

**TRANSALKYLATION PROCESS AND
CATALYST COMPOSITION USED THEREIN**

5 **INVENTORS:** Brett T. Loveless, Jean W. Beeckman, Christopher G. Oliveri, Scott J. Weigel,
Matthew S. Ide, Theresa A. Baumrucker.

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to and the benefits of U.S. Provisional Application
No. 62/450,122, filed January 25, 2017, and EP Application No. 17161741.8, filed March 20,
10 2017, the disclosures of which are incorporated by reference in their entireties.

FIELD OF THE INVENTION

[0002] The present invention relates to a process for the transalkylation of aromatics,
particularly the transalkylation of poly-isopropylbenzene (PIPB) with benzene to produce
cumene and the transalkylation of poly-ethylbenzene (PEB) with benzene to produce
15 ethylbenzene.

BACKGROUND OF THE INVENTION

[0003] Ethylbenzene is a valuable commodity chemical and is used in the production of
styrene monomer. Cumene (isopropylbenzene) is also a valuable commodity chemical and is
used in the production of phenol and acetone.

20 [0004] Presently, ethylbenzene is often produced by a liquid phase alkylation process from
benzene and ethylene in the presence of an alkylation catalyst. The liquid phase process
operates at a lower temperature than its vapor phase counterpart. One advantage of the liquid
phase alkylation is a lower yield of undesired by-products, poly-alkylated aromatic
compound(s). The alkylation of aromatic hydrocarbon compounds employing zeolite catalysts
25 is known and understood in the art. U.S. Pat. No. 5,334,795 describes the liquid phase
alkylation of benzene with ethylene in the presence of MCM-22 to produce ethylbenzene; and
U.S. Pat. No. 4,891,458 discloses liquid phase alkylation and transalkylation processes using
zeolite beta.

[0005] Cumene is often produced by a liquid phase alkylation process from benzene and
30 propylene in the presence of a zeolite-based alkylation catalyst. U.S. Pat. No. 4,992,606
discloses a process for preparing cumene using MCM-22 in liquid phase.

[0006] Commercial alkylation processes for the production of ethylbenzene and cumene
typically produce certain poly-alkylated by-products in addition to desired ethylbenzene and
cumene. The poly-alkylated aromatic compound(s) may be transalkylated with benzene or
35 other alkylatable aromatic compound(s) to produce additional ethylbenzene or cumene. This

5 transalkylation reaction may be accomplished by feeding the poly-alkylated aromatic compound(s) through a transalkylation reactor operated under suitable conditions and in the presence of a transalkylation catalyst. U.S. Pat. No. 5,557,024 discloses a process for preparing short chain alkyl aromatic compounds using MCM-56 and the use of zeolite catalysts such as MCM-22, zeolite X, zeolite Y and zeolite beta for the transalkylation of the poly-alkylated aromatic compound(s).

[0007] Despite the advances in the liquid phase aromatic alkylation process, there is a need for an improved transalkylation process which has a higher conversion of the poly-alkylated aromatic compounds to the desired mono-alkylated aromatic compound, such as ethylbenzene or cumene.

15 **SUMMARY OF THE INVENTION**

[0008] Higher conversion of the poly-alkylated aromatic compounds to the desired mono-alkylated aromatic compounds in transalkylation processes may be achieved by the use of a higher-activity transalkylation catalyst composition. It has been discovered that a higher-activity transalkylation catalyst composition may be produced by increasing the external surface area/volume (SA/V) ratio of the transalkylation catalyst composition to a selected range of 30 cm⁻¹ to 85 cm⁻¹ combined with reducing the silica-to-alumina (Si/Al₂) molar ratio of the zeolite in the composition to a range of 10 to 15.

[0009] In one aspect, the invention is a process for producing ethylbenzene or cumene comprising one or more steps. In step (a), a transalkylation catalyst composition, described below, is provided to a reaction zone. In step (b), a stream comprising poly-alkylated benzene and an alkylatable aromatic compound stream comprising benzene are provided to the reaction zone. The poly-alkylated benzene stream comprises di-ethylbenzene or di-isopropylbenzene. In step (c), the poly-alkylated benzene stream is contacted with the benzene stream in the presence of the aforementioned transalkylation catalyst composition under at least partial liquid phase transalkylation conditions to produce a transalkylation effluent stream. Such effluent comprises ethylbenzene or cumene. The liquid phase transalkylation conditions include a temperature of 100°C to 300°C and a pressure of 200 kPa-a to 6000 kPa-a.

[0010] In one or more embodiments of the process, the catalytic activity of the transalkylation catalyst composition of this invention is higher (i.e., lower molar silica-content) than the catalytic activity of a lower-activity (i.e., higher molar silica-content) transalkylation catalyst composition which comprises said zeolite and has a silica-alumina molar ratio in the range of 25 to 37 when the catalysts are compared under equivalent transalkylation conditions.

5 **[0011]** In one or more embodiments of the process, the higher-activity (i.e., lower silica-content) transalkylation catalyst composition of this invention when employed in a process for producing ethylbenzene or cumene, exhibits a weight hourly space velocity of the poly-alkylated benzene stream that is higher than the weight hourly space velocity of a lower-activity (i.e., higher silica-content) transalkylation catalyst composition employed in such process, 10 where the catalysts are compared under equivalent transalkylation conditions. In another embodiment, a portion of the stream comprising benzene is contacted with an alkylating agent stream under alkylation conditions and in the presence of an alkylation catalyst to produce an alkylation effluent which comprises a mono-alkylated benzene and the poly-alkylated benzene. Thereafter, the alkylation effluent is separated to recover the poly-alkylated benzene stream in 15 which a portion is supplied to step (b) of the process for producing ethylbenzene or cumene.

[0012] In still another embodiment, the benzene stream is an impure stream which further comprises nitrogenous impurities. The impure stream is contacted with a treatment material under treatment conditions to remove at least a portion of the nitrogenous impurities. The treatment material is selected from the group consisting of clay, resin, activated alumina, a 20 molecular sieve and combinations thereof.

[0013] In another aspect, the present invention is a transalkylation catalyst which comprises a zeolite having a framework structure selected from the group consisting of FAU, BEA*, MOR, MWW and mixtures thereof. The zeolite has a silica-alumina molar ratio in a range of 10 to 15. The transalkylation catalyst composition has an external surface area/volume 25 ratio in the range of 30 cm^{-1} to 85 cm^{-1} .

[0014] In an embodiment, the catalytic activity of the transalkylation catalyst composition is higher than the catalytic activity of a higher silica-content transalkylation catalyst composition which comprises the zeolite and has a silica-alumina molar ratio in the range of 25 to 37 when the catalysts are compared under equivalent transalkylation conditions.

30 **DETAILED DESCRIPTION OF THE INVENTION**

[0015] Improved catalytic activity is exhibited by the transalkylation catalyst composition of this invention, described herein, when used in a process for producing a mono-alkylated aromatic compound, preferably ethylbenzene or cumene, by the transalkylation of a poly-alkylated aromatic compound with an alkylatable aromatic compound, preferably benzene, in 35 the presence of such composition under at least partial liquid phase transalkylation conditions.

[0016] To achieve the improved catalytic activity, the external surface area/volume ratio of transalkylation catalyst composition is increased to a selected range of 30 cm^{-1} to 85 cm^{-1} ,

5 and the silica-to-alumina (Si/Al₂) molar ratio of the zeolite is reduced to a selected range of 10 to 15. The zeolite has a framework structure selected from the group consisting of FAU, BEA*, MOR, MWW and mixtures thereof.

Definitions

[0017] The term “alkylatable aromatic compound” as used herein means an aromatic
10 compound that may receive an alkyl group. One non-limiting example of an alkylatable aromatic compound is benzene.

[0018] The term “alkylating agent” as used herein means a compound which may donate an alkyl group to an alkylatable aromatic compound. Non-limiting examples of an alkylating agent are ethylene, propylene, and butylene. Another non-limiting example is any poly
15 alkylated aromatic compound that is capable of donating an alkyl group to an alkylatable aromatic compound.

[0019] The term “aromatic” as used herein in reference to the alkylatable aromatic compounds which are useful herein is to be understood in accordance with its art-recognized scope which includes substituted and unsubstituted mono- and polynuclear compounds.
20 Compounds of an aromatic character which possess a heteroatom (e.g., N or S) are also useful provided they do not act as catalyst poisons, as defined below, under the reaction conditions selected.

[0020] The term “at least partial liquid phase” as used herein, means a mixture having at least 1 wt.% liquid phase, optionally at least 5 wt.% liquid phase, at a given temperature,
25 pressure, and composition.

[0021] The term “framework type” as used herein has the meaning described in the “Atlas of Zeolite Framework Types,” by Ch. Baerlocher, W.M. Meier and D.H. Olson (Elsevier, 5th Ed., 2001).

[0022] The term “MCM-22 family material” (or “MCM-22 family molecular sieve”), as
30 used herein, can include:

(i) molecular sieves made from a common first degree crystalline building block “unit cell having the MWW framework topology.” A unit cell is a spatial arrangement of atoms which is tiled in three-dimensional space to describe the crystal as described in the “Atlas of Zeolite Framework Types,” by Ch. Baerlocher, W.M. Meier and D.H. Olson (Elsevier, 5th Ed.,
35 2001);

(ii) molecular sieves made from a common second degree building block, a 2-dimensional tiling of such MWW framework type unit cells, forming a “monolayer of one unit

5 cell thickness,” preferably one c-unit cell thickness;

(iii) molecular sieves made from common second degree building blocks, “layers of one or more than one unit cell thickness”, wherein the layer of more than one unit cell thickness is made from stacking, packing, or binding at least two monolayers of one unit cell thick of unit cells having the MWW framework topology. The stacking of such second degree building blocks can be in a regular fashion, an irregular fashion, a random fashion, and any combination thereof; or

(iv) molecular sieves made by any regular or random 2-dimensional or 3- dimensional combination of unit cells having the MWW framework topology.

[0023] The MCM-22 family materials are characterized by having an X-ray diffraction pattern including d-spacing maxima at 12.4 ± 0.25 , 3.57 ± 0.07 and 3.42 ± 0.07 Angstroms (either calcined or as-synthesized). The MCM-22 family materials may also be characterized by having an X-ray diffraction pattern including d-spacing maxima at 12.4 ± 0.25 , 6.9 ± 0.15 , 3.57 ± 0.07 and 3.42 ± 0.07 Angstroms (either calcined or as-synthesized). The X-ray diffraction data used to characterize the molecular sieve are obtained by standard techniques using the K-alpha doublet of copper as the incident radiation and a diffractometer equipped with a scintillation counter and associated computer as the collection system.

[0024] Members of the MCM-22 family include, but are not limited to, MCM-22 (described in U.S. Patent No. 4,954,325), PSH-3 (described in U.S. Patent No. 4,439,409), SSZ-25 (described in U.S. Patent No. 4,826,667), ERB-1 (described in European Patent 0293032), ITQ-1 (described in U.S. Patent No. 6,077,498), ITQ-2 (described in International Patent Publication No. WO97/17290), ITQ-30 (described in International Patent Publication No. WO2005118476), MCM-36 (described in U.S. Patent No. 5,250,277), MCM-49 (described in U.S. Patent No. 5,236,575), MCM-56 (described in U.S. Patent No. 5,362,697; and an EMM-10 family molecular sieve (described or characterized in U.S. Patent Nos. 7,959,899 and 8,110,176; and U.S. Patent Application Publication No. 2008/0045768), such as EMM-10, EMM-10-P, EMM-12 and EMM-13.

[0025] Related zeolites to be included in the MCM-22 family are UZM-8 (described in U.S. Patent No. 6,756,030) and UZM-8HS (described in U.S. Patent No. 7,713,513), UZM-37 (described in U.S. Patent No. 8,158,105), all of which are also suitable for use as the molecular sieve of the MCM-22 family. Typically, the molecular sieve of the MCM-22 family is in the hydrogen form and having hydrogen ions, for example, acidic.

5 [0026] Typically, the molecular sieve of the MCM-22 family is in the hydrogen form and having hydrogen ions, for example, acidic. The entire contents of each of the aforementioned patents are incorporated herein by reference.

[0027] The term “mono-alkylated aromatic compound” means an aromatic compound that has only one alkyl substituent. Non-limiting examples of mono-alkylated aromatic compounds
10 are ethylbenzene, iso-propylbenzene (cumene) and sec-butylbenzene.

[0028] The term “poly-alkylated aromatic compound” as used herein means an aromatic compound that has more than one alkyl substituent. A non-limiting example of a poly-alkylated aromatic compound is poly-ethylbenzene, e.g., di-ethylbenzene, tri-ethylbenzene, and poly-isopropylbenzene, e.g., di-isopropylbenzene, and tri-isopropylbenzene.

15 [0029] The term “regenerated” when used in connection with the alkylation catalyst or the transalkylation catalyst herein means an at least partially deactivated catalyst that has been treated under controlled conditions of oxygen content and temperature to remove at least a portion of the coke deposited or to remove at least a portion of adsorbed catalyst poisons and thereby increase the catalytic activity of such material or catalyst.

20 [0030] The term “fresh” when used in connection with the molecular sieve, the guard bed material, the alkylation catalyst, or the transalkylation catalyst herein means the molecular sieve or such catalyst has not been used in a catalytic reaction after being manufactured.

[0031] The term “impurities” as used herein includes, but is not limited to, compounds having at least one of the following elements: nitrogen, halogens, oxygen, sulfur, arsenic,
25 selenium, tellurium, phosphorus, and Group 1 through Group 12 metals.

Process

[0032] In one aspect, the invention is a process for producing a mono-alkylated aromatic compound, preferably, ethylbenzene or cumene, comprising one or more steps. In step (a) of the process, a transalkylation catalyst composition, described herein, is provided to a reaction
30 zone. In step (b) of the process, a stream comprising poly-alkylated benzene and an alkylatable aromatic compound stream comprising benzene are provided to the reaction zone. The poly-alkylated benzene stream used to produce ethylbenzene comprises di-ethylbenzene. The poly-alkylated benzene stream used to produce cumene is di-isopropylbenzene. In step (c) of the process, the poly-alkylated benzene stream is contacted with the benzene stream in the presence
35 of the aforementioned transalkylation catalyst composition under at least partial liquid phase transalkylation conditions to produce a transalkylation effluent stream comprising ethylbenzene or cumene.

5 **[0033]** The products of the transalkylation reaction of the invention include ethylbenzene from the transalkylation reaction of a poly-ethylbenzene, such as di-ethylbenzene, with benzene, or cumene from the transalkylation reaction of poly-isopropylbenzene, such as di-isopropylbenzene, with benzene.

10 **[0034]** The transalkylation effluent is separated in a conventional separation system to recover the desired ethylbenzene stream or a cumene stream. Such conventional separation system, includes, for example, a benzene column, an ethylbenzene or cumene column, and a poly-alkylated column to recover the poly-ethylbenzene stream or the poly-isopropylbenzene stream.

15 **[0035]** The poly-alkylated benzene stream is produced from an alkylation process step which is particularly intended to produce mono-alkylated aromatic compounds, such as ethylbenzene and cumene in an alkylation step; however, the alkylation step will normally produce some poly-alkylated aromatic compounds, such as poly-ethylbenzene or poly-isopropylbenzene.

20 **[0036]** In an alkylation step, a portion of the stream comprising benzene, or a portion thereof, is contacted with a stream comprising an alkylating agent under alkylation conditions and in the presence of an alkylation catalyst to produce an alkylation effluent. This effluent stream comprises mono-alkylated benzene and poly-alkylated benzene stream. Preferably, the alkylating agent is ethylene and used to alkylate benzene to produce ethylbenzene, or propylene and used to alkylate benzene to produce cumene. In one embodiment, the mono-alkylated benzene is ethylbenzene and said poly-alkylated benzene is poly-ethylbenzene. In another embodiment, the mono-alkylated benzene is cumene and said poly-alkylated benzene is poly-isopropylbenzene.

25 **[0037]** In one or more embodiments, the alkylation effluent is separated to recover said poly-alkylated benzene stream. The recovered poly-alkylated benzene stream may then be supplied to step (b) of the process to produce ethylbenzene or cumene.

30 **[0038]** In one or more embodiments, the stream comprising benzene is an impure stream which further comprises nitrogenous impurities. The process of this invention, may further comprising the step of contacting the impure stream with a treatment material under treatment conditions to remove at least a portion of the nitrogenous impurities. The treatment material is selected from the group consisting of clay, resin, activated alumina, Linde type X, Linde type A and combinations thereof.

5 **[0039]** When a treatment material is used to remove a portion of impurities, suitable treatment conditions include a temperature from about 30°C to 200°C, and preferably between about 60°C to 150°C, a weight hourly space velocity (WHSV) of from about 0.1 hr⁻¹ and about 200 hr⁻¹, preferably from about 0.5 hr⁻¹ to about 100 hr⁻¹, and more preferably from about 1.0 hr⁻¹ to about 50 hr⁻¹; and a pressure between about ambient and 3000 kPa-a.

10 **Transalkylation and Alkylation Conditions**

[0040] The process for producing a mono-alkylated aromatic compound, such as ethylbenzene or cumene, of this invention is conducted such that the organic reactants, i.e., the alkylatable aromatic compound, e.g. the benzene, and the alkylating agent, i.e. poly-alkylated benzene or ethylene or propylene, are brought into contact with an alkylation catalyst or a
15 transalkylation catalyst. The contact is made in a suitable reaction zone such as, for example, in a flow reactor containing a fixed bed of the catalyst composition, under effective alkylation or transalkylation conditions. Such conditions include at least partial liquid phase transalkylation conditions or at least partial liquid phase alkylation conditions.

[0041] In one or more embodiments, the reactants can be neat, i.e., free from intentional
20 admixture or dilution with other material, or they can include carrier gases or diluents such as, for example, hydrogen or nitrogen.

[0042] The at least partial liquid phase conditions for transalkylation can include at least one of the following: a temperature of about 100°C to about 300°C, or from about 150°C to about 260°C, a pressure of about 200 kPa to about 6000 kPa, or about 200kPa to about 500
25 kPa, a weight hourly space velocity (WHSV) based on the total feed of about 0.5 hr⁻¹ to about 100 hr⁻¹ on total feed, and aromatic/poly-alkylated aromatic compound weight ratio 1:1 to 6:1.

[0043] When the poly-alkylated aromatic compounds are poly-ethylbenzenes and are reacted with benzene to produce ethylbenzene, the transalkylation conditions include a temperature of from about 220°C to about 260°C, a pressure of from about 300 kPa to about
30 400 kPa, weight hourly space velocity of 2 to 6 on total feed and benzene/PEB weight ratio 2:1 to 6:1.

[0044] When the poly-alkylated aromatic compounds are poly-isopropylbenzenes (PIPBs) and are reacted with benzene to produce cumene, the conditions for transalkylation include a temperature of from about 100°C to about 200°C, a pressure of from about 300 kPa to about
35 400 kPa, a weight hourly space velocity of 1 to 10 on total feed and benzene/PIPB weight ratio 1:1 to 6:1.

5 **[0045]** The at least partial liquid phase conditions for alkylation can include at least one of the following: a temperature of from about 10°C and about 400°C, or from about 10°C to about 200°C, or from about 150°C to about 300°C, a pressure up to about 25000 kPa, or up to about 20000 kPa, or from about 100 kPa to about 7000 kPa, or from about 689 kPa to about 4601 kPa, a molar ratio of alkylatable aromatic compound to alkylating agent of from about 0.1:1 to
10 about 50:1, preferably from about 0.5:1 to 10:1, and a feed weight hourly space velocity (WHSV) of between about 0.1 and about 100 hr⁻¹, or from about 0.5 to 50 hr⁻¹, or from about 10 hr⁻¹ to about 100 hr⁻¹.

[0046] When benzene is alkylated with ethylene to produce ethylbenzene, the alkylation reaction may be carried out under at least partially liquid phase conditions for alkylation which
15 include a temperature between about 150°C and 300°C, or between about 200°C and 260°C, a pressure up to about 20000 kPa, preferably from about 200 kPa to about 5600 kPa, a WHSV of from about 0.1 hr⁻¹ to about 50 hr⁻¹, or from about 1 hr⁻¹ and about 10 hr⁻¹ based on the ethylene feed, and a ratio of the benzene to the ethylene in the alkylation reactor from 1:1 to 30:1 molar, preferably from about 1:1 to 10:1 molar.

20 **[0047]** When benzene is alkylated with propylene to produce cumene, the reaction may be carried out under at least partially liquid phase conditions for alkylation which include a temperature of up to about 250°C, preferably from about 10°C to about 200°C; a pressure up to about 25000 kPa, preferably from about 100 kPa to about 3000 kPa; and a WHSV of from about 1 hr⁻¹ to about 250 hr⁻¹, preferably from 5 hr⁻¹ to 50 hr⁻¹, preferably from about 5 hr⁻¹ to
25 about 10 hr⁻¹ based on the ethylene feed.

Alkylatable Aromatic Compounds

[0048] Substituted alkylatable aromatic compounds which can be alkylated herein must possess at least one hydrogen atom directly bonded to the aromatic nucleus. The aromatic rings can be substituted with one or more alkyl, aryl, alkaryl, alkoxy, aryloxy, cycloalkyl, halide,
30 and/or other groups which do not interfere with the alkylation reaction.

[0049] Suitable alkylatable aromatic hydrocarbons for any one of the embodiments of this invention include benzene, naphthalene, anthracene, naphthacene, perylene, coronene, and phenanthrene, with benzene being preferred.

[0050] Generally the alkyl groups, which can be present as substituents on the aromatic
35 compound, contain from 1 to about 22 carbon atoms and usually from about 1 to 8 carbon atoms, and most usually from about 1 to 4 carbon atoms.

5 [0051] Suitable alkyl substituted aromatic compounds for any one of the embodiments of this invention include toluene (also preferred), xylene, isopropylbenzene, normal propylbenzene, alpha-methylnaphthalene, ethylbenzene, cumene, mesitylene, durene, p-cymene, butylbenzene, pseudocumene, o-diethylbenzene, m-diethylbenzene, p-diethylbenzene, isoamylbenzene, isohexylbenzene, pentaethylbenzene, pentamethylbenzene; 1,2,3,4-
10 tetraethylbenzene; 1,2,3,5-tetramethylbenzene; 1,2,4-triethylbenzene; 1,2,3-trimethylbenzene, m-butyltoluene; p-butyltoluene; 3,5-diethyltoluene; o-ethyltoluene; p-ethyltoluene; m-propyltoluene; 4-ethyl-m-xylene; dimethylnaphthalene; ethylnaphthalene; 2,3-dimethylantracene; 9-ethylantracene; 2-methylantracene; o-methylantracene; 9,10-dimethylphenanthrene; and 3-methyl-phenanthrene. Higher molecular weight alkylated
15 aromatic hydrocarbons can also be used as starting materials and include aromatic hydrocarbons such as are produced by the alkylation of aromatic hydrocarbons with olefin oligomers. 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
20 high boiling fraction in which the alkyl group attached to the aromatic nucleus varies in size from about C₆ to about C₁₂. When cumene or ethylbenzene is the desired product, the present process produces acceptably little by-products such as xylenes. The xylenes made in such instances may be less than about 500 ppm.

[0052] Reformate containing substantial quantities of benzene, toluene and/or xylene
25 constitutes a useful feed for the process of this invention.

Alkylating Agents

[0053] The alkylating agents, which are useful in one or more embodiments of this invention, generally include any aliphatic or aromatic organic compound having one or more available alkylating olefinic groups capable of reaction with the alkylatable aromatic
30 compound. Preferably, the alkylating agent comprises an olefinic group having from 1 to 5 carbon atoms, or a poly-alkylated aromatics compound(s). More preferably, the alkylation agents are poly-ethylbenzene and poly-isopropylbenzene for the transalkylation reaction, and ethylene and propylene for the alkylation reaction. Examples of suitable alkylating agents for any one of the embodiments of this invention are olefins, preferably, ethylene, propylene, the
35 butenes, and the pentenes, and mixtures thereof; alcohols (inclusive of monoalcohols, dialcohols, trialcohols, etc.), such as methanol, ethanol, the propanols, the butanols, and the pentanols; aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde,

5 and n-valeraldehyde; and alkyl halides such as methyl chloride, ethyl chloride, the propyl chlorides, the butyl chlorides, and the pentyl chlorides, and so forth.

[0054] Mixtures of light olefins are especially useful as alkylating agents in the alkylation process of this invention. Accordingly, mixtures of ethylene, propylene, butenes, and/or pentenes which are major constituents of a variety of refinery streams, e.g., fuel gas, gas plant
10 off-gas containing ethylene, propylene, etc., naphtha cracker off-gas containing light olefins, refinery FCC propane/propylene streams, etc., are useful alkylating agents herein.

[0055] Poly-alkylated aromatic compounds suitable for one or more embodiments of this invention include, but are not limited to, di-ethylbenzenes, tri-ethylbenzenes and poly-ethylbenzene(s), as well as di-isopropylbenzenes (DIPBs), tri-isopropylbenzenes (TIPBs) and
15 poly-isopropylbenzene(s) or mixtures thereof.

Guard Bed

[0056] Generally, the alkylatable aromatic compound stream and the alkylating agent stream supplied to the present process are impure streams and will contain some level of reactive impurities (as defined above), such as, for example, nitrogen compounds, which are
20 small enough to enter the pores of the catalyst, preferably alkylation catalyst and/or transalkylation catalyst, and thereby poison the catalyst. Moreover, it is normal to supply all alkylatable aromatic compounds to the first alkylation and/or transalkylation reaction zone, but to divide and supply the alkylating agent between the alkylation and/or transalkylation catalyst beds. Thus, the catalyst in the first reaction zone is more likely to be poisoned by impurities.
25 Thus, to reduce the frequency with which the catalyst in the first reaction zone must be removed for replacement, regeneration or reactivation, the present process preferably employs a separate guard bed in the first alkylation and/or transalkylation reaction zone. Alternatively, the guard bed may be upstream of and separate from the first reaction zone. The effluent from the guard bed is a treated feed, such as, for example, a treated alkylatable aromatic compound and/or a
30 treated alkylating agent, which is then fed to the process of this invention.

[0057] The process of the invention, in one or more embodiments, further comprises the step of contacting said alkylatable aromatic compound and/or said alkylating agent with a treatment material to remove at least a portion of any impurities from said alkylatable aromatic compound or said alkylating agent. The treatment material may be selected from the group
35 consisting of clay, resin, activated alumina, a molecular sieve and combinations thereof. The molecular sieve may be selected from the group consisting Linde X, Linde A, zeolite beta, faujasite, zeolite Y, Ultrastable Y (USY), Dealuminized Y (Deal Y), Rare Earth Y (REY),

- 5 Ultrahydrophobic Y (UHP-Y), mordenite, TEA-mordenite, ZSM-3, ZSM-4, ZSM-14, ZSM-18, ZSM-20 and combinations thereof.

Transalkylation Catalyst Composition

[0058] In another aspect, the present invention is a transalkylation catalyst which comprises a zeolite having a framework structure selected from the group consisting of FAU, BEA*, MOR, MWW and mixtures thereof. The zeolite has a silica-alumina molar ratio in a
10 range of 10 to 15. The transalkylation catalyst composition has an external surface area/volume ratio in the range of 30 cm^{-1} to 85 cm^{-1} , or 40 cm^{-1} to 80 cm^{-1} , or 45 cm^{-1} or 75 cm^{-1} .

[0059] The zeolite having a FAU framework type may be selected from the group consisting of 13X, Ultrastable Y (USY) and its low sodium variant, dealuminized Y (Deal Y),
15 Ultrahydrophobic Y (UHP-Y), rare earth exchanged Y (REY), rare earth exchanged USY (RE-USY) and mixtures thereof. Preferably, the zeolite having a FAU framework type is USY.

[0060] The zeolite having a MOR framework type may be selected from the group consisting of mordenite, EMM-34, TEA-mordenite and mixtures thereof. Preferably, the zeolite having a BEA* framework type is EMM-34, which is disclosed and described in U.S.
20 Pub. 2016-0221832.

[0061] Preferably, the zeolite having a BEA* framework type is zeolite beta.

[0062] The zeolite having a MWW framework type is a MCM-22 family material. Such MCM-22 family material may be selected from the group consisting of MCM-22, PSH-3, SSZ-25, MCM-36, MCM-49, MCM-56, ERB-1, EMM-10, EMM-10-P, EMM-12, EMM-13, UZM-
25 8, UZM-8HS, ITQ-1, ITQ-2, ITQ-30 and mixtures of two or more thereof. Preferably, the MCM-22 family material of the zeolite having MWW framework type is MCM-22 or MCM-49.

[0063] In one or more embodiments, the transalkylation catalyst composition is acidic in active form and has protons. The zeolite can be combined in a conventional manner with an
30 oxide binder, such as alumina or silica, such that the final transalkylation contains between 1 and 100 wt.% of the zeolite, based on the weight of the catalyst composition. Alternatively, the acidic transalkylation catalyst composition comprises greater than 0 wt.% up to 99 wt.% of a binder, based on the weight of said transalkylation catalyst composition. The zeolite comprise from 1 wt.% up to 100 wt.%, or from 10 wt.% to 90 wt.%, or from 20 wt.% to 80
35 wt.% of the transalkylation catalyst composition. Preferably, the zeolite comprises from 65 wt.% to 80 wt.% of said transalkylation catalyst composition.

5 **[0064]** The binder may be a metal or a mixed metal oxide. The binder may be selected from the group consisting of alumina, silica, titania, zirconia, tungsten oxide, ceria, niobia and combinations thereof.

10 **[0065]** In a preferred embodiment, the transalkylation catalyst composition of this invention comprises a zeolite having a framework structure selected from the group consisting of FAU, BEA*, MOR, MWW and mixtures thereof, wherein the silica-alumina molar ratio of said zeolite is in a range of 10 to 15, or in the range 11 to 14, or in the range of 12 to 13:

 wherein said FAU framework structure is selected from the group consisting of 13X, low sodium ultrastable Y (USY), dealuminized Y (Deal Y), ultrahydrophobic Y (UHP-Y), rare earth exchanged Y (REY), rare earth exchanged USY (RE-USY), and mixtures thereof,

15 wherein said zeolite which has said BEA* framework structure is zeolite beta,

 wherein said zeolite which has MOR framework structure is selected from the group consisting of mordenite, EMM-34, TEA-mordenite, and mixtures thereof;

 wherein said zeolite which has said MWW framework structure is a MCM-22 family material, said MCM-22 family molecular sieve is any one of MCM-22, PSH-3, SSZ-25, MCM-36, MCM-49, MCM-56, ERB-1, EMM-10, EMM-10-P, EMM-12, EMM-13, UZM-8, UZM-8HS, UZM-37, ITQ-1, ITQ-2, ITQ-30, or combinations of two or more thereof;

 wherein said transalkylation catalyst has an external surface area/volume ratio in the range of 30 cm⁻¹ to 85 cm⁻¹; and

 wherein said zeolite comprises from 65 wt.% to 80 wt.% of said transalkylation catalyst composition.

25 **[0066]** The catalytic activity of the transalkylation catalyst composition of this invention is higher than the catalytic activity of a lower-activity (i.e., higher molar silica-content) transalkylation catalyst composition which comprises said zeolite and has a silica-alumina (Si/Al₂) molar ratio in the range of 25 to 37, or in the range 27 to 35, or in the range 29 to 33, when the catalysts are compared under equivalent transalkylation conditions. The higher catalytic activity of the transalkylation catalyst of this invention is achieved by decreasing the amount of silica in the composition which results in a lower silica-alumina molar ratio.

35 **[0067]** Accordingly, the higher-activity (i.e., lower silica-content) transalkylation catalyst composition of this invention when employed in a process for producing ethylbenzene or cumene, exhibits a weight hourly space velocity of the poly-alkylated benzene stream that is higher than the weight hourly space velocity of a lower-activity (i.e., higher silica-content) transalkylation catalyst composition employed in such process, where the catalysts are

5 compared under equivalent transalkylation conditions, such as equivalent transalkylation temperatures.

[0068] Alternatively, the higher-activity (i.e., lower silica-content) transalkylation catalyst composition of this invention when employed in a process for producing ethylbenzene or cumene, may be operated at a lower transalkylation temperature than that of a lower-activity
10 (i.e., higher silica-content) transalkylation catalyst composition employed in such process, where the catalysts are compared under equivalent transalkylation conditions.

[0069] Not to be bound by any theory, it is believed that the higher activity exhibited by the transalkylation catalyst composition of this invention is provided by the lower silica-alumina (Si/Al_2) molar ratio of the zeolite combined with the higher external surface
15 area/volume (SA/V) of the composition. The lower Si/Al_2 molar ratio provides higher alumina content which facilitates the transalkylation reaction. The higher SA/V ratio provides an increased surface area per unit volume for the transalkylation of the bulky reactants. This is particularly true of a reaction in the liquid phase.

Alkylation Catalyst

20 [0070] In one or more embodiments, the alkylation catalyst comprises an aluminosilicate. The aluminosilicate is any one of a MCM-22 family molecular sieve, faujasite, mordenite, zeolite-beta, or combinations of two or more thereof. The MCM-22 family molecular sieve is any one of MCM-22, PSH-3, SSZ-25, MCM-36, MCM-49, MCM-56, ERB-1, EMM-10, EMM-10-P, EMM-12, EMM-13, UZM-8, UZM-8HS, UZM-37, ITQ-1, ITQ-2, ITQ-30, or
25 combinations of two or more thereof.

[0071] In one or more embodiments, the alkylation catalyst is acidic in active form and has protons. The zeolite can be combined in a conventional manner with an oxide binder, such as alumina or silica, such that the final alkylation catalyst composition contains between 1 and 100 wt.% of the zeolite, based on the weight of said alkylation catalyst composition.
30 Alternatively, the acidic alkylation catalyst composition comprises greater than 0 wt.% up to 99 wt.% of a binder, based on the weight of said alkylation catalyst composition. The zeolite comprise from 1 wt.% up to 100 wt.%, or from 10 wt.% to 90 wt.%, or from 20 wt.% to 80 wt.% of the alkylation catalyst composition. Preferably, the zeolite comprises from 65 wt.% to 80 wt.% of said alkylation catalyst composition.

35 [0072] The binder may be a metal or a mixed metal oxide. The binder may be selected from the group consisting of alumina, silica, titania, zirconia, tungsten oxide, ceria, niobia and combinations thereof.

5 [0073] In one or more embodiments, said alkylation or transalkylation catalyst composition can be a fresh alkylation or transalkylation catalyst composition, an at least partially deactivated alkylation or transalkylation catalyst composition, or combinations thereof. In one or more embodiments, said at least partially deactivated alkylation or transalkylation catalyst was deactivated by coke deposition during its prior use in an alkylation or transalkylation
10 process.

Catalyst Regeneration

[0074] As the alkylation and/or transalkylation process of the invention proceeds, the alkylation and/or transalkylation catalyst composition will gradually lose its alkylation activity, such that the reaction temperature required to achieve a given performance parameter, such as,
15 for example, conversion of the alkylating agent, will increase. When the alkylation and/or transalkylation catalyst activity has decreased by some predetermined amount, typically 5% to 90% and, more preferably 10% to 50%, compared to the initial alkylation and/or transalkylation catalyst activity, the deactivated catalyst composition can be subjected to a regeneration procedure using any known method, such as the method disclosed in U.S. Patent No. 6,380,119
20 to BASF, incorporated herein by reference.

Examples

[0075] The invention will now be more particularly described with reference to the following Examples.

Effect of USY zeolite Si/Al₂ molar ratio on Transalkylation Performance

25 Examples 1 and 2 Catalyst Preparations

[0076] In Example 1, the catalyst composition (Catalyst A) contained 80 wt.% USY zeolite (Si/Al₂ = 30 molar) and 20 wt.% amorphous Al₂O₃ (alumina) in acidic form.

[0077] In Example 2, the catalyst composition (Catalyst B) contained 80 wt.% USY zeolite (Si/Al₂ = 12 molar) and 20 wt.% amorphous Al₂O₃ (alumina) in acidic form.

30

Catalyst Transalkylation Performance Evaluation for Examples 1 and 2

[0078] Following catalyst preparation, the transalkylation of poly-ethylbenzenes (PEB) with benzene was performed in a fixed bed reactor with Catalyst A and Catalyst B. The PEB stream included di-ethylbenzene (DEB). The test procedure consisted of loading the dried
35 catalyst into a batch reactor along with benzene. The reactor was then heated to 266°F (130°C) followed by the addition of PEB under an inert gas pressure of 300 psig (2068.43 kPa). For Catalyst A, the benzene/PEB ratio of 2:1 by weight and the weight hourly space velocity

5 (WHSV) of 1.1 hr^{-1} were set, and the reaction temperature increased stepwise to 190°C to achieve a target DEB conversion of 65%. For Catalyst B, the benzene/PEB ratio of 2:1 by weight and the weight hourly space velocity (WHSV) of 1.1 hr^{-1} were set, and the reaction temperature decreased stepwise to 177°C to achieve a target DEB conversion of 65%. Samples were removed periodically for the duration of the test and analyzed with gas chromatography
10 to determine the conversion of DEB.

[0079] Table 1 shows the performance data of Catalyst A and Catalyst B the transalkylation of poly-ethylbenzenes (PEB) with benzene as follows:

Table 1

	Catalyst A	Catalyst B	Catalyst A	Catalyst B
PEB WHSV, (hr^{-1})	1.1	1.1	0.86	1.74
Temp, $^{\circ}\text{C}$	190	177	190	190
DEB Conv.	65%	65%	65%	65%

15 As can be seen from Table 1, lower temperature operation is achieved at constant DEB conversion and at constant PEB throughput. Alternatively, higher PEB throughput is achieved at constant temperature and constant DEB conversion.

Effect of USY zeolite Catalyst Particle Size And Shape On Transalkylation Catalyst Activity
Examples 3 to 6 Catalyst Preparations

20 [0080] In Example 3, the catalyst composition (Catalyst C) contained 80 wt.% USY zeolite ($\text{Si}/\text{Al}_2 = 12$ molar) and 20 wt.% of an amorphous Al_2O_3 (alumina) in acidic form and having a particle size and shape of a 1/16 inch cylindrical extrudate.

[0081] In Example 4, the catalyst composition (Catalyst D) contained 80 wt.% USY zeolite ($\text{Si}/\text{Al}_2 = 12$ molar) and 20 wt.% of an amorphous Al_2O_3 (alumina) in acidic form and having
25 a particle size and shape of a 1/20 inch quadrulobe extrudate.

[0082] In Example 5, the catalyst composition (Catalyst C) contained 80 wt.% USY zeolite ($\text{Si}/\text{Al}_2 = 12$ molar) and 20 wt.% of an amorphous Al_2O_3 (alumina) in acidic form of Type 1 and having a particle size and shape of a 1/16 inch cylindrical extrudate.

[0083] In Example 6, the catalyst composition (Catalyst D) contained 80 wt.% USY zeolite
30 ($\text{Si}/\text{Al}_2 = 12$ molar) and 20 wt.% of an amorphous Al_2O_3 (alumina) in acidic form and having a particle size and shape of a 1/20 inch quadrulobe extrudate.

- 5 [0084] While the calculation of cylinder geometry is well known, the calculation of the quadrulobe geometry is more complex. The equations below detailed the calculations involved in determining the surface/volume (SA/V) of the quadrulobe materials.

Perimeter (P)	$6\pi r$
Cross Sectional Area (AX)	$(16+\pi)r^2$
Particle Surface Area (SA _i)	$SA_i = 2A_{xi} + P_iL$
Volume (Vi)	$V_i = A_{xi}L$
SA/V	$SA/V = \Sigma SA_i / \Sigma V_i$

- 10 [0085] Surface Area/Volume ratios were calculated for the quadrulobe and cylinder extrudates by approximating the particles as cylinders with a 0.25 mm diameter and 0.25 mm length. The following table below listed SA/V ratios for the particle sizes tested.

Name	1/20 inch Quadrulobe	1/16 inch Cylinder
Geometry	Quadrulobe	Cylinder
Diameter	1/20 inch*	1/16 inch
Length	¼ inch	¼ inch
SA/V (in ⁻¹)	198	88
SA/V (cm ⁻¹)	78	35

*Diameter was measured across the minimum.

Catalyst Activity Evaluation for Examples 3 to 6

- 15 [0086] Following catalyst preparation, the transalkylation of poly-ethylbenzenes (PEB) with benzene was performed in a fixed bed reactor with Catalyst C and Catalyst D and for Catalyst E and Catalyst F. The test procedure used was the same as described above. The Transalkylation activity was based on the DEB conversion. The transalkylation activity for Catalyst D was normalized to the transalkylation activity for Catalyst C. The transalkylation activity for Catalyst F was normalized to the transalkylation activity for Catalyst W.

Table 2

Catalyst	Alumina Type	Extrudate Particle Size/Shape	Normalized Transalkylation Activity
Catalyst C	Type 1	1/16 inch cylindrical	1
Catalyst D	Type 1	1/20 inch	1.5

		quadrulobe	
Catalyst E	Type 2	1/16 inch cylindrical	0.95
Catalyst F	Type 2	1/20 inch quadrulobe	1.3

5 **[0087]** As can be seen, Table 2 shows that the modification of the catalyst extrudate particle size and shape can influence significantly the transalkylation activity. Catalyst particles with smaller diameters and larger surface area to volume ratios are preferred for liquid phase reactions where mass transport limitations may persist.

10 **[0088]** Certain embodiments and features have been described using a set of numerical upper limits and a set of numerical lower limits. It should be appreciated that ranges from any lower limit to any upper limit are contemplated unless otherwise indicated. Certain lower limits, upper limits and ranges appear in one or more claims below. All numerical values take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

15 **[0089]** The term “comprising” (and its grammatical variations) as used herein is used in the inclusive sense of “having” or “including” and not in the exclusive sense of “consisting only of” or “consisting of.” The terms “a” and “the” as used herein are understood to encompass the plural as well as the singular.

20 **[0090]** Various terms have been defined above. To the extent a term used in a claim is not defined above, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Furthermore, all patents, test procedures, and other documents cited in this application are fully incorporated by reference to the extent such disclosure is not inconsistent with this application and for all jurisdictions in which such incorporation is permitted.

25 **[0091]** The foregoing description of the disclosure illustrates and describes the present disclosure. Additionally, the disclosure shows and describes only the preferred embodiments but, as mentioned above, it is to be understood that the disclosure is capable of use in various other combinations, modifications, and environments and is capable of changes or modifications within the scope of the concept as expressed herein, commensurate with the
30 above teachings and/or the skill or knowledge of the relevant art.

CLAIMS

5 *What is claimed is:*

1. A process for producing ethylbenzene or cumene comprising the steps of:

 (a) providing an transalkylation catalyst composition to a reaction zone, said transalkylation catalyst comprising a zeolite having a framework structure selected from the group consisting of FAU, BEA*, MOR, MWW and mixtures thereof, wherein the silica-
10 alumina molar ratio of said zeolite is in a range of 10 to 15, wherein said transalkylation catalyst composition is in the form of an extrudate having an external surface area/volume ratio in the range of 30 cm⁻¹ to 85 cm⁻¹;

 (b) providing a stream comprising a poly-alkylated benzene and a portion of an alkylatable aromatic compound stream to said reaction zone, wherein said poly-alkylated
15 benzene stream comprises di-ethylbenzene or di-isopropylbenzene and said alkylatable aromatic compound stream comprises benzene;

 (c) contacting said poly-alkylated benzene stream with said alkylatable aromatic compound stream in the presence of said transalkylation catalyst composition under at least partial liquid phase transalkylation conditions to alkylate the alkylatable aromatic compound
20 and produce a transalkylation effluent stream comprising ethylbenzene or cumene, wherein the catalytic activity of said transalkylation catalyst composition is higher than the catalytic activity of a higher silica-content transalkylation catalyst composition which comprises said zeolite and has a silica-alumina molar ratio in the range of 25 to 37 when said catalyst compositions are compared under equivalent transalkylation conditions.

25 (d) providing a stream comprising an alkylating agent and another portion of said alkylatable aromatic compound stream to another reaction zone;

 (e) contacting said another portion of said alkylatable aromatic compound stream with said stream comprising an alkylating agent under alkylation conditions in the presence of an alkylation catalyst to alkylate the alkylatable aromatic compound and produce an alkylation
30 effluent which comprises mono-alkylated benzene and said poly-alkylated benzene;

 (f) separating said alkylation effluent to recover said poly-alkylated benzene stream; and

 (g) supplying at least a portion of said poly-alkylated benzene stream to step (b).

35 2. The process of claim 1, wherein said alkylatable aromatic compound stream comprising benzene is an impure stream which further comprises nitrogenous impurities.

- 5
3. The process of claim 2, further comprising the step of contacting said impure stream with a treatment material under treatment conditions to remove at least a portion of said nitrogenous impurities, wherein said treatment conditions include a temperature from about 30°C to 200°C, a weight hourly space velocity (WHSV) of from about 0.1 hr⁻¹ and about 200
- 10 hr⁻¹, and a pressure between about ambient and 3000 kPa-a.
4. The process of any preceding claim, further comprising the step:
- (h) separating said transalkylation effluent stream to recover an ethylbenzene stream or a cumene stream.
- 15
5. The process of any preceding claim, further comprising the step:
- (i) separating said alkylation effluent stream to recover an ethylbenzene stream or a cumene stream.
- 20 6. The process of any preceding claim, wherein said mono-alkylated benzene is ethylbenzene, said poly-alkylated benzene is poly-ethylbenzene and said alkylating agent is ethylene.
7. The process of any preceding claim, wherein said mono-alkylated benzene is cumene,
- 25 said poly-alkylated benzene is poly-isopropylbenzene, and said alkylating agent is propylene.
8. The process of any preceding claim, wherein the weight hourly space velocity of said poly-alkylated benzene stream in said presence of said transalkylation catalyst composition is higher than the weight hourly space velocity in the presence of said higher silica-content transalkylation catalyst composition when said catalyst compositions are compared under
- 30 equivalent transalkylation conditions.
9. The process of claim 8, wherein the transalkylation temperatures are equivalent.
- 35 10. The process of any preceding claim, wherein said at least partial liquid phase transalkylation conditions include a temperature of 100°C to 200°C and a pressure of 200 kPa-a to 600 kPa-a.

5

11. The process of any preceding claim, wherein said alkylation conditions are at least partially liquid phase conditions and include a temperature of 150°C to 300°C and a pressure of up to about 20000 kPa, and a WHSV based on the weight of said alkylating agent from about 0.1 hr⁻¹ to about 30 hr⁻¹.

10

12. The process of any preceding claim, wherein the conversion of di-ethylbenzene or di-isopropylbenzene is in the range of about 25 wt. % to about 95 wt. %.

13. The process of any preceding claim, wherein said zeolite which has said FAU framework structure is selected from the group consisting of 13X, low sodium ultrastable Y (USY), dealuminized Y (Deal Y), ultrahydrophobic Y (UHP-Y), rare earth exchanged Y (REY), rare earth exchanged USY (RE-USY), and mixtures thereof.

14. The process of any preceding claim, wherein said zeolite which has said BEA* framework structure is zeolite beta.

15. The process of any preceding claim, wherein said zeolite which has said MOR framework structure is selected from the group consisting of mordenite, EMM-34, TEA-mordenite, and mixtures thereof.

25

16. The process of any preceding claim, wherein said zeolite which has said MWW framework structure is a MCM-22 family molecular sieve and combinations thereof.

17. The process of claim 16, wherein said MCM-22 family molecular sieve is any one of MCM-22, PSH-3, SSZ-25, MCM-36, MCM-49, MCM-56, ERB-1, EMM-10, EMM-10-P, EMM-12, EMM-13, UZM-8, UZM-8HS, UZM-37, ITQ-1, ITQ-2, ITQ-30, or combinations of two or more thereof.

18. The process of any preceding claim, wherein said alkylation catalyst comprises an aluminosilicate.

19. The process of claim 18, wherein said aluminosilicate is any one of a MCM-22 family

5 molecular sieve, faujasite, mordenite, zeolite-beta, or combinations of two or more thereof.

20. The process of any one of claim 3 to claim 19, wherein said treatment material is selected from the group consisting of a clay, a resin, an activated alumina, a molecular sieve and combinations thereof, wherein said molecular sieve is selected from the group consisting

10 Linde X, Linde A, zeolite beta, faujasite, zeolite Y, Ultrastable Y (USY), Dealuminized Y (Deal Y), Rare Earth Y (REY), Ultrahydrophobic Y (UHP-Y), mordenite, TEA-mordenite, ZSM-3, ZSM-4, ZSM-14, ZSM-18, ZSM-20 and combinations thereof.