phosphoric acid apparently occurs more readily by the reaction with methanol than with benzene since the former has a more reactive hydrogen atom than does benzene. Hence a higher temperature is required for methylation than for ether formation.

The use of a solid phosphoric acid catalyst permits the process of the present invention to be carried out continuously with a fixed catalyst bed and thus avoids mechanical problems and controls the time of contact of the reactants with the catalyst to form substantially the mono-methyl derivative of the aromatic hydrocarbon charged rather than more-highly methylated compounds. For the present purpose solid phosphoric acid catalyst has the advantage over composites of aluminum chloride and carriers in that the solid phosphoric acid catalyst forms substantially no addition compounds or complexes with aromatic hydrocarbons or methylated aromatic hydrocarbons.

The following examples are given to illustrate the character of results obtained by the use of the present process, although the data presented are not introduced with the intention of unduly limiting the generally broad scope of the invention.

Example I

80 parts by weight of benzene, 20 parts by weight of methanol and 10 parts by weight of 10-12 mesh solid phosphoric acid catalyst were placed in an autoclave to which hydrogen was added to 100 atmospheres initial pressure after which the resulting mixture was heated for 4 hours at 400° C. under a maximum pressure of 282 atmospheres. The resulting reaction products contained 9 parts by weight of toluene, 2.5 parts by weight of xylenes, and 8 parts by weight of higher methylated compounds including crystalline hexamethyl benzene. The respective yields

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of toluene, xylenes, and higher methylated benzenes obtained were 16, 8, and 36% of the theoretical based upon the amount of methanol available.

Example II

5.5 parts by weight of toluene, 1.0 part by weight of xylenes, and 2.5 parts by weight of more-highly methylated benzenes were obtained when 88 parts by weight of benzene, 23 parts by weight of di-methyl ether, and 10 parts by weight of 10-12 mesh solid phosphoric acid catalyst were heated in the presence of hydrogen at 400° C. for 4 hours under a maximum pressure of 298 atmospheres.

The nature of the present invention and its commercial utility can be seen from the specification and examples given, although neither section is intended to limit its generally broad scope.

I claim as my invention:

1. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon to contact with a methylating agent at a temperature of from about 350° to about 500° C. in the presence of a catalyst containing as its active ingredient an acid-acting compound of phosphorus.

2. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon to contact with a methylating agent at a temperature of from about 350° to about 500° C. in the presence of a catalyst comprising essentially a calcined composite of an acid of phosphorus and a generally siliceous adsorbent capable of undergoing compound formation with said acid of phosphorus.

3. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon to contact with a methylating agent at a temperature of from about 350° to about 500° C. in the presence of a catalyst comprising essentially a calcined composite of pyrophosphoric acid and diatomaceous earth.

4. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon to contact with a methylating agent at a temperature of from about 350° to about 500° C. in the presence of a catalyst containing as its active ingredient an acid-acting salt of phosphorus.

5. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon to contact with a methylating agent at a temperature of from about 350° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst containing as its active ingredient an acid-acting compound of phosphorus.

6. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon to contact with methanol at a temperature of from about 350° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst containing as its active ingredient an acid-acting compound of phosphorus.

7. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon to contact with methyl ether at a temperature of from about 350° to about 500° C. under a pressure of from sub-

stantially atmospheric to approximately 300 atmospheres in the presence of a catalyst containing as its active ingredient an acid-acting compound of phosphorus.

8. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon to contact with a methyl halide at a temperature of from about 350° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst containing as its active ingredient an acid-acting compound of phosphorus.

9. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon, hydrogen, and a methylating agent to contact at a temperature of from about 350° to about 500° C. in the presence of a catalyst containing as its active ingredient an acid-acting compound of phosphorus.

10. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon, hydrogen, and a methylating agent to contact at a temperature of from about 350° to about 500° C. in the presence of a catalyst comprising essentially a calcined composite of an acid of phosphorus and a generally siliceous adsorbent capable of undergoing compound formation with said acid of phosphorus.

11. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon, hydrogen, and a methylating agent to contact at a temperature of from about 350° to about 500° C. in the presence of a catalyst containing as its active ingredient an acid-acting salt of phosphorus.

12. A process for producing a substantial yield of toluene from benzene which comprises subjecting said benzene, hydrogen, and a methylating agent to contact at a temperature of from about 350° to about 500° C. in the presence of a catalyst containing as its active ingredient an acid-acting compound of phosphorus.

13. A process for producing a substantial yield of toluene from benzene which comprises subjecting said benzene, hydrogen, and a methylating agent to contact at a temperature of from about 350° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst containing as its active ingredient an acid-acting compound of phosphorus.

14. A process for producing a substantial yield of toluene from benzene which comprises subjecting said benzene, hydrogen, and methanol to contact at a temperature of from about 350° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst containing as its active ingredient an acid-acting compound of phosphorus.

15. A process for producing a substantial yield of toluene from benzene which comprises subjecting said benzene, hydrogen, and methyl ether to contact at a temperature of from about 350° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst containing as its active ingredient an acid-acting compound of phosphorus.

16. A process for producing a substantial yield of toluene from benzene which comprises subjecting said benzene, hydrogen, and a methyl halide to contact at a temperature of from about 350° to about 500° C. under a pressure of from

substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst containing as its active ingredient an acid-acting compound of phosphorus.

17. A process for producing a substantial yield of toluene from benzene which comprises subjecting said benzene, hydrogen, and methanol to contact at a temperature of from about 350° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst comprising essentially a calcined composite of an acid of phosphorus and a generally siliceous adsorbent.

18. A process for producing a substantial yield of toluene from benzene which comprises subjecting said benzene, hydrogen, and methanol to contact at a temperature of from about 350° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst comprising essentially a calcined composite of pyrophosphoric acid and diatomaceous earth.

19. A process for producing a substantial yield of toluene from benzene which comprises subjecting said benzene, hydrogen, and methanol to contact at a temperature of from about 350° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst containing as its active ingredient an acid-acting salt of phosphorus.

20. A continuous process for producing toluene from benzene which comprises subjecting from 1 to about 20 molecular proportions of said benzene and 1 molecular proportion of methanol to contact at a temperature of from about 350° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of hydrogen and of a catalyst containing as its active ingredient an acid-acting compound of phosphorus to form a product containing a substantial proportion of toluene; separating said product into unconverted benzene, toluene, and poly-methylated benzenes; and recycling said unconverted benzene and poly-methylated benzenes to commingle with the methanol and benzene being charged to contact with the catalyst.

21. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon to contact with methanol at a temperature of from about 350° to about 500° C. in the presence of a catalyst comprising essentially a calcined composite of an oxy-acid of phosphorus and a generally siliceous adsorbent capable of undergoing compound formation with said oxy-acid of phosphorus.

22. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon to contact with dimethyl ether at a temperature of from about 350° to about 500° C. in the presence of a catalyst comprising essentially a calcined composite of an oxy-acid of phosphorus and a generally siliceous adsorbent capable of undergoing compound formation with said oxy-acid of phosphorus.

23. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon to contact with a methylating agent at a temperature of from about 350° to about 500° C. in the presence of a catalyst comprising essentially a calcined composite of pyrophosphoric acid and a generally siliceous adsorbent capable of undergoing compound formation with said pyrophosphoric acid.

24. A process for producing methylated aromatic hydrocarbons which comprises subjecting an aromatic hydrocarbon to contact with a methylating agent at a temperature of from about 350° C. to about 500° C. in the presence of a calcined catalyst comprising essentially an oxy-acid of phosphorus and a generally silicious absorbent capable of undergoing compound formation with said oxy-acid of phosphorus.

LOUIS SCHMERLING.

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