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TREATMENT OF HYDROCARBONS

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This invention relates to the treatment of poly-alkyl aromatic hydrocarbons to produce substantial yields of mono-alkyl aromatic hydrocarbons. More specifically the process is concerned with the production of mono-alkyl aromatic hydrocarbons from poly-alkyl aromatic hydrocarbons in the presence of a granular catalytic material.

In the methylation of benzene to obtain toluene and in the ethylation of benzene to form ethyl benzene, which is an intermediate in the manufacture of styrene, substantial amounts of polymethylated and poly-ethylated benzenes are obtained. For economic reasons it is desirable that these poly-alkylated aromatic hydrocarbons be converted into the mono-alkyl aromatic hydrocarbons. Xylenes and higher methylated benzenes are also obtained from the coking of coal in quantities in excess of the usual demands for them. Also, poly-alkyl aromatic hydrocarbons in other synthetically produced hydrocarbon mixtures may be of less value than the corresponding lower boiling and less-highly alkylated derivatives.

In one specific embodiment the present invention comprises a process for producing substantial yields of mono-alkyl aromatic hydrocarbons from poly-alkyl aromatic hydrocarbons which comprises subjecting said poly-alkyl aromatic hydrocarbons, a non-alkylated aromatic hydrocarbon, hydrogen, and hydrogen chloride to contact with a catalyst comprising essentially a composite of zinc chloride and a carrier.

By the process of this invention an aromatic hydrocarbon having more than one side chain such as those prepared by catalytic alkylation of an aromatic hydrocarbon, separated from the constituents of coal tar, or present in other synthetically formed or naturally occurring material may be converted into mono-alkylated aromatic hydrocarbons. Thus xylenes, mesitylene, and higher methylated benzenes may be converted into toluene; while di-ethyl benzene, tri-ethyl benzene, and other poly-ethyl benzenes may be changed into mono-ethyl benzene utilizable in the production of styrene, which in turn may be converted into resins or rubber-like substances. Other poly-alkyl aromatic hydrocarbons may similarly be converted into mono-alkyl aromatic hydrocarbons.

Shifting of alkyl groups from one molecular nucleus to another has previously been observed in the presence of aluminum chloride or ferric chloride catalysts particularly in the treatment or xylenes as illustrated by the following equations:

(1) $2C_6H_4(CH_3)_2 \longrightarrow C_6H_5CH_3 + C_6H_3(CH_3)_3$
Xylene → Toluene + Trimethylbenzene

(2) $C_6H_4(CH_3)_2 + C_6H_6 \longrightarrow 2C_6H_5CH_3$
Xylene + Benzene → Toluene

Thus a poly-alkyl aromatic hydrocarbon may be used alone as indicated by a di-alkyl hydrocarbon, xylene, in Equation 1 or it may be mixed with an additional quantity of another aromatic hydrocarbon, usually a non-alkylated aromatic hydrocarbon as shown in Equation 2. For example, in the treatment of xylenes the addition of benzene increased the yield of toluene probably because the migrating methyl group can thus react more readily with benzene than with the xylene. Mesitylene and more highly alkylated aromatic hydrocarbons may also be converted into less highly alklated aromatic hydrocarbons such as toluene and xylenes.

As a catalyst for the process of the present invention zinc chloride has the advantage over aluminum chloride used for the same purpose in that the zinc chloride forms with aromatic hydrocarbons substantially no sludge-like complexes, generally termed lower layer complexes. The substantial absence of sludge formation thus permits continuous operation as well as a higher yield of desired mono-alkyl conversion product. Furthermore all of the desired product is present as a hydrocarbon liquid free from lower layer which may be washed with caustic to remove hydrogen chloride and then distilled directly, whereas with aluminum chloride catalyst much of the hydrocarbon is in the sludge or lower layer which must be hydrolyzed before all of the mono-alkylated aromatic hydrocarbon product is available for washing and distillation. Such hydrolyzing treatment also destroys the aluminum chloride, but used zinc chloride catalyst may be regenerated by extracting with water, filtering if necessary, and either evaporating the aqueous solution or impregnating a carrier therewith.

Another advantage of zinc chloride is the ease with which it may be handled. Thus while alu-

minum chloride and ferric chloride must be kept in anhydrous condition, zinc chloride is not harmed substantially by water. Accordingly it may be dissolved therein and later deposited upon a suitable carrier.

While zinc chloride may be used as catalyst in the form of the solid salt, in molten condition, or in aqueous solution, it is preferably supported by or composited with a carrier such as alumina, a silica-alumina composite, raw or acid-treated clays, diatomaceous earth, silica-gel, charcoal, etc. The preferred carrier for zinc chloride, however, is alumina, or a substantially inert material containing alumina or composited with a substantial proportion of alumina. The different carriers or supports which may be employed are not necessarily equivalent in their action.

The proportion of zinc chloride and carrier may be varied as desired to make catalyst composites of different activities. Thus it has been found possible and practical to make stable granular catalysts resistant to disintegrating influences by using from about 5 to about 50% by weight of zinc chloride and from about 95 to about 50% by weight of activated alumina or an alumina-containing carrier. These materials in finely powdered form, after thorough mechanical mixing, may be subjected to drying, pelleting, and heating operations to produce formed particles of catalyst suitable for use as reactor filling material. A suitable carrier may also be impregnated with an aqueous solution of zinc chloride, dried, and calcined at a temperature between about 300° and about 350° C. to form a zinc chloride-carrier composite suitable for use in promoting the dealkylation of poly-alkylated aromatic hydrocarbons to mono-alkylated aromatic hydrocarbons.

De-alkylations of poly-alkylated aromatic hydrocarbons of the types hereinabove set forth are effected preferably in the presence of hydrogen and/or of hydrogen chloride. There is little or no carbon formation upon the catalyst when the de-alkylation reaction is carried out under hydrogen pressure but carbon formation does occur to a substantial extent in the absence of hydrogen. By using high hydrogen pressure in the presence of a catalyst containing zinc chloride, mono-alkylated aromatic hydrocarbon will be formed not only by de-alkylation but also by destructive hydrogenation of the poly-alkylated aromatic hydrocarbon. Further, the introduction of hydrogen chloride to the reaction mixture promotes the de-alkylation reaction to give a substantially higher yield of mono-alkylated aromatic hydrocarbon per pass over the catalyst than is obtained in the absence of hydrogen chloride.

In de-alkylating a poly-alkylated aromatic hydrocarbon according to the process of the present invention, the exact method of procedure depends upon the nature of the hydrocarbons being treated, the activity of the catalysts, and other factors. A simple procedure utilizable in the case of a poly-alkylated aromatic hydrocarbon which is normally liquid or if solid is readily soluble in the added aromatic hydrocarbon or in a substantially inert liquid, consists in contacting the poly-alkylated aromatic hydrocarbon or its solution with a zinc chloride-carrier composite preferably in the presence of both hydrogen and hydrogen chloride. The reaction temperature used depends upon the nature of the alkyl groups present in the poly-alkylated aromatic hydrocarbon. For poly-methyl and poly-ethyl aromatic compounds a temperature of from about 300° to about 500° C. is suitable; while for poly-isopropyl derivatives and other poly-alkylated aromatic compounds containing more than 3 carbon atoms in the alkyl side chains, a lower temperature may be used from about 100° to about 400° C. Although zinc chloride melts at about 365° C. it may nevertheless be employed on a carrier such as alumina at a temperature as high as about 425° C. without substantial loss of zinc chloride therefrom. At higher temperatures of operation, zinc chloride may be employed in molten condition. The operating pressure is generally above atmospheric and up to about 300 atmospheres maximum under the conditions of operation.

Intimate contact of the poly-alkylated aromatic hydrocarbon or mixture of non-alkylated and poly-alkylated aromatic hydrocarbons with the catalyst is effected by passing the reaction mixture through a fixed bed of the granular catalyst containing zinc chloride or the reacting component or components may be mixed with finely divided catalyst in a substantially fluid type of operation. While the method of passing the aromatic and poly-alkylated aromatic hydrocarbons through a suitable reactor containing the granular catalyst is generally customary procedure, the de-alkylation reaction may also be effected in a closed vessel in which some of the reacting constituents are in liquid or fluid phase and in which the catalyst is preferably in finely divided form and is maintained in dispersion or suspension by some method of agitation. Reacting constituents may also be contacted 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 conversion to a mono-alkylated aromatic hydrocarbon.

In general the products formed by subjecting a poly-alkylated aromatic hydrocarbon to de-alkylation are separated into the desired mono-alkylated aromatic hydrocarbon, incompletely converted poly-alkylated aromatic hydrocarbons, and possibly an excess of non-alkylated aromatic hydrocarbon, and then the incompletely converted poly-alkylated aromatic hydrocarbons and excess of non-alkylated aromatic hydrocarbon are returned to the process and mixed with additional quantities of the fresh reactants being charged to contact with the zinc chloride-carrier catalyst contained in the de-alkylating reaction zone. Also di-alkyl aromatic hydrocarbons and other poly-alkyl derivatives may be separated from the reaction mixture as desired products of the process in addition to the mono-alkyl aromatic compound hereinabove set forth.

The following examples are given to illustrate the character of results obtained by the use of the present process, although the data presented are only from selected cases and are not introduced with the intention of unduly restricting the generally broad scope of the invention:

EXAMPLE I

50 to 52 parts by weight of tri-ethyl benzene and 15 parts by weight of a composite containing 25% by weight of zinc chloride and 75% by weight of alumina were placed in an autoclave together with the amounts of benzene and hydrogen chloride indicated in Table I, after which hydrogen or nitrogen was added to an initial pressure of 100 atmospheres. The charged auto-

clave was then heated for 4 hours at 400° C. with the results shown in Table I which indicates the yields of benzene, ethyl benzene, and di-ethyl benzene based upon the tri-ethyl benzene charged.

TABLE I

De-ethylation of tri-ethyl benzene

	Run No.							
	1	2	3	4	5	6	7	8
Reactants, parts by weight:								
Tri-ethyl benzene	50	50	50	50	52	52	51	50
Benzene	75	75	0	0	75	75	0	0
Hydrogen chloride	2	0	0	2	2	0	0	2
Initial pressure of—								
Hydrogen...atmospheres	100	100	100	100				
Nitrogen...do					100	100	100	100
Maximum pressure atmospheres	235	248	208	202	290	282	250	245
Yield, per cent of theoretical based on tri-ethyl benzene charged:								
Benzene			17	8				
Ethyl benzene	126	107	34	18	95	34	6	12
Di-ethyl benzene	39	51	36	29	41	46	15	27
Tri-ethyl benzene	4	4	6	18	14	50	50	30
Higher ethylated benzenes			2	4	13	11	9	13

The results given in Table I show that it is beneficial to have benzene, hydrogen, and hydrogen chloride all present when de-alkylating tri-ethyl benzene in the presence of a zinc chloride-alumina catalyst.

EXAMPLE II

The conversion of xylene into toluene in the presence of the catalyst used in Example I is illustrated by the results shown in Table II on a number of runs carried out at 300° and 400° C. under an initial hydrogen pressure of 100 atmospheres during periods of 4 hours each. When both benzene and hydrogen chloride were commingled with the xylene and the catalytic treatment was carried out under hydrogen pressure (run #3), 58% of the xylene was converted into toluene. In the absence of added benzene (run #2), 16% of toluene was formed at 400° C.

TABLE II

De-methylation of xylene to toluene

	Run No.		
	1	2	3
Reactants, parts by weight:			
Xylene	78	50	50
Benzene	0	0	50
Hydrogen chloride	0	2	2
Catalyst	15	20	20
Temperature ° C.	300	400	400
Maximum pressure atmospheres	217	218	245
Toluene formed:			
Parts by weight	0.5	7	25
Per cent of theoretical based on xylene charged	1	16	58

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.

We claim as our invention:

1. A process for producting a substantial yield of a mono-alkyl aromatic hydrocarbon from a poly-alkyl aromatic hydrocarbon which comprises subjecting said polyalkyl aromatic hydrocarbon, a non-alkylated aromatic hydrocarbon, hydrogen and hydrogen chloride at a de-alkylating temperature of from about 100° C. to about 500° C. to contact with a zinc chloride-containing catalyst.

2. A process for producing a substantial yield of a mono-alkyl aromatic hydrocarbon from a poly-alkyl aromatic hydrocarbon which comprises subjecting said poly-alkyl aromatic hydrocarbon, a non-alkylated aromatic hydrocarbon, hydrogen, and hydrogen chloride at a de-alkylating temperature of from about 100° C. to about 500° C. to contact with a catalyst comprising essentially a composite of zinc chloride and an aluminum oxide-containing carrier.

3. A process for producing a substantial yield of toluene from a poly-methylated benzene which comprises subjecting said poly-methylated benzene, benzene, hydrogen, and hydrogen chloride to contact at a temperature from about 300° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst comprising essentially a composite of zinc chloride and an aluminum oxide-containing carrier.

4. A process for producing a substantial yield of ethyl benzene from a poly-ethylated benzene which comprises subjecting said poly-ethylated benzene, benzene, hydrogen, and hydrogen chloride to contact at a temperature of from about 300° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst comprising essentially a composite of zinc chloride and an aluminum oxide-containing carrier.

5. A process for producing a substantial yield of a mono-alkyl aromatic hydrocarbon in which the alkyl group contains more than two carbon atoms from a poly-alkyl aromatic hydrocarbon in which at least one of the alkyl groups contains more than two carbon atoms which comprises subjecting said poly-alkyl aromatic hydrocarbon, hydrogen, and hydrogen chloride to contact at a temperature from about 100° to about 400° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst comprising essentially a composite of zinc chloride and an aluminum oxide-containing carrier.

6. A process for producing a substantial yield of toluene from a poly-methylated benzene which comprises subjecting said poly-methylated benzene, benzene, hydrogen, and hydrogen chloride to contact at a temperature from about 300° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst comprising essentially a composite of zinc chloride and alumina.

7. A process for producing a substantial yield of ethyl benzene from a poly-ethylated benzene which comprises subjecting said poly-ethylated benzene, benzene, hydrogen, and hydrogen chloride to contact at a temperature of from about 300° to about 500° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst comprising essentially a composite of zinc chloride and alumina.

8. A process for producing a substantial yield of a mono-alkyl aromatic hydrocarbon in which the alkyl group contains more than two carbon atoms from a poly-alkyl aromatic hydrocarbon in which at least one of the alkyl groups contains more than two carbon atoms which comprises subjecting said poly-alkyl aromatic hydrocarbon, hydrogen, and hydrogen chloride to contact at a temperature from about 100° to about

400° C. under a pressure of from substantially atmospheric to approximately 300 atmospheres in the presence of a catalyst comprising essentially a composite of zinc chloride and alumina.

9. A process for producing a substantial yield of a mono-alkyl aromatic hydrocarbon from a poly-alkyl aromatic hydrocarbon which comprises subjecting said poly-alkyl aromatic hydrocarbon, a non-alkylated aromatic hydrocarbon, hydrogen and hydrogen chloride at a dealkylating temperature of from about 100° C. to about 500° C. to contact with a catalyst comprising essentially from about 5 to about 50% by weight of zinc chloride and from about 95 to about 50% by weight of alumina.

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