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ALKYLATION OF AROMATICS AND CATALYST THEREFOR

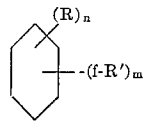
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17 Claims. (Cl. 260—671)

This invention relates to the alkylation of aromatics with alkylating agents and is particularly concerned with a catalytic alkylation process employing in the presence of free hydrogen, a hydrocarbon conversion catalyst consisting essentially of chromia, boria and alumina. Alkylated aromatics are of value in many fields and some are particularly desirable as constituents of high octane aviation fuels and as sources of synthetic detergents.

Although catalytic processes for the alkylation of aromatics have been suggested, the present process provides good utilization of alkylating agents, low carbon yields thus less carbon laydown on the catalyst, good catalyst aging characteristics, low disproportionation or isomerization, and a readily regenerable catalyst.

The aromatics, e.g. alkylatable aromatic hydrocarbons, suitable for alkylation in the present process includes mono- and polycyclic aromatic hydrocarbon compounds such as benzene and its lower alkyl homologues e.g. toluene and the xylenes, naphthalene, and indane, which may be substituted or unsubstituted. The substituted aromatic compounds must, however, contain at least one hydrogen attached to the aromatic nucleus and are preferably methyl-substituted. These compounds may correspond to the general formula



where R is an alkyl, including cyclo alkyl, radical containing generally from about 1 to 20, preferably from about 1 to 8, carbon atoms; n is 0 to 3 or 5; R' is an aromatic hydrocarbon ring, preferably C_4H_4; -f- indicates a fused ring relationship (two carbon atoms common to two aromatic nuclei e.g. as in naphthalene); and m is generally 0 to 1 or more. R may also be a divalent hydrocarbon group attached to the aromatic ring at two carbon atoms of the ring, e.g. alkylene, as in Decalin and Tetralin. The preferred aromatics, however, include benzene and alkyl benzenes corresponding to the above formula when m is 0. The aromatic rings and R groups may be substituted as with phenyl, hydroxy, alkoxy, halide and other radicals which do not prevent the desired reaction. Suitable aromatic hydrocarbons include benzene, toluene, ortho-xylene, meta-xylene, para-xylene, ethyl-benzene, ortho-ethyltoluene, meta-ethyltoluene, para-ethyltoluene, 1,2,3-trimethylbenzene, 1,2,4 - trimethylbenzene, 1,3,5 - trimethylbenzene or mesitylene, normal propylbenzene, isopropylbenzene, etc. Higher molecular weight alkylaromatic hydrocarbons are also suitable as starting materials and include aromatic hydrocarbons such as are produced by the alkylation of aromatic hydrocarbons with olefin polymers. Such products are frequently referred to in the art as alkylate, and include hexylbenzene, nonylbenzene, dodecylbenzene, pentadecylbenzene, hexyltoluene, nonyltoluene, dodecyltoluene, pentadecyltoluene, etc. Very often alkylate is obtained as a high boiling fraction in which the alkyl group attached to the aromatic nucleus varies in size from about C_9 to about C_{18}. Other suitable alkylatable aromatic hydrocarbons include those with two or more aryl groups such as diphenyl, diphenylmethane, triphenyl, triphenylmethane, fluorene, stilbene, etc. Examples of other alkylatable aromatic hydrocarbons containing condensed benzene rings include naphthalene, alpha-methylnaphthalene, beta-methylnaphthalene, anthracene, phenanthrene, naphthacene, rubrene, etc.

The alkylating agents suitable for use in the present process include organic compounds containing an alkyl, including cycloalkyl, radical which is transferable to the aromatic nucleus. These compounds are aliphatic and include alkyl halides, alkanols and ethers generally containing from about 1 to 20 carbon atoms, preferably from about 1 to 6 carbon atoms, and also contain a radical e.g. an hydroxyl or ether radical, which will displace a nuclear hydrogen of the aromatic through condensation. The alkylation agent is preferably saturated and frequently contains oxygen which produces water during the alkylation reaction.

A number of suitable alkylating agents correspond to the general formula

R—O—R'

where R is a monovalent hydrocarbon radical such as alkyl, including cycloalkyl, usually lower alkyl and preferably containing 1 to 4 carbon atoms and R' is hydrogen or R, such as a lower alkyl radical and preferably containing 1 to 4 carbon atoms. The alkylating agents usually do not have more than about 18 carbon atoms, preferably up to about 12 carbon atoms. Specific alkylating agents include alkanols such as ethanol, propanol, isopropanol, pentanol, octanol and preferably methanol; and alkyl ethers such as dimethyl ether, diethyl ether and like members whether substituted with non-interfering groups or not.

When the alkanols are employed, they may go through an intermediate ether stage. Examples of alkyl halides which may be used are of the formula RX, where R is as noted above and X is halogen and include ethyl chloride, normal propyl chloride, isopropyl chloride, normal butyl chloride, isobutyl chloride, secondary butyl chloride, tertiary butyl chloride, amyl chlorides, hexyl chlorides, etc., ethyl bromide, normal propyl bromide, isopropyl bromide, normal butyl bromide, isobutyl bromide, secondary butyl bromide, tertiary butyl bromide, amyl bromides, hexyl bromides, etc., ethyl iodide, normal propyl iodide, etc.

Methanol or dimethyl ether can be employed as the methylating agent. However, methanol holds an edge since dimethyl ether gives slightly lower utilization and higher carbon on the catalyst.

The alkylation is accomplished by employing a particularly effective catalyst which includes catalytically effective amounts of chromia and boria on an alumina base. The catalyst generally contains from about 1 to 20 weight percent and preferably from about 5 to 15 weight percent of chromia.

The boria component is surface dispersible on the support and is employed in amounts sufficient to enhance the utilization of the alkylating agent. The boria is prefer-

ably added in amounts in direct proportion to the area of the support and these amounts will usually be from about 1 to 20 weight percent and preferably from about 5 to 15 weight percent. These amounts are particularly effective on alumina having surface areas of about 350 to 600 square meters per gram (BET) before use. The boria component is preferably added to the alumina as a hot aqueous solution of boric acid and advantageously the alumina is precalcined and again calcined after addition of the boria.

The chromia and boria constituents of the catalyst are on an absorptive alumina base of the activated or calcined type. The base is usually the major component of the catalyst, generally constituting at least about 60 weight percent on the basis of the catalyst, preferably at least about 75 to 90. The catalyst base is an activated or gamma-alumina such as those derived by calcination of amorphous hydrous alumina, alumina monohydrate, alumina trihydrate or their mixtures. The catalyst base precursor most advantageously is a mixture predominating in, or containing a major proportion of, for instance about 65 to 95 weight percent, one or more of the alumina trihydrates bayerite I, bayerite II (randomite or nordstrandite) or gibbsite, and may have about 5 to 35 weight percent of alumina monohydrate (boehmite), amorphous hydrous alumina or their mixture. The alumina base can contain small amounts of other solid oxides such as silica, magnesia, natural or activated clays (such as kaolinite, montmorillonite, halloysite, etc.), titania, zirconia, etc., or their mixtures. An optimum catayst composition contains from about 5 to 10% chromia and about 10% boria supported on activated alumina.

The alkylation reaction conditions used in the method of the present invention generally include a temperature sufficient to maintain the aromatic and alkylating agent feeds in the vapor phase under the pressure employed. This temperature may be from about 400 to 1000° F., preferably from about 500 to 800° F. while the pressure may range from about ambient pressures or less up to about 2000 p.s.i.g., e.g. about 0 to 2000 p.s.i.g., and are preferably elevated pressures ranging from about 50 to 1000 p.s.i.g. The catalyst can be used as a fixed, moving or fluidized bed or in any other convenient type of handling system. The aromatic space velocity will in most cases be from about 0.1 to 10, preferably from about 0.1 to 5, weights of aromatic per weight of catalyst per hour (WHSV). The alkylating agent is generally employed in a molar ratio to the aromatic of about 0.1 to 4:1 and preferably of about 1 to 2:1. Free molecular hydrogen must be present in our reaction system in amounts sufficient to inhibit carbon yields and the hydrogen to alkylating agent molar ratio will usually be from about 0.01 to 20:1 or more, preferably about 2 to 10:1. Conveniently, the hydrogen concentration is maintained by recycling hydrogen-rich gases from the reaction zone. Diluent gases such as N_2 and CH_4 can also be utilized in the present process usually in the amounts specified for hydrogen.

As previously stated the preferred catalyst base material is an activated or gamma-alumina made by calcining a precuror predominating in alumina trihydrate. An alumina of this type is disclosed in U.S. Patent No. 2,838,444. The alumina base is derived from a precursor alumina hydrate composition containing about 65 to 95 weight percent of one or more of the alumina trihydrate forms gibbsite, bayerite I and bayerite II (randomite) as defined by X-ray diffraction analysis. The substantial balance of the hydrate is amorphous hydrous or monohydrate alumina. Trihydrates are present as well defined crystallites, that is they are crystalline in form when examined by X-ray diffraction means. The crystallite size of the precursor alumina trihydrate is relatively large and usually is in the 100 to 1000 Angstrom unit range. The calcined alumina has a large portion of its pore volume in the pore size range of about 100 to 1000 Angstrom units generally having about 0.1 to about 0.5 and preferably about 0.15 to about 0.3 cc./g. of pore volume in this range. As described in the patent the calcined catalyst base can be characterized by large surface area ranging from about 350 to about 550 or more square meters/gram when in the virgin state as determined, for example, by the BET absorption technique. A low area catayst base prepared by treating the predominantly trihydrate base precursor is described in U.S. Patent No. 2,838,445. This base when in the virgin state has substantially no pores of radius less than about 10 Angstrom units and the surface area of the catalyst base is less than about 350 square meters/gram and most advantageously is in the range of about 150 to 300 square meters/gram.

The chromia and boria components can be added to the catalyst by known procedures. However, the alumina in hydrate or calcined form is preferably impregnated simultaneously with a chronic acid-boric acid aqueous solution. This manner of impregnation is distinguished from, for instance, the addition of an aqueous chromia solution to a boria-alumina composite or the addition of boria to a chromia-alumina composite. A catalyst prepared by the addition of boria to a chromia-alumina composite had high alkylation activity and a higher coking rate than a catalyst prepared by the simultaneous addition of chromia and boria to alumina. After impregnation, the resulting impregnated product is dried generally at a temperature within the range of 170° F. to 400° F. for at least 6 hours and up to 24 hours or more with a slow stream of air circulated to carry off the water vapor. The dried alumina catalyst mixture than may be formed by a tabletting or extruding operation. If the catalyst is to be in finely divided form, a grinding operation may follow drying. In the case of tabletting it is customary to incorporate a die lubricant which advantageously is organic and can be burned out by oxidation in the calcination step.

The pellets so obtained are suitable for subjection to high temperature treatment or calcination at a temperature between about 500° F. and about 1400° F., usually about 700° F. and 1000° F., for a period of between about 2 and about 36 hours. It is generally preferred that the calcining operation be conducted to minimize contact time of the alumina-containing product with water vapor at the high temperatures encountered. During the drying and calcining steps, the alumina hydrate is converted to gamma or activated alumina. The product after drying generally contains a substantial amount of water, for example, from about 15 to about 28 percent of water, which is driven off at temperatures above 400° F. It is usually preferred to heat the alumina-containing composite at a rate of 2 to 20° F. per minute up to 600° F. with an air flow through the catalyst bed followed by heating at a slower rate to the final calcination temperature within the range of 500° F. to 1400° F. especially if an organic die lubricant is to be oxidized without localized overheating. While the calcination or heat treatment will generally be conducted in air, it is also feasible, although generally less desirable, to carry out the same in other oxidizing atmospheres, a reducing atmosphere such as for example, hydrogen or methane, or an inert atmosphere, such as nitrogen. In some instances, it may be desirable to carry out the calcination initially in a blend of air and nitrogen followed by heat treatment in an atmosphere of hydrogen. The alumina impregnated with the catalytically active components, is finally cooled the yield the finished product.

The catalyst of the present invention can be easily regenerated employing conventional procedures, for instance by subjecting it to an oxygen-containing gas at temperatures sufficient to burn off carbon deposited on the catalyst during the alkylation. This oxygen-containing gas, e.g. an oxygen-nitrogen mixture, can contain about 0.01 weight percent to 5 weight percent oxygen but preferably contains about 0.5 to 1.5 weight percent oxygen

and is introduced at a flow rate such that the maximum temperature at the site of combustion is below about 1000° F.

During processing, particularly when using alkanols, water is generally formed and may leach boria off of the alumina. To correct this, the boria can be replaced by adding the boria back as some easily decomposed feed soluble form of boron, e.g. a boria-yielding compound such as trimethylborate. Conveniently, this is done by including in the alkylation feeds, e.g. the aromatic hydrocarbon or alkylating agent feeds, usually less than about 1%, advantageously about 0.01 to 0.05, weight percent of the boria-yielding compound based on the catalyst inventory. These amounts are usually sufficient to provide the desired amounts of the boria-yielding compound although larger amounts can be used if the compound is added intermittently. The addition of the boria in these concentrations based on the feed, e.g. aromatic hydrocarbon, can be done as necessary or continued over the processing period in order to maintain an adequate concentration of this component on the alumina base. The boria-yielding compound is advantageously one which will yield boria under alkylation conditions. Suitable compounds include alkylborates such as trimethylborate.

The following examples will serve to illustrate the invention but they are not to be considered limiting.

EXAMPLE I

Preparation of alumina

(A) An alumina composition of the kind described in U.S. Patent No. 2,838,444 can be employed in preparing the catalyst used in the process of our invention. The alumina of this patent can be made as follows. Pure aluminum metal is dissolved in pure hydrochloric acid, and the resulting solution is mixed with deionized water to form an aqueous aluminum chloride solution and an alumina gel is prepared equivalent to approximately 65 grams of Al_2O_3 per liter. A separate deionized water solution of NH_4OH is prepared containing approximately 65 grams of ammonia per liter. These two reagents in approximate volume ratio of 1:1 are intimately mixed as a flowing stream at a pH of 8.0. The flowing stream is passed to a stoneware container and an alumina hydrate is visible. The precipitated hydrate is filtered from the mother liquid and washed to <0.2% chloride by successive filtrations and reslurryings in deionized water until the desired chloride concentration is reached. In each reslurrying ammonia is added to give a pH of about 9. The washed hydrate is covered with water in a container and aged at about 90° F. until it is approximately 70% trihydrate, the remaining being substantially of the amorphous or monohydrate forms. The total hydrate composition is comprised of 42% bayerite, 18% randomite, 11% gibbsite, 20% boehmite, and 9% amorphous as determined by X-ray diffraction analysis. The aged hydrate is dried on a horizontal drum drier to give a powder of generally less than 20 mesh. The drum dried powder is mixed in a planetary type dough beater with sufficient deionized water to indicate 26 weight percent water on a Central Scientific Company infra-red moisture meter containing a 125 watt bulb, Cat. No. 26675. The resulting mixture is forced through a die plate having holes 1/16" in diameter bolted to a 3½" Welding Engineers screw extruder. The resulting strands are broken to particles of length varying generally between about 1/16" to 1".

The particles are dried at 230° F. and calcined by heating to 925° F. in a flow of nitrogen gas followed by a flow of air while the composition is maintained at a temperature in the range of 865° F. to 920° F. After the calcination the composition has an area (BET method) within the range from about 350 to 550 square meters/gram. Essentially the same alumina composition is employed in Examples II to X below.

Preparation of chromia-boria-alumina catalysts

(B) An alumina composition prepared essentially as described above in (A), except that air was used for the complete calcination procedure is employed in preparing the chromia-boria-alumina catalyst by the following procedure. 300 g. of the alumina composition are weighed into an 8" crystallizing dish. A solution is made up of 49.3 g. of CrO_3, 66.7 g. of H_3BO_3 and 280 ml. of water by heating to boiling. The hot solution is poured rapidly over the alumina and stirred thoroughly with a rubber spatula. Excess water is boiled off on a hot plate. The resulting catalyst is placed in a forced air drying oven, set at 230° F., for about 16 hours. The catalyst is stirred occasionally while drying. The oven-dried catalyst is transferred to a sagger and heated in a muffle furnace 2 hours at 500° F. followed by 3 hours at 1000° F. The catalyst is cooled in a desiccator. Analysis: 1.5% volatile matter at 1000° C., 10.2% B_2O_3, 9.91% Cr_2O_3. Sample No. 900–255–5139. This catalyst was used for Examples II and IV (Runs 1063–55 and 67) Table I.

(C) An alumina composition prepared essentially as described above in (A), except that air was used for the complete calcination procedure is employed in preparing a chromia-boria-alumina catalyst by the following procedure. 300 g. of the alumina composition are weighed into a 3-neck, 1 liter round bottom flask. One neck of the flask is stoppered, one attached to the closed stop-cock of a buret, and the third attached to a vacuum line. One-half hour is allowed for removal of air from the flask and the alumina. A solution of 49.3 g. of CrO_3 dissolved in DI water to make 240 ml. is then admitted through the buret. The flask and contents are shaken vigorously while the solution is being added. The catalyst is transferred to an 8" crystallizing dish and placed in a forced-air drying oven, set at 230° F., for about 16 hours. The oven-dried catalyst is transferred to a sagger and heated in a muffle furnace 2 hours at 500° F. followed by 3 hours at 1000° F. The catalyst is cooled in a desiccator. This chromia-alumina composition is transferred to an 8" crystallizing dish. 66.7 g. of H_3BO_3 are dissolved in 280 ml. of deionized water by heating to boiling and poured over the chromia-alumina. The resulting mixture is stirred thoroughly with a rubber spatula and excess water is boiled off on a hot plate. The catalyst is placed in a forced-air drying oven, set at 230° F., for about 16 hours. The catalyst is stirred occasionally while drying. The over-dried catalyst is transferred to a sagger and heated in a muffle furnace 2 hours at 500° F. followed by 3 hours at 1000° F. The catalyst is cooled in a desiccator. Analysis: 1.5% volatile matter at 1000° C., 11.9% B_2O_3, 9.87% Cr_2O_3. Sample No. 900–255–5140. This catalyst was used for Example III (Run 1063–77) Table I.

EXAMPLES II TO IV

The examples were conducted according to the following procedure. A 1-inch internal diameter Universal stainless steel reactor heated by radiant heat and bronze-block furnace was employed. The temperature of the reactor was controlled by Fenwall thermostats and the temperature of the catalyst bed was measured by means of iron-constantan thermocouples located throughout the bed.

The aromatic and alkylating agents were blended in the proper ratio and charged to the reactor from a graduated blowcase by nitrogen (diluent gas) placement. Both the diluent gas and liquid feed were metered to the reactor through Fischer-Porter rotameters.

The liquid products were separated from the effluent gases in a Jerguson liquid-level gauge and then released to atmospheric pressure at room temperature. The volume of dry gas was measured by means of a wet test meter and spot and continuous gas samples were taken. The gas samples were analyzed by mass spectrometer

techniques. Total hydrocarbon analyses were by vapor phase chromatography. The examples were conducted under the conditions specified in Table I and the results for each of the examples are also presented in this table.

TABLE I

[Conditions: 700° F., 200 p.s.i.g., .25 WHSV, about 3/1 H_2/aromatic mol ratio, 1 o-xylene/1 alkylating agent mol ratio, 4 hrs. test]

Example	II 1063-55	III 1063-77	IV 1063-67
Catalyst	10% Cr_2O_3 on 10% B_2O_3, Al_2O_3.	10% Cr_2O_3 10% B_2O_3 Al_2O_3.	10% Cr_2O_3 10% B_2O_3 alumina.
Alkylating Agent	Methanol	Methanol	Dimethyl Ether.
Percent Alkylating Agent Utilization.	56	59	50.
WHSV	.25	.25	.22.
C on Catalyst, Wt. Percent.	0.15	0.45	.40.
Method of Preparation.	Cr_2O_3–B_2O_3 added Simultaneously to Al_2O_3.	B_2O_3 added to Cr_2O_3/Al_2O_3.	Cr_2O_3–B_2O_3 added Simultaneously to Al_2O_3.

EXAMPLES V TO VIII

Essentially the same procedure employed in Example II is followed except the alkylating agents and aromatics listed below in their respective examples are substituted for the methanol and o-xylene respectively, of Example II.

Example	Alkylating Agent	Aromatic
V	Dibutyl ether	Benzene.
VI	Butanol	Naphthalene.
VII	Methanol	Indane.
VIII	t-Octanol	Toluene.
VIIIa	t-Butyl chloride	o-Xylene.

EXAMPLE IX

Essentially the same procedure employed in Example II is followed except isodurene was substituted for o-xylene and the conditions employed included a temperature of 600° F., a pressure of 100 p.s.i.g., a WHSV of .22, a H_2/aromatic mol ratio of 7/1, and an isodurene/methanol mol ratio of 2/1. The results of this procedure are as follows.

Recovery, wt. percent/feed:

Gas	2.3
Coke	0.1
H_2O layer	4.1
Unconverted MeOH and COC	0.3
HC	91.1
Total	97.9

Product HC:

C_8's ——Weight percent feed—	.15
C_9's ——do——	1.19
C_{10}'s ——do——	60.10
C_{11}'s ——do——	27.50
C_{12}'s ——do——	3.85
Percent methylation	64
Carbon on catalyst	0.07

EXAMPLE X

In the following example boria is added during processing to a 10% Cr_2O_3–6.3% B_2O_3–Al_2O_3 catalyst. Essentially the same procedure employed in Example II was followed except that the catalyst was contacted with an ortho-xylene-methanol-trimethylborate feed at a rate such that 0.5 weight percent boria per hour, based on the catalyst weight, was added on the catalyst. The conditions and results for this example are set forth below.

[Conditions: 700° F., 200 p.s.i.g., .25 WHSV, 3/1 H_2, 1 o-xylene/1 MeOH]

Run No.	1122–2.
Percent B_2O_3	6.3→11.8.
Special treatment of catalyst	Boria added as $(CH_3O)_3B$ 0.5%/hr.
Methanol utilization	70.
Carbon on catalyst, wt. percent MeOH/hr.	.12.

EFFECT OF HYDROGEN PARTIAL PRESSURE

At approximately zero hydrogen pressure (H_2/alkylating agent molar ratio of about 0/1) carbon laydown was equivalent to 16.1 wt. percent of the methanol feed/hr. (Run 1063–59) and a hydrogen partial pressure of 310 p.s.i.a. (H_2/alkalating agent molar ratio of 7/1) carbon laydown was 0.06 wt. percent/hr. (Run 1122–12).

TABLE II.—EFFECT OF HYDROGEN PARTIAL PRESSURE

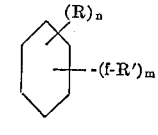
Catalyst: 10% Cr_2O_3–10% B_2O_3–Al_2O_3
Feed: ortho-xylene

Run 1063	59	1122-12
Temp.,° F	700	700
Pressure, p.s.i.g	100	400
P_{H_2}, p.s.i.a	10	310
Arom./MeOH Mole Ratio	1/1	1/1
H_2/MeOH Mole Ratio	.22	6.0
Methanol Utilization	55	55
Carbon on Catalyst, Wt. Percent MeOH/hr	16.1	.06

It is claimed:

1. In the process of alkylating an alkylatable aromatic hydrocarbon with an alkylating agent comprising contacting the alkylatable aromatic hydrocarbon with an alkylating agent under alkylation conditions in the presence of free hydrogen and an alkylation catalyst consisting essentially of a minor amount of chromia, a minor amount of boria sufficient to enhance the utilization of the alkylating agent, and a major amount of activated alumina.

2. The method of claim 1 wherein the alkylatable aromatic hydrocarbon corresponds to the structural formula



where R is an alkyl radical containing from about 1 to 8 carbon atoms; n is 0 to 3; R' is an aromatic hydrocarbon ring; m is 0 to 1 and -f- indicates a fused ring relationship.

3. The method of claim 2 wherein the alkylating agent corresponds to the structural formula

R—O—R'

where R is a lower alkyl radical of 1 to 4 carbon atoms and R' is selected from the group consisting of R and H.

4. The method of claim 3 wherein the catalyst consists essentially of about 5 to 15 weight percent chromia, about 5 to 15 weight percent boria and activated alumina.

5. The method of claim 4 wherein the alkylation conditions include a temperature from about 500 to 800° F., an aromatic space velocity from about 0.1 to 5 WHSV, and an alkylating agent/aromatic molecular ratio of about 0.1 to 4:1.

6. The method of claim 5 in which the activated alumina is derived by calcination of an alumina hydrate

percursor having a major amount of alumina trihydrate.

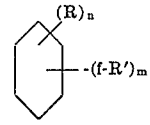
7. A catalyst composition useful in the alkylation of alkylatable aromatic hydrocarbons with an alkylating agent consisting essentially of about 1 to 20 weight percent chromia, about 1 to 20 weight percent boria and activated alumina, the alumina being essentially composed of gamma alumina modifications resulting from drying at a temperature of 170° F. to 400° F. and calcining at a temperature between about 500° F. and 1400° F. of a mixture of precursor hydrous alumina phases containing a major amount of trihydrate.

8. In a method for preparing a catalyst composition useful in the alkylation of alkylatable aromatic hydrocarbons with an alkylating agent consisting essentially of about 1 to 20 weight percent chromia, about 1 to 20 weight percent boria, and activated alumina, the alumina being essentially composed of gamma alumina modifications resulting from drying at a temperature of 170° F. to 400° F. and calcining at a temperature between about 500° F. and 1400° F. of a mixture of precursor hydrous alumina phases the step comprising simultaneously introducing the chromia and boria onto the alumina.

9. In a method for preparing a catalyst composition useful in the alkylation of alkylatable aromatic hydrocarbons with an alkylating agent consisting essentially of about 1 to 20 weight percent chromia, about 1 to 20 weight percent boria, and activated alumina, the alumina being essentially composed of gamma alumina modifications resulting from drying at a temperature of 170° F. to 400° F. and calcining at a temperature between about 500° F. and 1400° F. of a mixture of precursor hydrous alumina phases containing a major amount of trihydrate; the step comprising simultaneously introducing the chromia and boria onto the alumina.

10. The process of alkylating an alkylatable aromatic hydrocarbon with an alkylating agent comprising contacting the alkylatable aromatic hydrocarbon with an alkylating agent under alkylation conditions in the presence of free hydrogen and an alkylation catalyst consisting essentially of about 1 to 20 weight percent of chromia, about 1 to 20 weight percent of boria and a major amount of activated alumina.

11. The process of claim 10 wherein the alkylatable aromatic hydrocarbon corresponds to the structural formula



where R is an alkyl radical containing from about 1 to 8 carbon atoms; *n* is 0 to 3; R′ is an aromatic hydrocarbon ring; *m* is 0 to 1 and *-f-* indicates a fused ring relationship.

12. The process of claim 11 wherein the alkylating agent corresponds to the structural formula R—O—R′ where R is a lower alkyl radical of 1 to 4 carbon atoms and R′ is selected from the group consisting of R and H.

13. The method of claim 9 in which the chromia and boria are simultaneously introduced by impregnating the alumina with a chromic acid-boric acid aqueous solution.

14. The method of claim 13 wherein the alumina is in a hydrous phase, is calcined prior to the chromia-boria addition, and is then recalcined.

15. The method of claim 4 wherein the chromia and boria components are added to the alumina simultaneously.

16. The method of claim 15 wherein the chromia and boria are simultaneously introduced by impregnating the alumina with a chromic acid-boric acid aqueous solution.

17. The method of claim 16 wherein the alumina is in a hydrous phase, is calcined prior to the chromia-boria addition, and is then recalcined.

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