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3,109,038 CATALYTIC ALKYLATION OF AROMATICS WITH PARAFFINS

John W. Myers, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware
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This invention relates to the production of alkyl aromatic compounds. In one aspect, the invention relates to the formation of alkyl derivatives from aromatic hydrocarbons. In another aspect, the invention relates to the formation from aromatic hydrocarbons of derivatives containing one or more alkyl groups more than are contained in the original aromatic hydrocarbon. In another aspect, this invention relates to a method of producing alkylated aromatic compounds from aromatic compounds and paraffins. In another aspect, the invention relates to the utilization of an improved catalytic process for reacting paraffins and aromatics. In a still further aspect, the invention relates to the alkylation of an aromatic hydrocarbon with an aliphatic hydrocarbon in the presence of a catalyst of at least one of platinum, rhodium, palladium, iridium, nickel, and cobalt on an acid support.

It has been known for some time how to prepare alkylated aromatic hydrocarbons wherein an alkyl group is attached to the aromatic molecule through utilization of a catalytic means or condensing agent. These are illustrated by the well known synthesis of Friedel and Crafts, in which an alkyl halide is caused to alkylate an aromatic molecule by the aid of aluminum chloride, by the reaction of an olefin and an aromatic hydrocarbon in the presence of some condensation agents such as phosphoric acid or aluminum chloride and by other similar means.

Aromatic hydrocarbons such as benzene, naphthalene, toluene, xylene, and others are produced in relative abundance in the destructive distillation of coal, in the enrichment of manufactured gas by the cracking of petroleum, and in gas reforming pyrolysis. However, only relatively small amounts of alkylated derivatives such as ethylbenzene, propylbenzene, alkyl naphthalenes, are formed in these operations. The alkylated derivatives of the aromatics differ from the purely cyclic aromatics in properties and are valuable in a variety of special uses.

I have found that alkylation of aromatic compounds with paraffins is greatly improved when carried out in the presence of a catalyst of at least one of platinum, rhodium, palladium, iridium, nickel, and cobalt on an acid support.

Therefore, it is an object of this invention to provide an improved process for the alkylation of aromatics with paraffins. A further object of this invention is to provide an improved method for effecting the formation of alkyl derivatives from aromatic hydrocarbons in the presence of a catalyst of platinum, rhodium, palladium, iridium, nickel, and cobalt on an acid support. Another object of this invention is the formation of alkyl derivatives from aromatic hydrocarbons with a higher yield of alkyl aromatics.

Other aspects, objects, and the several advantages of the invention are apparent from a study of the disclosure and the appended claims.

According to this invention, there is provided an improved catalytic process for reacting paraffins and aromatics. In this process, paraffins such as ethane, propane, butane, and the like, and aromatics such as benzene, toluene, xylene, and the like, are contacted with an acidic

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catalyst containing a promoter having dehydrogenation activity, at elevated temperatures and preferably at elevated pressures. The process is carried out by passing a mixed paraffin-aromatic feed over the catalyst at temperatures usually in the range of about 400° F. to 900° F., preferably in the range of about 550° F. to 850° F., at pressures usually in the range from about 0 to 5,000 p.s.i.g. or even higher, preferably in the range from about 250 to 3,000 p.s.i.g., and liquid hourly space velocities usually in the range from about 0.1 to 10, preferably in the range from about 0.1 to 5.

The catalyst is at least one of platinum, rhodium, palladium, iridium, nickel, and cobalt supported on an acidic support such as halogenated alumina, silica-alumina, boria-alumina, or zinc chloride-alumina. Suitable catalysts are platinum-halogen-alumina, platinum-silica-alumina, platinum-boria-alumina, and platinum-zinc chloride-alumina, and the corresponding composites of rhodium, iridium, palladium, cobalt, and nickel. The catalyst will usually contain in the range of about 0.01 to 10 weight percent, preferably in the range of about 0.1 to 2 weight percent of the metal, the remainder being the support. These catalysts can be made by any known process, such as impregnation. The supports should have surface areas of at least about 25 square meters per gram, preferably at least about 50 square meters per gram. The impregnation of the support can be effected by using an aqueous salt solution of the metallic component, and the impregnated support dried and then reduced at elevated temperatures to decompose the salt and form the metallic component.

A preferred catalyst composition is platinum or palladium on halogenated alumina. The metallic component is ordinarily in the range of about 0.01 to 10 weight percent, preferably in the range of about 0.1 to 2 weight percent. The halogen is ordinarily in the range of about 0.5 to 10 weight percent, preferably in the range of about 1 to 7 weight percent. The remainder is substantially alumina. Chlorine and fluorine are suitable for use as the halogen component. This type of catalyst is well known in the art as are methods of production.

The feed to the process consists essentially of at least one aromatic to be alkylated and at least one paraffin alkylating agent. The aromatic can be benzene, naphthalene, an incompletely alkylated benzene or naphthalene, and the like. Mixtures of these aromatics can also be used. The alkylating agent can be either straight- or branched-chain and can have 2 to about 10 carbon atoms. Mixtures of these paraffins can also be used. The feed should have a mol ratio of paraffin to aromatic of at least about 0.2:1 to 10:1, preferably at least about 0.5:1 to 5:1. As the paraffin is relatively non-reactive in condensing with itself, high mol ratios of alkylatable hydrocarbon to alkylating agent are of less importance in this process than in the more conventional processes using more reactive alkylating agents.

When using a platinum family metal on halogenated alumina as the catalyst, it is desirable to include a small amount of hydrogen halide, alkyl halide or alkylene halide in the feed as an activator. Amounts in the range of about 0.05 to 0.5 weight percent, based on the hydrogen halide available on decomposition are satisfactory. Chlorides are preferred as activators.

Example

A mixture of 35.7 weight percent propane, 64.0 weight

percent benzene, and 0.3 weight percent ethylene dichloride was contacted with a catalyst of 0.37 weight percent platinum, 3.4 percent fluorine, less than 0.05 percent chlorine and the remainder alumina. The process was operated continuously at 900 p.s.i.g., 694° F., and 0.6 LHSV.

The effluent contained 6.6 weight percent of components boiling above benzene. The analysis of the higher boiling material was

Component:	Weight Percent
Toluene -----	3
n-Propylbenzene -----	22
i-Propylbenzene -----	45
Heavier -----	30

It is evident that the predominant products were propylbenzenes, and the amount was close to the estimated thermodynamic equilibrium.

Reasonable variation and modification are possible within the scope of the foregoing disclosure and the appended claims to the invention, the essence of which is an improved process for the catalytic alkylation of aromatics with paraffins in the presence of a catalyst of at least one of platinum, rhodium, iridium, palladium, nickel, and cobalt on an acid support.

I claim:

1. A method for adding an alkyl group to an aromatic hydrocarbon which comprises subjecting a feed consisting essentially of at least one aromatic to be alkylated and at least one paraffin selected from the group consisting of ethane, propane, and butane to a reacting temperature in the range of about 400° F. to about 900° F., at a pressure in the range of about 0 to about 5,000 p.s.i.g., at a liquid hourly space velocity in the range of about 0.1 to about 10, and in the presence of a catalyst of at least one element selected from the group consisting of palladium, platinum, rhodium, iridium, nickel and cobalt on an acid support, to form alkyl substituted derivatives, and separating from the process the alkyl substituted derivatives so produced.

2. A method in accordance with claim 1 wherein said catalyst is a platinum-halogen-alumina catalyst.

3. A method in accordance with claim 1 wherein said reaction temperature is in the range of about 550° F. to about 850° F., said pressure is in the range of about 250 to about 3000 p.s.i.g. and said liquid hourly space velocity is in the range of about 0.1 to about 5.

4. A method in accordance with claim 1 further comprising adding to said feed a small amount of an element selected from the group consisting of hydrogen halide, alkyl halide, and an alkylene halide as an activator.

5. A method in accordance with claim 1 wherein said aromatic is benzene and said catalyst is a platinum-fluorine-alumina catalyst.

6. A method in accordance with claim 1 wherein said catalyst comprises said element in the range of about 0.01 to about 10 weight percent, a halogen in the range of about 0.5 to about 10 weight percent, and alumina.

7. A method in accordance with claim 6 wherein said element is in the range of about 0.01 to about 2 weight percent and said halogen is in the range of about 1 to about 7 weight percent.

8. A method in accordance with claim 1 wherein the mol ratio of paraffin to aromatic is in the range of about 0.2:1 to about 10:1.

9. A method in accordance with claim 1 wherein the mol ratio of paraffin to aromatic is in the range of about 0.5:1 to about 5:1, said temperature is in the range of about 550° F. to about 850° F., said pressure is in the range of about 250 to about 3000 p.s.i.g., and said liquid hourly space velocity is in the range of about 0.1 to about 5.

References Cited in the file of this patent

UNITED STATES PATENTS

2,642,384	Cox	June 16, 1953
2,752,289	Haensel	June 26, 1956
2,777,805	Lefrancois et al.	Jan. 15, 1957

OTHER REFERENCES

Sachanen, "Chemical Constituents of Petroleum," 1945, published by Reinhold Publishing Co. (New York), page 214 relied upon.