

HIGHLY SELECTIVE ALKYLATION PROCESS
WITH LOW ZEOLITE CATALYST COMPOSITION

STATEMENT OF PRIORITY

5 **[0001]** This application claims priority to U.S. Application No. 14/674832 which was filed March 31, 2015, the contents of which are hereby incorporated by reference in its entirety.

TECHNICAL FIELD

10 **[0002]** The present subject matter relates to a process for alkylation of a feedstock, and more specifically to a highly active, stable and selective alkylation process with a low zeolite catalyst composition having a low nitrogen to zeolite aluminum molar ratio

BACKGROUND

15 **[0003]** Alkylation of aromatic compounds with a C₂ to C₄ olefin and transalkylation of polyalkylaromatic compounds are two common reactions for producing monoalkylated aromatic compounds. Examples of these two reactions that are practiced industrially to produce ethylbenzene are the alkylation of benzene with ethylene and the transalkylation of benzene and diethylbenzene.

20 **[0004]** Combining alkylation and transalkylation can thus maximize ethylbenzene production. Such a combination can be carried out in a process having two reaction zones, one for alkylation and the other for transalkylation, or in a process having a single reaction zone in which alkylation and transalkylation both occur.

25 **[0005]** A key operating variable directly related to operating efficiency of alkylation process is the molar ratio of aryl groups per alkyl group. The lower the ratios, the lower the amounts of benzene required to recover/recycle, the lower the capital and utility cost would be. The numerator of this ratio is the number of moles of aryl groups passing through the reaction zone during a specified period of time. The number of moles of aryl groups is the sum of all aryl groups, regardless of the compound in which the aryl group happens to be. In the context of ethylbenzene production, for example, one mole of benzene, one mole of ethylbenzene, and one mole of diethylbenzene each contribute one mole of aryl group to the

sum of aryl groups. The denominator of this ratio is the number of moles of alkyl groups that have the same number of carbon atoms as that of the alkyl group on the desired monoalkylated aromatic and which pass through the reaction zone during the same specified period of time. The number of moles of alkyl groups is the sum of all alkyl and alkenyl groups with the same number of carbon atoms as that of the alkyl group on the desired monoalkylated aromatic, regardless of the compound in which the alkyl or alkenyl group happens to be, except that paraffins are not included. In the context of ethylbenzene production, the number of moles of ethyl groups is the sum of all ethyl and ethenyl groups, regardless of the compound in which the ethyl or ethenyl group happens to be, except that paraffins, such as ethane, propane, n-butane, isobutane, pentanes, and higher paraffins are excluded from the computation of the number of moles of ethyl groups. For example, one mole of ethylene and one mole of ethylbenzene each contribute one mole of ethyl group to the sum of ethyl groups, whereas one mole of diethylbenzene contributes two moles of ethyl groups and one mole of triethylbenzene contributes three moles of ethyl groups. Butylbenzene and octylbenzene contribute no moles of ethyl groups

[0006] Advancements in zeolites and catalysts have enabled the aromatic alkylation process to operate at lower aryl to alkyl ratios. The catalysts typically include a relatively high content of zeolite in order to ensure good activity, activity stability and stable long-term operation. Currently, aromatic alkylation catalysts including UZM-8 zeolite have a zeolite content greater than 50 wt%.

[0007] Many aromatic alkylation catalysts containing a variety of zeolites have been proposed and used for alkylating and transalkylating aromatics. Regardless whether the reaction is alkylation or transalkylation, it is important that such catalysts exhibit acceptable activity to convert the reactants and acceptable yield to the desired product. Although compounds containing nitrogen may be used in the synthesis and/or treatment of such zeolites, nitrogen is known to reduce the activity of the resulting catalysts. Therefore it is well known in the art to remove nitrogen such as by heating for sufficient time and temperature to obtain the hydrogen form of the zeolite. It is also known that nitrogen compounds in the reactants may be adsorbed on the active catalyst sites and cause rapid deactivation of the catalyst. The effect of nitrogen on the selectivity of such catalysts is inconsistent as both increased and decreased selectivity has been reported. The source or

sources of the inconsistent selectivity changes is uncertain as differences in one or more variables, such as, types of zeolites, zeolite treatments steps, catalyst compositions and preparation steps, the reactants, desired products, and various reaction conditions have been reported.

- 5 **[0008]** Zeolite is synthesized using organic templates, which are removed via calcinations in the catalyst preparation. Because of the heat and steam evolved during the calcination, the zeolite would incur appreciable structural and framework damages. The degree of damage is related to the degree of hydrothermal severity, which is proportional to the amount the zeolite in the catalyst. Furthermore, at high zeolite contents, the zeolite in the catalyst tends to
10 agglomerate, reducing the effective utilization of zeolite. Lastly because of the high cost of zeolites, catalysts containing high levels of zeolites and processes using those catalysts are also expensive.

SUMMARY

- 15 **[0009]** One aspect of the invention is a method for alkylation of a feedstock. In one embodiment, the method includes contacting the feedstock comprising at least one alkylatable aromatic compound and an alkylating agent with a first alkylating catalyst composition under alkylating conditions to convert the majority of alkylating reagent, followed by having a second alkylating catalyst composition to contact the effluent exiting the first alkylating catalyst composition to convert the remaining unconverted alkylating
20 reagent. In a further aspect, the first alkylating catalyst composition comprises UZM-8 zeolite, nitrogen, and a binder, the first alkylating catalyst composition having 2-20 wt% UZM-8 zeolite, and the catalyst having a nitrogen to zeolite aluminum molar ratio of between 0.01 to 0.040; the second alkylating catalyst composition comprises zeolite UZM-8, UZM-37, MCM-22, BEA, FAU with zeolite contents greater than 30%; wherein a total alkylated
25 selectivity at a temperature and a molar ratio of alkylatable aromatic compound to alkylating agent is greater than 99.0%.

BRIEF DESCRIPTION OF THE DRAWING

- [0010]** The Figure is a graph showing the effect of zeolite content on catalyst activity measured by the position of the end of the active zone (EAZ).

DETAILED DESCRIPTION

[0011] To ensure high olefin conversion, maintain activity stability, and attain high alkylated product selectivity and long-term operating stability, the alkylation catalyst typically contains a zeolite content of greater than 50%. The activity is measured as olefin conversion determined by the amount of olefin at the reactor inlet and that unconverted at the outlet of the reactor. Alternatively the catalyst activity is measured by the size of the active zone required to reach to maximal temperatures, and the activity stability is measured by the stability of the size of the active zone as a function of time on stream. In commercial operation, the size of the active zone is a fraction of the total catalyst bed in a fixed bed reactor, while the remaining catalyst bed functions as the catalyst life zone. It is advantageous to have a highly active catalyst, which ensures a minimal size of the active zone and maximal life zone to attain long-term stable operation. Total alkylated selectivity is defined as the production of mono- and poly-alkylated benzene out of the total benzene and olefin consumed on a carbon basis. The total alkylated selectivity represents the possibly maximal amounts of recoverable alkylated products through the alkylation and trans-alkylation reactor, a measurement of the efficiency of feed utilization. Again, to maintain a long-term stable and efficient commercial production of cumene, a minimal amount of zeolite is required.

[0012] It was unexpectedly found that the alkylation catalysts containing significantly less than 50% UZM-8 zeolite maintained high activity and activity stability under process conditions of low benzene to olefin ratios and temperatures, which are severe but economically advantageous. The activity measured on the basis of olefin conversions remains unchanged, when the zeolite contents of the catalyst are reduced to very low amounts. Most unexpectedly the activity measured by the size of EAZ remains unchanged as the zeolite content is reduced and only expands slightly when the zeolite contents are reduced below 10%. It is also unexpectedly found that the total alkylated product selectivity remains unchanged with catalysts containing very low UZM-8 zeolite contents. For example, the total alkylated selectivity can be greater than 99.0%, or greater than 99.1%, or greater than 99.2%, or greater than 99.3%, or greater than 99.4%, or greater than 99.5%, or greater than 99.6%, or greater than 99.7%.

[0013] In one embodiment of the invention the alkylation reactor is made up entirely of a catalyst containing less than 20 wt% UZM-8 zeolite. The alkylation catalyst comprises a UZM-8 zeolite and a binder. The zeolite is present in an amount of at least 1 wt% and less than between 20 wt% of the catalyst composition, with the remainder being the binder. There can be between 2 and 20 wt% zeolite, or less than 20 wt% zeolite, or less than 15 wt% zeolite, or less than 10 wt% zeolite. The binder comprises one or more conventional zeolite binder materials such as those described below.

[0014] In one embodiment of the invention, the alkylation reaction is carried out by two catalysts with the lead catalyst containing less than 20 wt% UZM-8 zeolite and the lag catalyst containing greater than 30 wt% zeolite selected from zeolite UZM-8, UZM-37, MCM-22, BEA, FAU or a mixture of thereof. The lead alkylation catalyst comprises a UZM-8 zeolite and a binder with the zeolite present in an amount of at least 1 wt% and less than 50 wt% of the catalyst composition, with the remainder being the binder. There can be less than 30 wt% zeolite, or less than 25 wt% zeolite, or 25 wt% zeolite. The binder comprises one or more conventional zeolite binder materials such as those described below. The lag catalyst contains greater than 30 wt% zeolite UZM-8, UZM-37, MCM-22, BEA, FAU or a mixture of thereof with the balance comprising one or more conventional binder materials such as those described below. The two alkylation catalysts can be installed in the same or preferably separate reactor vessels. In this embodiment, the first alkylation catalyst is made up of more than 50% and preferably at least 70% of the total alkylator reactor volume with the balance being the second alkylation catalyst. In the same embodiment the majority of alkylating reagent is converted by the first alkylation catalyst with the remaining converted by the second alkylation catalyst. The second alkylation zone may or may not have a dedicated injection of alkylatable aromatic compound into the bed. The second alkylation zone if installed in a separate reactor vessel can have two beds operating in lead and lag configuration. Lead and lag operation of the second zone allows for independent regeneration and reload of the finishing catalyst while ensuring continuous operation without olefin breakthrough.

[0015] In ethyl benzene (EB), cumene, and heavier alkylates such as linear alkylbenzenes used in the manufacture of detergents, lower UZM-8 zeolite content maintains high catalyst activity, activity stability and total alkylate selectivity. As the zeolite content was reduced,

the catalysts did not show debits in activity, activity stability or total alkylated selectivity based on the conversion of benzene and propylene on a carbon basis. The catalyst showed greater than 90% propylene conversion and stable activity at relatively severe conditions of low inlet temperatures and low benzene to olefin ratios for zeolite contents greater than 2 wt%. This is in comparison to normal processing conditions of greater than 90% conversion achieved at 130°C using a catalyst of a much higher zeolite content of 50% or more. The conversion (e.g., ethylene, propylene, or butene) was typically greater than 90%, or greater than 95%, or greater than 96%, or greater than 97%, or greater than 98%, or greater than 99%.

[0016] In another preferred embodiment of the invention, the process comprises the alkylation reactor made up of the first alkylation catalyst or a combination of the first and second alkylation catalysts as previously prescribed and guard beds to remove contaminants from the feed streams. The long-term deactivation of UZM-8 based catalysts is typically caused by contaminants, specifically basic nitrogen compounds, oxygen including oxygenates, and highly unsaturated aliphatic hydrocarbons in benzene. Sulfur can also have an impact on activity and/or activity stability on zeolite UZM-8, UZM-37, MCM-22, BEA and FAU-containing catalysts. Metals, including but not limited to, As, Hg, and Pb, can also impact performance at the low zeolite levels.

[0017] By incorporating one or more guard beds to remove oxygenate species, nitrogen and sulfur containing compounds, and/or highly unsaturated aliphatic hydrocarbons and metals, alkylation process with low zeolite contents can be used. The guard bed essentially eliminates contaminants from the benzene and olefin feed streams, protecting the alkylation catalyst. The importance of protecting the alkylation catalyst from contaminants increases in importance as the zeolite content decreases because the contaminants can reduce the catalyst activity.

[0018] The process significantly reduces the overall cost of the adsorbent and catalyst. The cost of manufacturing the guard bed material is much less than the alkylation catalyst because of the pressurized synthesis of the UZM-8 catalyst.

[0019] Suitable guard beds for nitrogen, oxygenates, sulfur containing compounds, and/or highly unsaturated acyclic and cyclic hydrocarbons and metals are known in the art. In one

embodiment, the guard bed can utilize an adsorbent made of steamed modified zeolite Y/ Al_2O_3 . In another embodiment, the guard bed is made up of Ni-Mo-O on a steamed modified zeolite Y/ Al_2O_3 support. In another embodiment, the adsorbent can be Ni-Mo-O on a cation exchanged zeolite X and Y support with the cations being Mg, Y (yttrium), and rare earth elements. The guard bed can be operated at a temperature in the range of 25°C to 260°C, and a pressure of 0.7 MPa (100 psig) to 4.1 MPa (600 psig).

[0020] The catalyst for the process disclosed herein contains one or more members of the family of aluminosilicate and substituted aluminosilicate zeolites designated UZM-8 and UZM-8HS, which are described in US Patent Nos. 6,756,030; 7,091,390; 7,268,267; and 7,638,667; for example, each of which is incorporated herein by reference. U.S. Pat. No. 6,756,030 describes UZM-8 and its preparation, and therefore it is not necessary herein to describe these in detail. Briefly, UZM-8 zeolites are prepared in an alkali-free reaction medium in which only one or more organoammonium species are used as structure directing agents. In this case, the microporous crystalline zeolite (UZM-8) has a composition in the as-synthesized form and on an anhydrous basis expressed by the empirical formula:



where R is at least one organoammonium cation selected from the group consisting of protonated amines, protonated diamines, quaternary ammonium ions, diquaternary ammonium ions, protonated alkanolamines and quaternized alkanolammonium ions. Preferred organoammonium cations are those that are non-cyclic or those that do not contain a cyclic group as one substituent. Of these those that contain at least two methyl groups as substituents are especially preferred. Examples of preferred cations include without limitation DEDMA, ETMA, HM and mixtures thereof. The ratio of R to (Al+E) is represented by "r" which varies from 0.05 to 5. The value of "p" which is the weighted average valence of R varies from 1 to 2. The ratio of Si to (Al+E) is represented by "y" which varies from 6.5 to 35. E is an element which is tetrahedrally coordinated, is present in the framework and is selected from the group consisting of gallium, iron, chromium, indium and boron. The mole fraction of E is represented by "x" and has a value from 0 to 0.5, while "z" is the mole ratio of O to (Al+E) and is given by the equation

$$z = (\text{rp} + 3 + 4y) / 2.$$

[0021] The UZM-8 zeolites can be prepared using both organoammonium cations and alkali and/or alkaline earth cations as structure directing agents. As in the alkali-free case above, the same organoammonium cations can be used here. Alkali or alkaline earth cations are observed to speed up the crystallization of UZM-8, often when present in amounts less than 0.05 M⁺/Si. For the alkali and/or alkaline earth metal containing systems, the microporous crystalline zeolite (UZM-8) has a composition in the as-synthesized form and on an anhydrous basis expressed by the empirical formula:



where M is at least one exchangeable cation and is selected from the group consisting of alkali and alkaline earth metals. Specific examples of the M cations include but are not limited to lithium, sodium, potassium, rubidium, cesium, calcium, strontium, barium and mixtures thereof. Preferred R cations include without limitation DEDMA, ETMA, HM and mixtures thereof. The value of "m" which is the ratio of M to (Al+E) varies from 0.01 to 2. The value of "n" which is the weighted average valence of M varies from 1 to 2. The ratio of R to (Al+E) is represented by "r" which varies from 0.05 to 5. The value of "p" which is the weighted average valence of R varies from 1 to 2. The ratio of Si to (Al+E) is represented by "y" which varies from 6.5 to 35. E is an element which is tetrahedrally coordinated, is present in the framework and is selected from the group consisting of gallium, iron, chromium, indium and boron. The mole fraction of E is represented by "x" and has a value from 0 to 0.5, while "z" is the mole ratio of O to (Al+E) and is given by the equation

$$z = (mn + rp + 3 + 4y)/2$$

where M is only one metal, then the weighted average valence is the valence of that one metal, i.e. +1 or +2. However, when more than one M metal is present, the total amount of

$$M_m^{n+} = M_{m1}^{(n1)+} + M_{m2}^{(n2)+} + M_{m3}^{(n3)+}$$

and the weighted average valence "n" is given by the equation:

$$n = \frac{m1 \cdot n1 + m2 \cdot n2 + m3 \cdot n3 + \dots}{m1 + m2 + m + \dots}$$

Similarly when only one R organic cation is present, the weighted average valence is the

valence of the single R cation, i.e., +1 or +2. When more than one R cation is present, the total amount of R is given by the equation.

$$R_r^{p+} = R_{r1}^{(p1)+} + R_{r2}^{(p2)+} + R_{r3}^{(p3)+}$$

and the weighted average valence "p" is given by the equation

$$p = \frac{p1 \cdot r1 + p2 \cdot r2 + p3 \cdot r3 + \dots}{p1 + p2 + p3 + \dots}$$

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[0022] The microporous crystalline zeolites used in the process disclosed herein are prepared by a hydrothermal crystallization of a reaction mixture prepared by combining reactive sources of R, aluminum, silicon and optionally M and E. The sources of aluminum include but are not limited to aluminum alkoxides, precipitated aluminas, aluminum metal, sodium aluminate, organoammonium aluminates, aluminum salts and alumina sols. Specific examples of aluminum alkoxides include, but are not limited to aluminum ortho sec-butoxide and aluminum ortho isopropoxide. Sources of silica include but are not limited to tetraethylorthosilicate, colloidal silica, precipitated silica, alkali silicates and organoammonium silicates. A special reagent consisting of an organoammonium aluminosilicate solution can also serve as the simultaneous source of Al, Si, and R. Sources of the E elements include but are not limited to alkali borates, boric acid, precipitated gallium oxyhydroxide, gallium sulfate, ferric sulfate, ferric chloride, chromium nitrate and indium chloride. Sources of the M metals include the halide salts, nitrate salts, acetate salts, and hydroxides of the respective alkali or alkaline earth metals. R can be introduced as an organoammonium cation or an amine. When R is a quaternary ammonium cation or a quaternized alkanolammonium cation, the sources include but are not limited the hydroxide, chloride, bromide, iodide and fluoride compounds. Specific examples include without limitation DEDMA hydroxide, ETMA hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide, hexamethonium bromide, tetrapropylammonium hydroxide, methyltriethylammonium hydroxide, tetramethylammonium chloride and choline chloride. R may also be introduced as an amine, diamine, or alkanolamine that subsequently hydrolyzes to form an organoammonium cation. Specific non-limiting examples are N,N,N',N'-tetramethyl-1,6-hexanediamine, triethylamine, and triethanolamine. Preferred sources of R

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without limitation are ETMAOH, DEDMAOH, and hexamethonium dihydroxide (HM(OH)₂).

[0023] The reaction mixture containing reactive sources of the desired components can be described in terms of molar ratios of the oxides by the formula:



where "a" varies from 0 to 25, "b" varies from 1.5 to 80, "c" varies from 0 to 1.0, "d" varies from 10 to 100, and "e" varies from 100 to 15000. If alkoxides are used, it is preferred to include a distillation or evaporative step to remove the alcohol hydrolysis products. The reaction mixture is now reacted at a temperature of 85°C to 225°C (185 to 437°F) and preferably from 125°C. to 150°C. (257 to 302°F) for a period of 1 day to 28 days and preferably for a time of 5 days to 14 days in a sealed reaction vessel under autogenous pressure. After crystallization is complete, the solid product is isolated from the heterogeneous mixture by means such as filtration or centrifugation, and then washed with deionized water and dried in air at ambient temperature up to 100°C. (212°F.).

15 **[0024]** The UZM-8 aluminosilicate zeolite, which is obtained from the above-described process, is characterized by an x-ray diffraction pattern, having at least the d-spacings and relative intensities set forth in Table A below.

TABLE A

d-Spacings and Relative Intensities for as-synthesized UZM-8

20	2- Θ	d(Å)	I/I ₀ %
	6.40-6.90	13.80-12.80	w-s
	6.95-7.42	12.70-11.90	m-s
	8.33-9.11	10.60-9.70	w-vs
	19.62-20.49	4.52-4.33	m-vs
25	21.93-22.84	4.05-3.89	m-vs
	24.71-25.35	3.60-3.51	w-m
	25.73-26.35	3.46-3.38	m-vs

30 **[0025]** The UZM-8 compositions are stable to at least 600°C. (1112°F.) (and usually at least 700°C. (1292°F.)). The characteristic diffraction lines associated with typical calcined

UZM-8 samples are shown below in table B. The as-synthesized form of UZM-8 is expandable with organic cations, indicating a layered structure.

TABLE B

d-Spacings and Relative Intensity for Calcined UZM-8

5	2- Θ	d(Å)	I/I ₀ %
	4.05-4.60	21.80-19.19	w-m
	7.00-7.55	12.62-11.70	m-vs
	8.55-9.15	10.33-9.66	w-vs
	12.55-13.15	7.05-6.73	w
10	14.30-14.90	6.19-5.94	m-vs
	19.55-20.35	4.54-4.36	w-m
	22.35-23.10	3.97-3.85	m-vs
	24.95-25.85	3.57-3.44	w-m
	25.95-26.75	3.43-3.33	m-s

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[0026] An aspect of the UZM-8 synthesis that contributes to some of its unique properties is that it can be synthesized from a homogenous solution. In this chemistry, soluble aluminosilicate precursors condense during digestion to form extremely small crystallites that have a great deal of external surface area and short diffusion paths within the pores of the crystallites. This can affect both adsorption and catalytic properties of the material.

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[0027] As-synthesized, the UZM-8 material will contain some of the charge balancing cations in its pores. In the case of syntheses from alkali or alkaline earth metal-containing reaction mixtures, some of these cations may be exchangeable cations that can be exchanged for other cations. In the case of organoammonium cations, they can be removed by heating under controlled conditions. In the cases where UZM-8 is prepared in an alkali-free system, the organoammonium cations are best removed by controlled calcination, thus generating the acid form of the zeolite without any intervening ion-exchange steps. The controlled calcination conditions include the calcination conditions described herein below for the composite catalyst, and it may sometimes be desirable to perform the controlled calcination of the zeolite after the zeolite has been combined with a binder. On the other hand, it may sometimes be possible to remove a portion of the organoammonium via ion exchange. In a

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special case of ion exchange, the ammonium form of UZM-8 may be generated via calcination of the organoammonium form of UZM-8 in an ammonia atmosphere.

[0028] The catalyst used in the process disclosed herein preferably contains calcined UZM-8. Calcination of as-synthesized UZM-8 effects changes such as in the x-ray diffraction pattern. The UZM-8 zeolite used in the catalyst used in the process disclosed herein contains preferably less than 0.1 wt-%, more preferably less than 0.05 wt-%, and even more preferably less than 0.02 wt-% of alkali and alkaline earth metals. The alkali or alkaline earth metals can be removed from the as synthesized UZM-8 or calcined as synthesized UZM-8 prior to formulating the zeolite into the catalysts. The alkali or the alkali earth metals can also be removed after the as synthesized UZM-8 or calcined as synthesized UZM-8 zeolite being formulated into the catalyst and calcined. The removal of alkali or alkaline earth elements are performed using ammonium exchange using solutions of 0.1 to 20wt% ammonium salts at temperatures ranging from 20 to 95°C.

[0029] For use in the process disclosed herein, the zeolite preferably is mixed with a binder for convenient formation of catalyst particles in a proportion of 1 to 100 mass % zeolite and 0 to 99 mass-% binder, with the zeolite preferably comprising from 2 to 50 mass-% of the composite. The binder should preferably be porous, have a surface area of 5 to 800 m²/g, and be relatively refractory to the conditions utilized in the hydrocarbon conversion process. Non-limiting examples of binders are aluminas, titania, zirconia, zinc oxide, magnesia, boria, silica-alumina, silica-magnesia, chromia-alumina, alumina-boria, silica-zirconia, etc.; silica, silica gel, and clays. Preferred binders are amorphous silica and alumina, including gamma-, eta-, and theta-alumina, with gamma- and eta-alumina being especially preferred.

[0030] The zeolite with or without a binder can be formed into various shapes such as pills, pellets, extrudates, spheres, etc. Preferred shapes are extrudates and spheres. Extrudates are prepared by conventional means which involves mixing of zeolite either before or after adding metallic components, with the binder and a suitable peptizing agent to form a homogeneous dough or thick paste having the correct moisture content to allow for the formation of extrudates with acceptable integrity to withstand direct calcination. The dough then is extruded through a die to give the shaped extrudate. A multitude of different extrudate shapes are possible, including, but not limited to, cylinders, cloverleaf, dumbbell and

symmetrical and asymmetrical polylobates. It is also within the scope of this invention that the extrudates may be further shaped to any desired form, such as spheres, by any means known to the art.

[0031] Spheres can be prepared by the well known oil-drop method which is described in U.S. Pat. No. 2,620,314, which is hereby incorporated herein by reference in its entirety. The method involves dropping a mixture of zeolite, and for example, alumina sol, and gelling agent into an oil bath maintained at elevated temperatures. The droplets of the mixture remain in the oil bath until they set and form hydrogel spheres. The spheres are then continuously withdrawn from the oil bath and typically subjected to specific aging treatments in oil and an ammoniacal solution to further improve their physical characteristics. The resulting aged and gelled particles are then washed and dried at a relatively low temperature of 50-200°C. (122-392°F.) and subjected to a calcination procedure at a temperature of 450-700°C. (842-1292°F.) for a period of 1 to 20 hours. This treatment effects conversion of the hydrogel to the corresponding alumina matrix.

[0032] The catalyst composite is dried at a temperature of from 100°C (212°F) to 320°C (608°F) for a period of from 2 to 24 or more hours and, usually, calcined at a temperature of from 400° C (752°F) to 650°C (1202°F) in an air atmosphere for a period of from 1 to 20 hours. The calcining in air may be preceded by heating the catalyst composite in nitrogen to the temperature range for calcination and holding the catalyst composite in that temperature range for from 1 to 10 hours. A catalyst composite used in the process disclosed herein preferably has an x-ray diffraction pattern having at least the d-spacings and relative intensities set forth in Table B.

[0033] The binder used in the catalyst composite for the process disclosed herein preferably contains less alkali and alkaline earth metals than the UZM-8 zeolite used in the catalyst composite, and more preferably contains little or no alkali and alkaline earth metals. Therefore, the catalyst composite has a content of alkali and alkaline earth metals of less than that of the UZM-8 zeolite used in forming the catalyst composite, owing to the binder effectively lowering the alkali and alkaline earth metals content of the catalyst composite as a whole.

[0034] The ion exchange step may be followed by an optional water wash step and multiple ion exchange steps may be used to obtain the desired amount of alkali and alkaline earth metals on the aromatic alkylation catalyst. In an embodiment, the aromatic alkylation catalyst contains less than 0.1 mass %, preferably less than 0.05 mass %, and more preferably less than 0.02 mass % of alkali and alkaline earth metals on a metal oxide, e.g. Na_2O , volatile free basis. Water washing after ion exchange is well known. Suitable conditions for the optional water washing step include a water to catalyst weight ratio ranging from 1:1 to 10:1 and a temperature ranging from 15°C to 100°C. The water / catalyst contacting time will vary as is known in the art with the equipment and the type of contacting, e.g. flow through fixed bed, counter-current flows, and contact and decant. The ion exchanged catalyst may optionally be dried prior to the final calcining step. Suitable drying conditions include a temperature of from 100°C to 320°C for a period of from 1 to 24 or more hours. This optional drying step may be conducted in air or in an inert atmosphere such as nitrogen.

[0035] The ion exchanged catalyst is heated in a final calcining step wherein the nitrogen content of the catalyst may be controlled to produce the aromatic alkylation catalyst having a nitrogen to zeolite aluminum molar ratio (N/Alz) of at least 0.01. In an embodiment, the nitrogen to zeolite aluminum molar ratio of the catalyst ranges from 0.01 to 0.040. The nitrogen to zeolite aluminum molar ratio, is calculated from the mass of nitrogen on the aromatic alkylation catalyst as determined by method ASTM 5291 and the total mass (framework and non framework) of aluminum in the UZM-8 zeolite in the catalyst. Thus, the zeolite aluminum mass is determined by the aluminum content of the zeolite as measured by inductively coupled plasma – atomic emission spectroscopy (ICP-AES) and the zeolite weight percentage in the catalyst. Unless otherwise noted, the analytical methods used herein such as ASTM 5291 are available from ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA, USA.

[0036] In the final calcining step, the ion exchanged catalyst may be heated at conditions including a temperature of from 450°C to 650°C for a period of from 10 minutes to 20 hours to produce the aromatic alkylation catalyst. In an embodiment, the final calcining conditions include a temperature of from 500°C to 650°C for a period of from 10 minutes to 10 hours; and the period may be from 10 minutes to 5 hours. In an embodiment, the final calcining step is conducted at a pressure from 69 kPa(a) to 138 kPa(a) (10 to 20 psia). The final

calcining step atmosphere may be inert, such as nitrogen. In another embodiment the final calcining step atmosphere may comprise oxygen, for example, from 1 to 21 mole % oxygen; the atmosphere may be air. Other constituents such as water vapor and/or ammonia may also be present in the final calcining step atmosphere. The final calcining step may be conducted
5 in a variety of batch and/or continuous equipment as is known in the art such as box ovens, belt ovens, and rotating kilns. The conditions of the final calcining step may be the same as or different from the conditions of the first calcining step.

[0037] The final calcining conditions are adjusted as needed to obtain the level of nitrogen on the aromatic alkylation catalyst that will result in the desired nitrogen to zeolite
10 aluminum molar ratio. The precise final calcining conditions may vary with number, type, and conditions of the prior processing steps employed and with the specific equipment and conditions, such as the atmosphere and heating and cooling rates, used to perform the final calcining step. In general, adjustments to the final calcining step temperature and time at temperature provide the greatest change in the nitrogen content and N/Al₂O₃ of the aromatic
15 alkylation catalyst produced. For example, with other variables held constant, the nitrogen content of the catalyst will increase as the calcination time and/or temperature are decreased. Generally, calcination conditions that are less severe, i.e. causing less zeolite dealumination will result in catalysts with higher nitrogen contents.

[0038] The process disclosed herein can be expected to be applicable generally to the
20 alkylation of an alkylation substrate with an alkylation agent. The process disclosed herein is more specifically applicable to the production of an alkyl aromatic by alkylation of a feed aromatic with a feed olefin. Although benzene is the principal feed aromatic of interest, feed aromatics such as alkyl-substituted benzenes, condensed ring systems generally, and alkylated derivatives thereof may be used. Examples of such feed aromatics are toluene,
25 ethylbenzene, propylbenzene, and the like; xylene, mesitylene, methylethylbenzene, and the like; naphthalene, anthracene, phenanthrene, methylnaphthalene, dimethyl-naphthalene, and tetralin. More than one feed aromatic can be used. The feed aromatic may be introduced into an alkylation catalyst bed in one or more aromatic feed stream. Each aromatic feed stream may contain one or more feed aromatics. In addition to the feed aromatic(s), an aromatic feed
30 stream may contain non-aromatics, including but not limited to, saturated and unsaturated cyclic hydrocarbons that have the same, one more, or one less, number of carbon atoms as the

feed aromatic. For example, an aromatic feed stream containing benzene may also contain cyclohexane, cycloheptane, cyclohexenes, or cycloheptenes, as well as methylated versions of any of these hydrocarbons, or mixtures thereof. The concentration of each feed aromatic in each aromatic feed stream may range from 0.01 to 100 wt-%.

5 **[0039]** Feed olefins containing from 2 to 6 carbon atoms are the principal alkylating agents contemplated for the process disclosed herein. Examples of such feed olefins include C2-C4 olefins, namely ethylene, propylene, butene-1, cis-butene-2, trans-butene-2, and iso-butene. However, feed olefins having from 2 to 20 carbon atoms may be used effectively in the process disclosed herein. More than one feed olefin may be used. The feed olefin may be
10 introduced into an alkylation catalyst bed in one or more olefinic feed streams. Each olefinic feed stream may contain one or more feed olefins. In addition to the feed olefin(s), an olefinic feed stream may contain non-olefins, such as paraffins that have the same number of carbon atoms as the olefin. For example, a propylene-containing olefinic feed stream may also contain propane, while an olefinic feed stream containing ethylene may also contain ethane.
15 The concentration of each feed olefin in each olefinic feed stream may range from 0.01 to 100 wt-%.

[0040] The most widely practiced hydrocarbon conversion processes to which the present invention is applicable are the catalytic alkylation of benzene with ethylene to produce ethylbenzene, the catalytic alkylation of benzene with propylene to produce cumene, and the
20 catalytic alkylation of benzene with butene to produce butylbenzene. Although the discussion herein of the present invention refers to a catalytic cumene reaction system, the discussion is also in reference to its application to a catalytic ethylbenzene reaction system. It is not intended that this discussion limit the scope of the present invention as set forth in the claims.

[0041] In practicing the process disclosed herein, a portion of the effluent of the
25 alkylation reaction zone can be reintroduced into the alkylation reaction zone. Unless otherwise noted in this specification, the term "portion," when describing a process stream, refers to either an aliquot portion of the stream or a dissimilar fraction of the stream having a different composition than the total stream from which it was derived. An aliquot portion of the stream is a portion of the stream that has essentially the same composition as the stream
30 from which it was derived. The ratios of the effluent to combined fresh feeds range from 0 to 20 and preferably from 0 to 10 on a weight basis. Alkylation is preferably performed in

either mixed or the liquid phase. Consequently, reaction pressure needs to be sufficiently high to ensure at least a partial liquid phase. Where ethylene is the olefin, the pressure range for the reactions is usually from 1379 kPa(g) (200psi(g)) to 6985 kPa(g) (1000 psi(g)), more commonly from 2069 kPa(g) (300psi(g)) to 4137 kPa(g) (600 psi(g)), and even more commonly from 3103 kPa(g) (450psi(g)) to 4137 kPa(g) (600 psi(g)). Preferably, the reaction conditions are sufficient to maintain benzene in a liquid phase and are supercritical conditions for ethylene. Pressure is not a critical variable in the success of the process disclosed herein, however, and the only criterion is that the pressure be sufficiently great to ensure at least partial liquid phase. For olefins other than ethylene, the process disclosed herein may be practiced generally at a pressure of from 345 kPa(g) (50psi(g)) to 6985 kPa(g) (1000 psi(g)).

[0042] The overall weight hourly space velocity (WHSV) of the feed olefin may range from 0.01 to 8.0 hr⁻¹. As used herein, weight hourly space velocity of a component means the weight flow rate of the component per hour divided by the catalyst weight, where the weight flow rate of the component per hour and the catalyst weight are in the same weight units. The WHSV of aromatics, including benzene and a polyalkylaromatic having at least two C₂+ groups, if any, is generally from 0.3 to 480 hr⁻¹. In a preferred embodiment, in which the polyalkyl aromatic is a diethylbenzene or a triethylbenzene, the molar ratio of benzene per ethylene is from 1.5:1 to 6:1, the WHSV of ethylene is from 0.1 to 6.0 hr⁻¹, and the WHSV of aromatics including benzene and the polyethylbenzenes is from 0.5 to 70 hr⁻¹.

EXAMPLES

[0043] As synthesized UZM-8 of Si/Al₂ molar ratio of 20 is prepared as per the following method. In a large beaker, 160.16 grams of diethyldimethylammonium hydroxide is added to 1006.69 grams de-ionized water, followed by 2.79 grams of 50 wt% NaOH solution. Next, 51.48 grams of liquid sodium aluminate is added slowly and stirred for 20 minutes. Then, 178.89 grams of SiO₂ (sold in commerce as Ultrasil) is slowly added to the gel and stirred for 20 minutes. Next, 24 grams of UZM-8 seed is added to the gel, and stirred for an additional 20 minutes. The gel is then transferred to a 2-liter stirred reactor and heated to 160° C in 2 hours and subsequently crystallized for 115 hours. After digestion, the material is filtered and washed with de-ionized water and dried at 100° C. XRD (X-Ray Diffraction) analysis of

the resulting material shows pure UZM-8. The elemental analysis by inductively coupled plasma – atomic emission spectroscopy (ICP-AES) shows a Si/Al₂ molar ratio of 20.

[0044] Example 1 is a comparative example that is made of 70 wt% UZM-8 and 30 wt% alumina. In preparing the catalyst, the as synthesized UZM-8 is first mixed and mulled with HNO₃ peptized Catapal C alumina (made using a HNO₃ to alumina weight ratio of 0.17) to attain dough consistency readily to be extruded into pellets of a cylindrical shape of 1/16" diameter. The extrudate was calcined at 600°C in flowing air for 1 hour. The calcined catalyst was then ammonium ion exchanged to remove sodium using 10 wt% ammonium nitrate solution at a dosage of 1 gram ammonium nitrate per gram of calcined catalyst at 60°C.

[0045] Example 2 is also a comparative example that is made in the same manner as example 1 with the exception that it contains 50 wt% UZM-8 and 50 wt% alumina in a trilobed shape of 1/16" circumference.

[0046] Examples 3 and 4 represent those used in this invention, and contain 30 and 12 wt% UZM-8 zeolite, respectively, with the balance being alumina in a trilobed shape of 1/16" circumference.

[0047] To test the catalyst performance, 25 grams of catalyst was mixed with quartz sand to fill the interstitial voids to ensure proper flow distribution before being loaded into a 7/8" ID standard steel reactor. The catalyst was dried down with flowing benzene pretreated using 3A dryer at 200°C for 12 hours. After the drydown, the recycle benzene was introduced followed by propylene. The benzene to propylene molar ratio for the test was targeted at 2.0, with a product effluent to combined fresh feed ratio of 7.4 on a weight basis, propylene weight hourly space velocity of 1.04 hr⁻¹, an inlet temperature of 115°C, and an outlet pressure of 3549 kPa (500 psig). The product effluent was monitored by on-line GC. The performance of catalyst examples 1 through 4 is summarized in the following table. The catalyst activity measured by olefin conversions across the reactor is consistently near 100% and shows no indication of lowered activity with reduced zeolite contents from 70 to 2 wt%. Furthermore, the total alkylated product selectivity is consistently close to 100%, even at very low zeolite contents under very severe but economic process conditions of a benzene to olefin molar ratio of 2.0 and an inlet temperature of 115°C.

Table 1

Ex.	UZM-8 Zeolite %	% C3= Conv.	total alkylated selectivity, %	Size of Active Zone, inches	catalyst bed length, inches	% Active Zone	cumene/(cumene +DIPB+TIPB)
#1	70	99.8	99.76	1.75	6.18	28	80.8
#2	50	99.86	99.7	2.5	6.15	41	78.9
#3	30	99.86	99.75	1.5	5.66	27	78.7
#4	12	99.87	99.75	1.75	4.75	37	81.5
#5	7	99.67	99.74	2.93	6.35	46	81.4
#6	2	99.63	99.73	-----	-----	-----	83.5

[0048] The catalyst activity measured by the size of the active zone is summarized in Figure 1. It is unexpected to discover that the size of the active zone going from 70 to 7 wt% zeolite stays relatively constant and the variability is within the reproducibility of catalyst bed locations. Furthermore, the total alkylated selectivity is maintained at 99.7% or higher with decreasing zeolite contents, and the mono-alkylate selectivity increase from 80 to 84%.

SPECIFIC EMBODIMENTS

While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

A first embodiment of the invention is a method for alkylation of feedstock comprising contacting the feedstock comprising at least one alkylatable aromatic compound and an alkylating agent with a first alkylating catalyst composition under alkylating conditions, the first alkylating catalyst composition comprising UZM-8 zeolite, nitrogen, and a binder, the first alkylating catalyst composition having 2-20 wt% UZM-8 zeolite, and the catalyst having a nitrogen to zeolite aluminum molar ratio of between 0.01 to 0.040 to produce a product stream; wherein a total alkylated selectivity at a temperature and a molar ratio of alkylatable aromatic compound to alkylating agent is greater than 99.0%; and

contacting the product stream with a second alkylating catalyst to convert the unconverted olefins existing from the first alkylating catalyst. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the first alkylating catalyst composition has 10 wt% UZM-8 zeolite. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph comprises zeolite UZM-8, UZM-37, MCM-22, BEA, FAU or a mixture of thereof at a combined zeolite content of greater than 30wt%. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph comprises zeolite UZM-8, UZM-37, MCM-22, BEA, FAU or a mixture of thereof at a combined zeolite content of greater than 30wt%. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising contacting the feedstock with at least one additional catalyst composition before contacting the feedstock with the first alkylating catalyst composition, the at least one additional catalyst composition capable of reacting with one or more of nitrogen, oxygenate species, sulfur, or metals, to reduce a level of nitrogen, oxygen, sulfur, or metals in the feedstock. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising contacting the effluent exiting the first alkylating catalyst with the second alkylating catalyst composition comprising a zeolite and a binder, the second alkylating catalyst composition having greater than 30 wt% zeolite. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the alkylating conditions include a temperature of from 90°C to 230°C, a pressure of from 1.3 MPa to 4.8 MPa, a molar ratio of alkylatable aromatic compound to alkylating agent of from 1 to 5, and a feed hourly weight space velocity based on the alkylating agent of from 0.5 to 10 hr⁻¹. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the alkylatable aromatic compound is benzene, the alkylating agent is propylene, and the propylene conversion across the first catalyst composition is greater than 90%. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the alkylatable aromatic compound is benzene, the alkylating agent is propylene, and the propylene conversion across the first catalyst composition is greater than 95%. An

embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the alkylatable aromatic compound is benzene, the alkylating agent is ethylene, and the ethylene conversion across the first catalyst composition is greater than 80%. An embodiment of the invention is one, any or all of prior
5 embodiments in this paragraph up through the first embodiment in this paragraph wherein the alkylatable aromatic compound is benzene, the alkylating agent is ethylene, and the ethylene conversion across the first catalyst composition is greater than 90%. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first
10 embodiment in this paragraph wherein the alkylatable aromatic compound is benzene, the alkylating agent is butene, and the butene conversion across the first catalyst composition is greater than 95%. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the alkylatable
aromatic compound is benzene, the alkylating agent is butene, and the butene conversion across the first catalyst composition is greater than 97%. An embodiment of the invention is
15 one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the second alkylating catalyst is made up of less than 50% and preferably less than 30% of the total alkylating catalysts.

A second embodiment of the invention is a method for alkylation of feedstock comprising contacting the feedstock comprising at least one alkylatable aromatic compound
20 and an alkylating agent with at least one additional catalyst composition, the at least one additional catalyst composition capable of reacting with one or more of nitrogen, oxygen, sulfur, or metals, forming a feedstock having a reduced level of nitrogen, oxygen, sulfur, or metals; contacting the feedstock with the reduced level of nitrogen, oxygen, sulfur, or metals
with a first alkylating catalyst composition under alkylating conditions, the first alkylating
25 catalyst composition comprising UZM-8 zeolite and a binder, the first alkylating catalyst composition having 2-20 wt% UZM-8 zeolite; wherein a total alkylated selectivity at a temperature and a molar ratio of alkylatable aromatic compound to alkylating agent is greater than 99.0%; and contacting the product stream with a second alkylating catalyst to convert
the unconverted olefins existing from the first alkylating catalyst. An embodiment of the
30 invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the first alkylating catalyst composition has 2 wt% to 10 wt% UZM-8 zeolite. An embodiment of the invention is one, any or all of prior

embodiments in this paragraph up through the second embodiment in this paragraph further comprising contacting the effluent exiting the first alkylating catalyst with a second alkylating catalyst composition comprising a zeolite and a binder, the second alkylating catalyst composition having greater than 30 wt% zeolite. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprises second alkylating catalyst composition comprises a zeolite selected from zeolite UZM-8, UZM-37, MCM-22, BEA, FAU, and a mixture of thereof at a combined zeolite content of greater than 30wt%. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the alkylating conditions include a temperature of from 90°C to 230°C, a pressure of from 1.3 MPa to 4.8 MPa, a molar ratio of alkylatable aromatic compound to alkylating agent of from 1 to 5, and a feed hourly weight space velocity based on the alkylating agent of from 0.5 to 10 hr⁻¹. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph where the second alkylating catalyst is made up of less than 50 and preferably less than 30% of the total alkylating catalysts.

Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present invention to its fullest extent and easily ascertain the essential characteristics of this invention, without departing from the spirit and scope thereof, to make various changes and modifications of the invention and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

CLAIMS

1. A method for alkylation of feedstock comprising:

contacting the feedstock comprising at least one alkylatable aromatic compound and an alkylating agent with a first alkylating catalyst composition under alkylating conditions, the first alkylating catalyst composition comprising UZM-8 zeolite, nitrogen, and a binder, the first alkylating catalyst composition having 2-10 wt% UZM-8 zeolite, and the catalyst having a nitrogen to zeolite aluminium molar ratio of between 0.01 to 0.040 to produce a product stream;

wherein a total alkylated selectivity at a temperature and a molar ratio of alkylatable aromatic compound to alkylating agent is greater than 99.0%; and

contacting the product stream with a second alkylating catalyst to convert the unconverted olefins exiting from the first alkylating catalyst, the second alkylating catalyst composition having greater than 30 wt% zeolite, the second alkylating catalyst composition is made of less than 30% of the total alkylating catalyst composition.

2. The method of claim 1 wherein the first alkylating catalyst composition has 10 wt% UZM-8 zeolite.

3. The second alkylating catalyst of claim 1 comprises zeolite UZM-8, UZM-37, MCM-22, BEA, FAU or a mixture of thereof at a combined zeolite content of greater than 30wt%.

4. The second alkylating catalyst of claim 2 comprises zeolite UZM-8, UZM-37, MCM-22, BEA, FAU, or a mixture of thereof at a combined zeolite content of greater than 30wt%.

5. The method of claim 1 further comprising contacting the feedstock with at least one additional catalyst composition before contacting the feedstock with the first alkylating catalyst composition, the at least one additional catalyst composition capable of reacting with one or more of nitrogen, oxygenate species, sulfur, or metals, to reduce a level of nitrogen, oxygen, sulfur, or metals in the feedstock.

6. The method of claim 1 further comprising contacting the effluent exiting the first alkylating catalyst with the second alkylating composition comprising a zeolite and a binder.

7. The method of claim 1 wherein the alkylating conditions include a temperature of 90°C to 230°C, a pressure of from 1.3 MPa to 4.58 MPa, a molar ratio of alkylatable

aromatic compound to alkylating agent of from 1 to 5, and a feed hourly weight space velocity based on the alkylating agent of from 0.5 to 10 hr⁻¹.

8. The method of claim 1 wherein the alkylatable aromatic compound is benzene, the alkylating agent is propylene, and the propylene conversion across the first catalyst composition is greater than 90%.

9. The method of claim 1 wherein the alkylatable aromatic compound is benzene, the alkylating agent is propylene, and the propylene conversion across the first catalyst composition is greater than 95%.

10. The method of claim 1 wherein the alkylatable aromatic compound is benzene, the alkylating agent is ethylene, and the ethylene conversion across the first catalyst composition is greater than 80%.