

ALKYLATED AROMATIC COMPOSITIONS, ZEOLITE CATALYST COMPOSITIONS AND PROCESSES FOR MAKING THE SAME

FIELD OF THE INVENTION

4 The present invention is directed to novel alkylated aromatic compositions,
5 zeolite catalyst compositions and processes for making the same. The
6 catalyst compositions comprise zeolite Y and mordenite zeolite having a
7 controlled macropore structure. The present invention is also directed to the
8 preparation of the catalyst compositions and their use in the preparation of
9 novel alkylated aromatic compositions. The catalyst compositions of the
10 present invention exhibit reduced deactivation rates during the alkylation
11 process, thereby increasing the life of the catalysts.

BACKGROUND OF THE INVENTION

13 It is well known to catalyze the alkylation of aromatics with a variety of Lewis
14 or Bronsted acid catalysts. Typical commercial catalysts include phosphoric
15 acid/kieselguhr, aluminum halides, boron trifluoride, antimony chloride,
16 stannic chloride, zinc chloride, onium poly(hydrogen fluoride), and hydrogen
17 fluoride. Alkylation with lower molecular weight olefins, such as propylene,
18 can be carried out in the liquid or vapor phase. For alkylations with higher
19 olefins, such as C₁₆ olefins, the alkylations are done in the liquid phase,
20 usually in the presence of hydrogen fluoride. Alkylation of benzene with
21 higher olefins is especially difficult, and requires hydrogen fluoride treatment.
22 However, hydrogen fluoride is not environmentally attractive.

23 The use of the above listed acids is extremely corrosive, thus requiring special
24 handling and equipment. Also, the use of these acids might involve
25 environmental problems. Another problem is that the use of these acids can
26 give less than desirable control on the precise chemical composition of the
27 product produced. Thus, it is preferable to use a safer, simpler catalyst.

1 preferably in solid state. This simpler process would result in less capital
2 investment, which would result in a less expensive product.

3 Solid crystalline aluminosilicate zeolite catalysts have been known to be
4 effective for the alkylation of aromatics with olefins. Zeolitic materials which
5 are useful as catalysts are usually inorganic crystalline materials that possess
6 uniform pores with diameters in micropore range that is less than
7 20 angstroms. Zeolites occur naturally and may also be prepared
8 synthetically. Synthetic zeolites include, for example, zeolites A, X, Y, L and
9 omega. It is also possible to generate metaloaluminophosphates and
10 metalosilicophosphates. Other materials, such as boron, gallium, iron or
11 germanium, may also be used to replace the aluminum or silicon in the
12 framework structure.

13 These zeolite catalyst materials are commercially available as fine crystalline
14 powders for further modification to enhance their catalytic properties for
15 particular applications. Processes for the further modification to enhance
16 catalytic properties of the zeolite catalysts are well known in the art, such as
17 forming the zeolite catalysts into shaped particles, exchanging the cations in
18 the catalyst matrix, etc.

19 Forming zeolite powders into shaped particles may be accomplished by
20 forming a gel or paste of the catalyst powder with the addition of a suitable
21 binder material such as a clay, an inorganic compound, or an organic
22 compound and then extruding the gel or paste into the desired form. Zeolite
23 powders may also be formed into particles without the use of a binder.
24 Typical catalyst particles include extrudates whose cross sections are circular
25 or embrace a plurality of arcuate lobes extending outwardly from the central
26 portion of the catalyst particles.

27 One problem with catalyst particles used in fixed bed reactors is catalyst
28 deactivation. In most hydrocarbon conversion processes, including alkylation,

1 the primary catalyst deactivation is caused by coke formation. This catalyst
2 deactivation is a serious problem in the use of zeolite catalysts for alkylation
3 reactions. This deactivation problem is well known in the art and it is well
4 understood that the deactivation mechanism can involve polymerization of the
5 olefin into large molecular species that cannot diffuse out of the pores
6 containing the active sites in the zeolitic material.

7 The use of zeolite catalysts for preparation of alkyl aromatics is typically
8 conducted by the catalytic alkylation of aromatic hydrocarbons with normal
9 alpha olefins or branched-chain olefins, and optionally a promotor. The
10 alkylated aromatic hydrocarbons can be converted into corresponding sulfonic
11 acids which can be further converted into alkylated aromatic sulfonates.

12 A number of patents have discussed processes for the preparation of zeolite
13 catalysts and the further shaping and forming of the catalyst particles and
14 extrudates with and without the use of binders. There are also a number of
15 patents disclosing the use of zeolite catalysts for alkylation of aromatic
16 hydrocarbons.

17 U.S. Pat. No. 3,094,383 discloses the preparation of synthetic zeolite
18 materials which upon hydration yield a sorbent of controlled effective pore
19 diameter and in which the sorbent and its zeolite precursor are provided
20 directly in the form of an aggregate.

21 U.S. Pat. No. 3,130,007 discloses the method of preparing sodium zeolite Y
22 with silica to alumina ratios ranging from greater than 3 to about 3.9.

23 U.S. Pat. No. 3,119,660 discloses a process for making massive bodies or
24 shapes of crystalline zeolites. The patent also discloses methods for the
25 identification of the catalyst materials using X-ray powder diffraction patterns
26 in conjunction with chemical analyses.

1 U.S. Pat. No. 3,288,716 discloses that the high "heavy content" of the
2 alkylated aromatic product can be controlled during the alkylation step and
3 has advantages over distilling the alkylated aromatic product to obtain the
4 desired molecular weight.

5 U.S. Pat. Nos. 3,641,177 and 3,929,672 disclose the technique to remove
6 sodium or other alkali metal ions from zeolite catalysts. The '177 patent also
7 discloses that such removal of the sodium or other alkali metal ions activates
8 the zeolite catalysts for the alkylation of aromatic hydrocarbons with olefins by
9 liquid phase reaction.

10 U.S. Pat. Nos. 3,764,533, 4,259,193 and 5,112,506 disclose the "heavy
11 alkylate" content influences neutral sulfonates and overbased sulfonates. In
12 U.S. Pat. No. 5,112,506, the effect of molecular weight distribution or "heavy
13 alkylate" is shown to influence the performance of both Neutral and HOB
14 sulfonates and the di-alkylate content is shown to influence the rust
15 performance of the corresponding sulfonate in U.S. Pat. No. 3,764,533. In
16 U.S. Pat. No. 4,259,193, a mono-alkylate sulfonate is preferred. U.S. Pat.
17 Nos. 3,288,716; 3,764,533; 4,259,193; and 5,112,506 are hereby
18 incorporated by reference for all purposes.

19 U.S. Pat. No. 3,777,006 discloses the use of nucleating centers for the
20 crystallization of crystalline aluminosilicate zeolites having a size in excess of
21 200 microns and characterized by high strength and excellent adsorptive
22 properties.

23 U.S. Pat. No. 4,185,040 discloses the preparation of highly stable and active
24 catalysts for the alkylation of aromatic hydrocarbons with C₂-C₄ olefins. The
25 catalysts are acidic crystalline aluminosilicate zeolites which exhibit much
26 improved deactivation rates.

- 1 U.S. Pat. No. 4,395,372 discloses an alkylation process for alkylating benzene
2 comprising contacting benzene and lower olefins with a rare earth exchanged
3 X or Y zeolite catalyst in the presence of sulfur dioxide.
- 4 U.S. Pat. No. 4,570,027 discloses the use of a low crystallinity, partially
5 collapsed zeolite catalyst for producing alkylaromatic hydrocarbons. The
6 alkylation reaction also involves conditioning the catalyst bed with hydrogen
7 prior to conducting the alkylation reaction.
- 8 U.S. Pat. Nos. 4,762,813; 4,767,734; 4,879,019 and 5,111,792 disclose the
9 preparation of a hydrocarbon conversion catalyst using a low silica to alumina
10 ratio zeolite Y bound into an extrudate and steamed to modify the catalyst.
- 11 U.S. Pat. No. 4,764,295 discloses a process for making non-foaming
12 detergent-dispersant lubricating oil additives. The process further involves
13 carbonation for making the products more basic.
- 14 U.S. Pat. No. 4,876,408 discloses an alkylation process using an ammonium-
15 exchanged and steam stabilized zeolite Y catalyst having an increased
16 selectivity for mono-alkylation. The process involves the presence of at least
17 one organic compound under conditions such that sufficient amount of
18 carbonaceous material evenly deposits on the alkylation catalyst to
19 substantially suppress its alkylation activity.
- 20 U.S. Pat. No. 4,891,448 discloses a process for alkylation of polycyclic
21 aromatic compounds in the presence of an acidic mordenite zeolite catalyst
22 having a silica to alumina molar ratio of at least 15:1 to produce a mixture of
23 substituted polycyclic aromatic compounds enriched in the para alkylated
24 isomers.
- 25 U.S. Pat. No. 4,916,096 discloses use of a zeolite Y catalyst for
26 hydroprocessing. The zeolite Y catalyst comprises a modified crystalline

1 aluminosilicate zeolite Y, a binder and at least one hydrogenation component
2 of a Group VI or a Group VIII metal.

3 U.S. Pat. No. 5,004,841 discloses a process for alkylation of polycyclic
4 aromatic compounds in the presence of an acidic mordenite zeolite catalyst
5 having a silica to alumina molar ratio of at least 15:1 to produce substituted
6 polycyclic aromatic compounds enriched in the linear alkylated isomers.

7 U.S. Pat. No. 5,026,941 discloses the use of a zeolite Y catalyst having a
8 silica to alumina ratio of 15 to 110 for the alkylation of naphthalene or
9 mono-isopropylnaphthalene.

10 U.S. Pat. No. 5,118,896 discloses an aromatic alkylation process comprising
11 the steps of contacting a hydrocarbon feed with an alkylating agent under
12 liquid phase alkylation conditions in the presence of a silica-containing large
13 macropore, small particle size zeolite catalyst, the catalyst having a pore
14 volume of about 0.25 to 0.50 cc/g in pores having a radius of 450 angstroms
15 and a catalyst particle diameter of not more than 1/32 of an inch.

16 U.S. Pat. No. 5,175,135 discloses the use of an acidic mordenite zeolite
17 catalyst for alkylation of aromatic compounds with an alkylating agent having
18 from one carbon atom to eight carbon atoms to produce substituted aromatic
19 compounds enriched in the linear alkylated isomers. The acidic mordenite
20 catalyst is characterized by its silica to alumina molar ratio, its porosity and a
21 Symmetry Index.

22 U.S. Pat. No. 5,191,135 discloses the process for making long-chain
23 alkyl-substituted aromatic compounds from naphthalenes, the process
24 comprising a zeolite alkylation catalyst in the presence of 0.5 to 3.0 weight
25 percent water. The presence of water increases the selectivity for making
26 mono-alkylated products.

1 U.S. Pat. Nos. 5,240,889 and 5,324,877 disclose processes for the
2 preparation of a catalyst composition having alkylation and/or transalkylation
3 activity and wherein the catalyst composition contains greater than 3.5 weight
4 percent water based on the total weight of the catalyst composition and the
5 aromatic alkylation process using said catalyst composition and olefins
6 containing 2 carbon atoms to 25 carbon atoms.

7 U.S. Pat. No. 5,198,595 discloses a process for alkylation of benzene or
8 substituted benzene in the presence of an acidic mordenite zeolite catalyst
9 having a silica to alumina ratio of at least 160:1 and a Symmetry Index above
10 about 1.0. A process for the preparation of the catalyst is also disclosed.

11 U.S. Pat. No. 5,243,116 discloses the production of alkylated benzenes by
12 alkylation and/or transalkylation in the presence of an acidic mordenite zeolite
13 catalyst having a silica to alumina molar ration of at least 30:1 and a specific
14 crystalline structure determined by X-ray diffraction.

15 U.S. Pat. No. 5,453,553 discloses a process for the production of linear alkyl
16 benzenes which process comprises co-feeding a mixture of benzene, linear
17 olefins and molecular hydrogen in the presence of a zeolite catalyst
18 containing a transition metal under alkylation condition such that the catalyst
19 is not deactivated.

20 U.S. Pat. No. 5,506,182 discloses the preparation of a catalyst composition
21 comprising 10 to 90 percent of a modified zeolite Y catalyst formed from a
22 modified zeolite Y and 10 to 90 percent binder using slurries of the modified
23 zeolite Y and the binder to form the catalyst composition having a clear
24 absorption peak in an IR spectrum of a wavelength of 3602 per centimeter.
25 The patent also discloses the substitution of iron for the alumina in the
26 zeolite Y structure.

1 U.S. Pat. No. 5,922,922 discloses a process for isomerizing a normal alpha
2 olefin in the presence of an acidic catalyst having a one-dimensional pore
3 system, and then using the isomerized olefin to alkylate aromatic
4 hydrocarbons in the presence of a second acidic catalyst, which can be
5 zeolite Y having a silica to alumina ratio of at least 40 to 1.

6 U.S. Pat. No. 5,939,594 discloses the preparation of a superalkalinized
7 alkylaryl sulfonate of alkaline earth metal. The alkyl group of the alkylaryl
8 sulfonate contains between 14 to 40 carbon atoms and the aryl sulfonate
9 radical of alkaline earth metal is fixed in a molar proportion comprised
10 between 0 and 13% in positions 1 or 2 of the linear alkyl chain.

11 U.S. Pat. No. 6,031,144 discloses a process for reducing the residual olefin
12 content of an alkylation reaction product by removing at least a portion of the
13 non-alkylated single-ring aromatic hydrocarbon and then reacting the
14 remaining alkylation reaction product in the presence of an acidic catalyst
15 such as a molecular sieve or clay.

16 U.S. Pat. No. 6,337,310 discloses the preparation of alkylbenzene from
17 preisomerized normal alpha olefins for making low overbased and high
18 overbased sulfonates having a TBN in the range of 3 to 500. The process
19 uses HF as catalyst or a solid acidic alkylation catalyst, such as a zeolite
20 having an average pore size of at least 6 angstroms.

21 U.S. Pat. No. 6,525,234 discloses a process for alkylating aromatic using a
22 porous crystalline material, e.g., MCM-22 and in situ regenerating the catalyst
23 by use of a polar compound having a dipole moment of at least 0.05 Debyes.

24 It is known that most solid acid catalysts produce high 2-aryl attachment when
25 alkylating with alpha-olefins. See S. Sivasanker, A. Thangaraj, "Distribution of
26 Isomers in the Alkylation of Benzene with Long-Chain Olefins over Solid Acid

Catalysts," *Journal of Catalysis*, 138, 386-390 (1992). This is especially true for mordenite zeolite.

Two general treatises on zeolite are: Handbook of Molecular Sieves by Rosemarie Szostak (Van Nostrand Reinhold, New York 1992) and Molecular Sieves: Principles of Synthesis and Identification, 2nd Edition, by Rosemarie Szostak (Chapman and Hall, London, UK 1999).

SUMMARY OF THE INVENTION

Disclosed herein are novel alkylated aromatic compositions and processes for preparation of carbonated, overbased alkylated aromatic sulfonates, which processes comprise the alkylation in the presence of the disclosed catalyst composites, and further sulfonation and carbonation, overbasing of the alkylated aromatic sulfonic acids.

Disclosed herein are zeolite catalyst compositions having a controlled macropore structure comprising zeolite Y and mordenite zeolite. Disclosed herein is a process for preparing the catalyst compositions. The catalysts and catalyst compositions may exhibit reduced deactivation rates during the alkylation process, thereby increasing the life of the catalysts and the catalyst compositions.

In particular, disclosed herein is an alkylated aromatic composition comprising a mixture of:

- (a) an alkylated aromatic hydrocarbon alkylation product wherein the alkylation reaction is conducted in the presence of an alkylation catalyst having a macropore structure comprising zeolite Y, and wherein the peak macropore diameter of the catalyst, measured by ASTM Test No. D 4284-03, is less than or equal to about 2000 angstroms and the cumulative pore volume of the catalyst

1 at pore diameters less than or equal to about 500 angstroms,
2 measured by ASTM Test No. D 4284-03, is less than or equal to
3 about 0.30 milliliters per gram; and
4

5 (b) an alkylated aromatic hydrocarbon alkylation product wherein the
6 alkylation reaction is conducted in the presence of an alkylation
7 catalyst having a macropore structure comprising mordenite
8 zeolite having a silica to alumina molar ratio of about 50 to about
9 105 and wherein the peak macropore diameter of the catalyst,
10 measured by ASTM Test No. D 4284-03, is less than or equal to
11 about 900 angstroms and the cumulative pore volume of the
12 catalyst at pore diameters less than or equal to about 500
13 angstroms, measured by ASTM Test No. D 4284-03, is less than
14 or equal to about 0.30 milliliters per gram.
15

16 The weight percent of the alkylated aromatic hydrocarbon of (a) in the mixture
17 may be in the range of about 40 percent to about 99 percent based on the
18 total alkylated aromatic composition. Preferably the weight percent of the
19 alkylated aromatic hydrocarbon of (a) in the mixture is in the range of about
20 50 percent to about 90 percent based on the total alkylated aromatic
21 composition, and more preferably the weight percent of the alkylated aromatic
22 hydrocarbon of (a) in the mixture is in the range of about 70 percent to about
23 80 percent based on the total alkylated aromatic composition.
24

25 The alkyl groups of the alkylated aromatic composition may be derived from
26 alpha olefins, isomerized olefins, branched-chain olefins, or mixtures thereof.
27 The alpha olefins or the isomerized olefins have from about 6 carbon atoms to
28 about 40 carbon atoms. Preferably, the alpha olefins or the isomerized olefins
29 have from about 20 carbon atoms to about 40 carbon atoms. The branched-
30 chain olefins have from about 6 carbon atoms to about 70 carbon atoms.
31 Preferably, the branched-chain olefins have from about 8 carbon atoms to

1 about 50 carbon atoms. More preferably, the branched-chain olefins have
2 from about 12 carbon atoms to about 18 carbon atoms.

3
4 The alkyl groups of the alkylated aromatic composition may be partially-
5 branched-chain isomerized olefins wherein the olefins have from about
6 6 carbon atoms to about 40 carbon atoms. Preferably, the partially-branched-
7 chain isomerized olefins have from about 20 carbon atoms to about 40 carbon
8 atoms.

9
10 The aromatic hydrocarbon of the alkylated aromatic composition may be
11 benzene, toluene, xylene, cumene, or mixtures thereof. Preferably, the
12 aromatic hydrocarbon is toluene or benzene.

13
14 The zeolite Y in step (a) and the mordenite zeolite in step (b) may contain a
15 binder. Preferably, the binder in the zeolite Y in step (a) and the binder in the
16 mordenite zeolite in step (b) is alumina.

17
18 The zeolite Y in step (a) and the mordenite zeolite in step (b) may be in the
19 form of a tablet.

20
21 In a first aspect, there is provided a process for preparing an alkylated aromatic
22 composition comprising:

23
24 (a) contacting at least one aromatic hydrocarbon with at least one
25 olefin under alkylation conditions in the presence of a zeolite
26 catalyst having a macropore structure comprising zeolite Y, and
27 wherein the peak macropore diameter of the catalyst, measured by
28 ASTM Test No. D 4284-03, is less than or equal to about
29 2000 angstroms and the cumulative pore volume of the catalyst at
30 pore diameters less than or equal to about 500 angstroms,
31 measured by ASTM Test No. D 4284-03, is less than or equal to

1 about 0.30 milliliters per gram to form a first alkylated aromatic
2 hydrocarbon product;
3
4 (b) contacting at least one aromatic hydrocarbon with at least one
5 olefin under alkylation conditions in the presence of a zeolite
6 catalyst having a macropore structure comprising mordenite zeolite
7 having a silica to alumina molar ratio of about 50 to about 105, and
8 wherein the peak macropore diameter of the catalyst, measured by
9 ASTM Test No. D 4284-03, is less than or equal to about
10 900 angstroms and the cumulative pore volume of the catalyst at
11 pore diameters less than or equal to about 500 angstroms,
12 measured by ASTM Test No. D 4284-03, is less than or equal to
13 about 0.30 milliliters per gram to form a second alkylated aromatic
14 hydrocarbon product; and
15
16 (c) combining the first alkylated aromatic hydrocarbon product and the
17 second alkylated aromatic hydrocarbon product to form the
18 alkylated aromatic composition;

19
20 wherein steps (a) and (b) can be conducted in any order.

21
22 The above process may further comprise in step (b) the reactivation of the
23 deactivated zeolite catalyst with a suitable solvent flush, preferably the solvent
24 is an aromatic hydrocarbon. More preferably, the aromatic hydrocarbon is
25 benzene.

26
27 The above process may further comprise sulfonating the alkylated aromatic
28 composition to form an alkylated aromatic sulfonic acid. The alkylated
29 aromatic sulfonic acid may be reacted with an alkaline earth metal and carbon
30 dioxide to produce a carbonated, overbased alkylated aromatic sulfonate.

31

1 The first alkylated aromatic hydrocarbon product in the alkylated aromatic
2 composition may be in the range of about 40 percent to about 99 percent
3 based on the total alkylated aromatic composition. Preferably, the first
4 alkylated aromatic hydrocarbon product in the alkylated aromatic composition
5 is in the range of about 50 percent to about 90 percent based on the total
6 alkylated aromatic composition. More preferably, the first alkylated aromatic
7 hydrocarbon product in the alkylated aromatic composition is in the range of
8 about 70 percent to about 80 percent based on the total alkylated aromatic
9 composition.

10

11 The olefin in step (a) and step (b) may be independently an alpha olefin, an
12 isomerized olefin, a branched-chain olefin, or mixtures thereof. The alpha
13 olefin or isomerized olefin may have from about 6 carbon atoms to about
14 40 carbon atoms. Preferably, the alpha olefin or isomerized olefin has from
15 about 20 carbon atoms to about 40 carbon atoms. The branched-chain olefin
16 may have from about 6 carbon atoms to about 70 carbon atoms. Preferably,
17 the branched-chain olefin has from about 8 carbon atoms to about 50 carbon
18 atoms. More preferably, the branched-chain olefin has from about 12 carbon
19 atoms to about 18 carbon atoms.

20

21 The olefin in step (a) or step (b) may be independently a partially-branched-
22 chain isomerized olefin, and the olefin may have from about 6 carbon atoms
23 to about 40 carbon atoms. Preferably, the partially-branched-chain
24 isomerized olefin has from about 20 carbon atoms to about 40 carbon atoms.

25

26 The aromatic hydrocarbon of the alkylated aromatic composition may be
27 benzene, toluene, xylene, cumene, or mixtures thereof. Preferably, the
28 aromatic hydrocarbon is toluene or benzene.

29

30 The cumulative pore volume of the zeolite catalyst at pore diameters less than
31 or equal to about 400 angstroms in step (a) and step (b) may be less than or equal
32 to about 0.30 milliliters per gram. Preferably, cumulative pore volume of the

1 zeolite catalysts at pore diameters less than or equal to about 300 angstroms
2 in steps (a) and (b) is less than about 0.25 milliliters per gram, more
3 preferably at pore diameters less than or equal to about 300 angstroms is less
4 than about 0.20 milliliters per gram, and most preferably at pore diameters
5 less than or equal to about 300 angstroms is in the range of about
6 0.08 milliliters per gram to about 0.16 milliliters per gram.

7 The cumulative pore volume of the zeolite catalysts at pore diameters less
8 than or equal to about 400 angstroms in steps (a) and (b) may be in the range of
9 about 0.05 milliliters per gram to about 0.18 milliliters per gram. Preferably,
10 the cumulative pore volume of the zeolite catalysts at pore diameters less
11 than or equal to about 300 angstroms in steps (a) and (b) is in the range of
12 about 0.08 milliliters per gram to about 0.16 milliliters per gram.

13

14 The zeolite Y catalyst in step (a) has a peak macropore diameter in the range
15 of about 700 angstroms to about 1800 angstroms. Preferably, the peak
16 macropore diameter of the zeolite Y catalyst in step (a) is in the range of
17 about 750 angstroms to about 1600 angstroms. More preferably, the peak
18 macropore diameter of the zeolite Y catalyst in step (a) is in the range of
19 about 900 angstroms to about 1400 angstroms.

20

21 In step (b), the peak macropore diameter of the mordenite zeolite catalyst may be in
22 the range of about 400 angstroms to about 800 angstroms. Preferably in
23 step (b), the peak macropore diameter of the mordenite zeolite catalyst is in
24 the range of about 400 angstroms to about 700 angstroms. More preferably
25 in step (b), the peak macropore diameter of the mordenite zeolite catalyst is in
26 the range of about 450 angstroms to about 600 angstroms.

27

28 In steps (a) in the above process, the zeolite Y catalyst has a silica to alumina
29 ratio of about 5:1 to about 100:1. Preferably in step (a), the zeolite Y catalyst
30 has a silica to alumina ratio of about 30:1 to about 90:1. More preferably in

step (a), the zeolite Y catalyst has a silica to alumina ratio of about 60:1 to about 80:1.

In step (b) in the above process, preferably the mordenite zeolite catalyst has a silica to alumina ratio of about 60:1 to about 80:1.

The zeolite Y in step (a) and the mordenite zeolite in step (b) may contain a binder. Preferably, the binder in the zeolite Y in step (a) and the binder in the mordenite zeolite in step (b) is alumina.

The zeolite Y in step (a) and the mordenite zeolite in step (b) may be in the form of a tablet.

In a second aspect, there is provided a process for preparing an alkylated aromatic composition comprising contacting at least one aromatic hydrocarbon with at least one olefin in the presence of a zeolite catalyst having a macropore structure comprising zeolite Y and mordenite zeolite having a silica to alumina ratio of about 50:1 to about 105:1, and wherein the peak macropore diameter of the catalyst, measured by ASTM Test No. D 4284-03, is less than or equal to about 2000 angstroms and the cumulative pore volume of the catalyst at pore diameters less than or equal to about 500 angstroms, measured by ASTM Test No. D 4284-03, is less than or equal to about 0.30 milliliters per gram.

The cumulative pore volume of the zeolite catalyst at pore diameters less than or equal to about 400 angstroms may be less than or equal to about 0.30 milliliters per gram. Preferably, the cumulative pore volume zeolite catalyst at pore diameters less than or equal to about 300 angstroms is less than or equal to about 0.25 milliliters per gram. More preferably, the cumulative pore volume zeolite catalyst at pore diameters less than or equal to about 300 angstroms is less than or equal to about 0.20 milliliters per gram.

1 The cumulative pore volume of the zeolite catalyst at pore diameters less than
2 or equal to about 400 angstroms may be in the range of about 0.05 milliliters
3 per gram to about 0.18 milliliters per gram. Preferably, the cumulative pore
4 volume of the zeolite catalyst at pore diameters less than or equal to about
5 300 angstroms is in the range of about 0.08 milliliters per gram to about
6 0.16 milliliters per gram.

7
8 The peak macropore diameter of the zeolite catalyst is in the range of about
9 400 angstroms to about 1500 angstroms. Preferably, the peak macropore
10 diameter of the zeolite catalyst is in the range of about 500 angstroms to
11 about 1300 angstroms. More preferably the peak macropore diameter of the
12 zeolite catalyst is in the range of about 600 angstroms to about
13 1100 angstroms, and most preferably the peak macropore diameter of the
14 zeolite catalyst is in the range of about 750 angstroms to about
15 900 angstroms.

16
17 The zeolite Y has a silica to alumina molar ratio of about 5:1 to about 100:1
18 and the mordenite zeolite has a silica to alumina molar ratio of about 50:1 to
19 about 105:1. Preferably the zeolite Y has a silica to alumina molar ratio of
20 about 30:1 to about 90:1, and more preferably the zeolite Y and the mordenite
21 zeolite independently has a silica to alumina molar ratio of about 60:1 to about
22 80:1.

23
24 The zeolite catalyst may contain a binder. Preferably, the binder is alumina.

25
26 The zeolite catalyst may be in the form of a tablet.

27
28 In a third aspect, there is provided a zeolite catalyst composition having a macropore
29 structure comprising:

30
31 (a) zeolite Y; and

32

1 (b) mordenite zeolite having a silica to alumina molar ratio in the
2 range of about 50:1 to about 105:1;
3
4 wherein the peak macropore diameter of the catalyst composition, measured
5 by ASTM Test No. D 4284-03, is less than about 2000 angstroms and the
6 cumulative pore volume of the catalyst at pore diameters less than or equal to
7 about 500 angstroms, measured by ASTM Test No. D 4284-03, is less than or
8 equal to about 0.30 milliliters per gram.
9
10 The cumulative pore volume of the zeolite catalyst composition at pore
11 diameters less than or equal to about 400 angstroms may be less than or equal to
12 about 0.30 milliliters per gram. Preferably, the cumulative pore volume zeolite
13 catalyst composition at pore diameters less than or equal to about
14 300 angstroms is less than or equal to about 0.25 milliliters per gram. More
15 preferably, the cumulative pore volume zeolite catalyst composition at pore
16 diameters less than or equal to about 300 angstroms is less than or equal to
17 about 0.20 milliliters per gram.
18
19 The cumulative pore volume of the zeolite catalyst composition at pore
20 diameters less than or equal to about 400 angstroms may be in the range of
21 about 0.05 milliliters per gram to about 0.18 milliliters per gram. Preferably,
22 the cumulative pore volume of the zeolite catalyst composition at pore
23 diameters less than or equal to about 300 angstroms is in the range of about
24 0.08 milliliters per gram to about 0.16 milliliters per gram.
25
26 The peak macropore diameter of the zeolite catalyst composition may be in the
27 range of about 400 angstroms to about 1500 angstroms. Preferably, the peak
28 macropore diameter of the zeolite catalyst composition is in the range of
29 about 500 angstroms to about 1300 angstroms. More preferably the peak
30 macropore diameter of the zeolite catalyst composition is in the range of
31 about 600 angstroms to about 1100 angstroms, and most preferably the peak

1 macropore diameter of the zeolite catalyst composition is in the range of
2 about 750 angstroms to about 900 angstroms.

3

4 The zeolite Y in step (a) having a silica to alumina ratio of about 5:1 to about
5 100:1, preferably the zeolite Y has a silica to alumina molar ratio of about 30:1
6 to about 90:1, and more preferably the zeolite Y has a silica to alumina molar
7 ratio of about 60:1 to about 80:1.

8

9 The mordenite zeolite in step (b) preferably has a silica to alumina molar ratio
10 of about 60:1 to about 80:1.

11

12 The zeolite catalyst composition may contain a binder. Preferably, the binder
13 is alumina.

14

15 The zeolite catalyst composition may be in the form of a tablet.

16

17 DETAILED DESCRIPTION OF THE INVENTION

18

DEFINITIONS

19 The term "alkylate" means an alkylated aromatic hydrocarbon.

20 The term "2-aryl content" is defined as the percentage of total alkylate (the
21 alkylate species in which the alkyl chain derived from the olefin employed in
22 the present alkylation process is attached to the aromatic ring) that is
23 comprised of those chemical species in which the attachment of the alkyl
24 chain to the aromatic ring is at the 2-position along the alkyl chain.

25 The term "binder" means any suitable inorganic material which can serve as
26 matrix or porous matrix to bind the zeolite particles into a more useful shape.

1 The term "branched-chain olefins" means olefins derived from the
2 polymerization of olefin monomers higher than ethylene and containing a
3 substantial number of branches wherein the branches are alkyl groups having
4 from about one carbon atom to about 30 carbon atoms. Mixtures of ethylene
5 and higher olefins are also contemplated.

6 The term "calcining" as used herein means heating the catalyst to about
7 400°C to about 1000°C in a substantially dry environment.

8 The term "carbonated, overbased" is used to describe those alkaline earth
9 metal alkyl aromatic sulfonates in which the ratio of the number of equivalents
10 of the alkaline earth metal moiety to the number of equivalents of the aromatic
11 sulfonic acid moiety is greater than one, and is usually greater than 10 and
12 may be as high as 20 or greater.

13 The term "cumulative pore volume" obtained by Mercury Intrusion Porosimetry
14 as used herein refers to that part of the total volume in milliliters per gram
15 derived from the graphical, cumulative pore volume distribution, measured by
16 Section 14.1.6 of ASTM D 4284-03, or the corresponding tabular presentation
17 of the same data between defined upper and lower pore diameters. When no
18 lower diameter limit is defined, the lower limit is the lowest detection limit or
19 lowest radius measured by Section 14.1.6 of ASTM D 4284-03.

20 The terms "dry basis", "anhydrous basis", and "volatiles-free basis" shall refer
21 to the dry weight of catalyst composite or raw materials expressed on a metal
22 oxides basis such as $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$.

23 The term "flush" as used herein means contacting the deactivated mordenite
24 catalysts and mordenite catalyst composites of this invention in the reactor
25 with a suitable solvent, such as an aromatic hydrocarbon for reactivation of
26 the mordenite catalysts and mordenite catalyst composites.

1 The term "loss-on-ignition (LOI)" as used herein means the percent weight
2 loss of the zeolite composite and raw material samples which volatilize or
3 evaporate when heated to 538°C for 1 hour. When the temperature is greater
4 than or equal about 538°C, the "loss-on-ignition" approximates the percent
5 volatiles.

6 The terms "macropore", "mesopore", and "micropore" as used herein follow
7 the definitions set forth by the International Union of Pure and Applied
8 Chemistry (IUPAC), Division of Physical Chemistry, in Manual of Symbols and
9 Terminology for Physicochemical Quantities and Units, Appendix II
10 Definitions, Terminology and Symbols in Colloid and Surface Chemistry Part I,
11 Adopted by the IUPAC Council at Washington, D. C., USA, on 23 July, 1971.
12 Pores with widths or diameters exceeding ~50 nanometers (500 angstroms)
13 are called "macropores". Pores with widths or diameters not exceeding
14 ~2.0 nanometers (20 angstroms) are called "micropores". Pores of
15 intermediate size (2.0 nanometers < width or diameter ≤ 50 nm) are called
16 "mesopores".

17 The term "Mercury Intrusion Porosimetry" refers to the ASTM Test
18 No. D 4284-03 used to determine pore volume distribution of catalysts by
19 Mercury Intrusion Porosimetry. Mercury pore distribution was measured
20 using a Quantachrome Scanning Mercury Porosimeter Model SP-100. The
21 software version used by the instrument is V2.11 (dated 10/27/93). Surface
22 tension used in the calculation is 473 dynes per centimeter and the contact
23 angle is 140 degrees.

24 The terms "normal alpha olefin" and "linear alpha olefin" mean those
25 straight-chain olefins without a significant degree of alkyl branching in which
26 the carbon to carbon double bond resides primarily at the end or "alpha"
27 position of the carbon chain, i.e., between C₁ and C₂. Normal alpha olefins
28 are derived from polymerization of ethylene.

1 The term "normal alpha olefin isomerization" means the conversion of normal
2 alpha olefins into isomerized olefins having a lower alpha olefin content (the
3 double bond is between C₁ and C₂), higher internal olefin content (the double
4 bond is in positions other than between C₁ and C₂), and optionally a higher
5 degree of branching.

6 The term "partially-branched chain olefin" is defined as the olefin product of
7 isomerization of normal alpha olefins wherein the degree of branching is
8 higher than in the starting normal alpha olefins.

9 The term "peak macropore diameter" as used herein means the peak
10 diameter (i.e., the diameter within the macropore region at which the
11 differential plot of pore size distribution, as defined by Section 14.2, reaches a
12 maximum) in the macropore range determined by ASTM Test No. 4284-03 for
13 the macropore peak in the catalysts of the present invention.

14 The term "peptizing" means the dispersion of large aggregates of binder
15 particles, including hydrated aluminas, into much smaller primary particles by
16 the addition of acid.

17 The term "percent volatiles" as used herein means the difference between the
18 actual weight of the catalyst composite or the raw materials and the weight of
19 the material on a dry, anhydrous, or volatiles-free basis, expressed as a
20 percentage of the actual sample weight.

21 The term "SAR" or "silica to alumina ratio" refers to the molar ratio of silicon
22 oxide to aluminum oxide; mol SiO₂:mol AlO₃.

23 The term "sufficient water to shape the catalyst material" means quantity of
24 water required to make an acid peptized mixture of zeolite and alumina
25 powders into an extrudable mass.

1 The term "tableting" as used herein refers to the process of forming a catalyst
2 aggregate from zeolite powder or a mixture of zeolite and binder powders by
3 compressing the powder in a die.

4 The term "total pore volume" obtained by Mercury Intrusion Porosimetry as
5 used herein refers to the total pore volume in milliliters per gram derived from
6 the graphical, cumulative pore volume distribution (Section 14.1.6 of ASTM
7 D 4284-03) or the corresponding tabular presentation of the same data.

8 As used herein, all percentages are weight percent, unless otherwise
9 specified.

10 As noted above, the present invention is directed to novel alkylated aromatic
11 compositions and their sulfonated and carbonated products. The alkylation of
12 the aromatic hydrocarbons is carried out in the presence of the zeolite catalyst
13 compositions of the present invention having a controlled macropore structure
14 comprising zeolite Y and mordenite zeolite. The catalysts of the present
15 invention were characterized by pore volume distribution obtained by Mercury
16 Intrusion Porosimetry, ASTM Test No. D 4284-03. Mercury Intrusion
17 Porosimetry provides a graph of cumulative pore volume (pv) versus pore
18 diameter (pd). Mercury Intrusion Porosimetry also is used to determine the
19 macropore peak diameter from the derivative, delta pv (Δpv) divided by delta
20 pd (Δpd). The graphs are used to characterize the catalysts of the present
21 invention.

22 The zeolite catalyst compositions were prepared using zeolite Y and
23 mordenite zeolite. Zeolite Y and mordenite zeolite may also be combined to
24 prepare zeolite catalyst compositions of the present invention. When the
25 zeolite catalyst compositions contain both zeolite Y and mordenite zeolite, the
26 zeolite catalyst composite may be prepared by mixing zeolite Y and mordenite
27 zeolite powders before the binding and shaping steps. The zeolite Y
28 CBV 760® and CBV 600® available from Zeolyst International having a

1 nominal silica to alumina ratio of 60 and 6.7, respectively, may be used for
2 preparing the zeolite catalyst compositions of this invention. However,
3 zeolite Y having a silica to alumina ratio between 5 and 110 may be used for
4 the preparation of the zeolite catalysts compositions of the present invention.
5 The mordenite zeolite 90A® having a nominal silica to alumina ratio of 90,
6 also available from Zeolyst International, may be used for preparing the
7 zeolite catalyst compositions of this invention. Mordenite zeolite having a
8 silica to alumina ratio of 50 to 105 may be used in the preparation of the
9 zeolite catalyst compositions of this invention.

10 The catalysts of the present invention may be shaped or formed into tablets,
11 extrudates or any other shape using procedures well known in the prior art.
12 The preparation of extrudates requires the presence of a binder, such as
13 alumina. The tabletted catalysts do not require the presence of a binder, but
14 a binder may be present in a tabletted zeolite catalyst. The crystalline zeolite
15 powder may be compressed to form a tablet. The tabletted catalysts of the
16 present invention provide exceptionally low deactivation rates in alkylation
17 reactions.

18 The alkylation of aromatic hydrocarbons with one or more olefins may be
19 carried out in a fixed bed reactor in the presence of the zeolite catalysts
20 compositions of the present invention comprising only zeolite Y, only
21 mordenite zeolite, or both zeolite Y and mordenite zeolite. The alkylation
22 process is conducted without the addition of water and using dried aromatic
23 hydrocarbon and olefin feed. It is believed that the presence of water during
24 the alkylation increases the deactivation rate of the catalysts of this invention.
25 When the alkylation using zeolite Y and mordenite zeolite is carried out in
26 separate fixed bed reactors, the alkylated aromatic hydrocarbons may be
27 combined to obtain the desired amount of alpha olefins versus branched-
28 chain olefins. Alkylation reactions using normal alpha olefins and zeolite
29 catalysts compositions comprising only mordenite zeolite give predominantly
30 alkylated aromatic hydrocarbons wherein the attachment of the of the alkyl

1 chain to the aromatic ring is at the 2-position along the alkyl chain. On the
2 other hand, alkylation reactions using zeolite catalysts compositions
3 comprising only zeolite Y and normal alpha olefins give predominantly
4 attachments at other than the 2-position along the alkyl chain.

5 The alkylation reaction may be carried out by any conventionally known
6 process. The aromatic hydrocarbon is reacted with one or more olefins in the
7 presence of a catalyst of the present invention under alkylation reaction
8 conditions. The above alkylation process is conducted without the addition of
9 water and using dried aromatic hydrocarbon and olefin feed. It is believed
10 that the presence of water during the alkylation process increases the
11 deactivation rate of the catalysts of this invention.

12 The aromatic hydrocarbon may be single-ring or double-ring, preferably the
13 aromatic hydrocarbon is a single-ring aromatic hydrocarbon. The aromatic
14 hydrocarbon may be an alkylated aromatic hydrocarbon, such as a
15 mono-alkylated aromatic hydrocarbon, wherein the alkyl group has from about
16 4 carbon atoms to about 80 carbon atoms. When the aromatic hydrocarbon
17 used is a mono-alkylated aromatic, the product of the alkylation reaction is a
18 di-alkylated aromatic hydrocarbon.

19 The olefins useful for alkylation of the aromatic hydrocarbons may be
20 linear-chain olefins or branched-chain olefins having from about 4 carbon
21 atoms to about 80 carbon atoms. In addition, normal alpha olefins may be
22 isomerized to obtain partially-branched-chain olefins for use in alkylation
23 process of the present invention. These resulting partially-branched-chain
24 olefins may be alpha-olefins, beta-olefins, internal-olefins, tri-substituted
25 olefins, and vinylidene olefins.

26 Alkylated aromatic hydrocarbon sulfonic acids of the alkylated aromatic
27 hydrocarbons of the present invention may be prepared by any known
28 sulfonation reaction. The alkylated aromatic sulfonic acids may be further

1 reacted with an alkaline earth metal and carbon dioxide to obtain carbonated,
2 overbased alkylated aromatic sulfonates useful as detergents in lubricating
3 oils. Carbonation may be carried out by any conventionally known process.
4 The degree of overbasing may be controlled by changing the reaction
5 conditions and the amount of the alkaline earth metal and carbon dioxide
6 used in the carbonation process.

7 The novel alkylation compositions of the present invention may be obtained
8 by conducting the alkylation reactions as described above in the presence of
9 the zeolite catalyst compositions of the present invention prepared as
10 described in Examples 1-4 below.

11 Procedure for Isomerization of Normal Alpha Olefins

12 The isomerization process may be carried out in batch or continuous mode.
13 The process temperatures can range from 50°C to 250°C. In the batch mode,
14 a typical method is to use a stirred autoclave or glass flask, which may be
15 heated to the desired reaction temperature. A continuous process is most
16 efficiently carried out in a fixed bed process. Space rates in a fixed bed
17 process can range from 0.1 to 10 or more weight hourly space velocity.

18 In a fixed bed process, the isomerization catalyst is charged to the reactor and
19 activated or dried at a temperature of at least 150°C under vacuum or flowing
20 inert, dry gas. After activation, the temperature of the isomerization catalyst is
21 adjusted to the desired reaction temperature and a flow of the olefin is
22 introduced into the reactor. The reactor effluent containing the partially-
23 branched, isomerized olefins is collected. The resulting partially-branched,
24 isomerized olefins contain a different olefin distribution (alpha olefin, beta
25 olefin, internal olefin, tri-substituted olefin, and vinylidene olefin) and
26 branching content than the unisomerized olefin.

1 Procedure for Alkylation of Aromatic Hydrocarbons

2 Alkylation of aromatic hydrocarbons with normal alpha olefins, partially-
3 branched-chain isomerized olefins, and branched-chain olefins may be carried
4 out by any method known by a person skilled in the art.

5 The alkylation reaction is typically carried out with an aromatic hydrocarbon
6 and an olefin in molar ratios from 1:15 to 25:1. Process temperatures can
7 range from about 100°C to about 250°C. The process is carried out without
8 the addition of water. As the olefins have a high boiling point, the process is
9 preferably carried out in the liquid phase. The alkylation process may be
10 carried out in batch or continuous mode. In the batch mode, a typical method
11 is to use a stirred autoclave or glass flask, which may be heated to the
12 desired reaction temperature. A continuous process is most efficiently carried
13 out in a fixed bed process. Space rates in a fixed bed process can range from
14 0.01 to 10 or more weight hourly space velocity.

15 In a fixed bed process, the alkylation catalyst is charged to the reactor and
16 activated or dried at a temperature of at least 150°C under vacuum or flowing
17 inert, dry gas. After activation, the alkylation catalyst is cooled to ambient
18 temperature and a flow of the aromatic hydrocarbon compound is introduced,
19 optionally toluene. Pressure is increased by means of a back pressure valve
20 so that the pressure is above the bubble point pressure of the aromatic
21 hydrocarbon feed composition at the desired reaction temperature. After
22 pressurizing the system to the desired pressure, the temperature is increased
23 to the desired reaction temperature. A flow of the olefin is then mixed with the
24 aromatic hydrocarbon and allowed to flow over the catalyst. The reactor
25 effluent comprising alkylated aromatic hydrocarbon, unreacted olefin and
26 excess aromatic hydrocarbon compound are collected. The excess aromatic
27 hydrocarbon compound is then removed by distillation, stripping, evaporation
28 under vacuum, or any other means known to those skilled in the art.

1 Procedure for Sulfonation of Alkylated Aromatic Hydrocarbons

2 Sulfonation of alkylated hydrocarbons may be carried out by any method
3 known by a person skilled in the art.

4 The sulfonation reaction is typically carried out in a falling film tubular reactor
5 maintained at about 65°C. The alkylated aromatic hydrocarbon is placed in
6 the tube and sulfur trioxide diluted with nitrogen is added to the alkylated
7 aromatic hydrocarbon. The molar ratio of alkylated aromatic hydrocarbon to
8 sulfur trioxide is maintained at about 1.05:1. The resulting alkylated aromatic
9 sulfonic acid may be diluted with about 10% 100 Neutral oil followed by
10 thermal treatment with nitrogen bubbling at a rate of about 10 liters per
11 kilogram of product and stirring while maintaining the temperature at about
12 85°C until the desired residual sulfuric acid content is obtained (maximum of
13 about 0.5%).

14 Procedure for Carbonation, Overbasing of Alkylated Aromatic Sulfonic Acids

15 Carbonation, overbasing of alkylaromatic sulfonic acids may be carried out by
16 any method known by a person skilled in the art to produce alkylaromatic
17 sulfonates.

18
19 Generally, the carbonation, overbasing reaction is carried out in a reactor in
20 the presence of the alkylated aromatic sulfonic acid, diluent oil, an aromatic
21 solvent, and an alcohol. The reaction mixture is agitated and alkaline earth
22 metal and carbon dioxide are added to the reaction while maintaining the
23 temperature between about 20°C and 80°C.

24
25 The degree of carbonation, overbasing may be controlled by the quantity of
26 the alkaline earth metal and carbon dioxide added to the reaction mixture, the
27 reactants and the reaction conditions used during the carbonation process.

1 Reactivation of Deactivated Mordenite Zeolite Catalysts and Composites

2 Once the mordenite zeolite catalysts and catalyst composites are completely
3 deactivated, the alkylation reaction stops because of the polymerization of the
4 olefin into large molecular species that cannot diffuse out of the crystal
5 micropores containing the active sites in the zeolitic material. However,
6 reactor bed need not be changed to remove the deactivated mordenite zeolite
7 catalysts and catalyst composites. The deactivated mordenite zeolite
8 catalysts and catalyst composites are reactivated at the end of an alkylation
9 run by stopping the olefin feed stream to the reactor and permitting the
10 aromatic hydrocarbon stream to continue to be flushed through the reactor for
11 a sufficient time, typically from about 12 hours to about 24 hours.

12 EXAMPLES

13 Example 1

14 Preparation of Zeolite Catalyst Composition 1

15 Zeolite Catalyst Composition 1 is prepared by mixing zeolite Y powder and
16 mordenite zeolite powder available from Zeolyst International or any other
17 commercial source. The zeolite Y and mordenite zeolite powders are mixed
18 in any proportion based on the desired alkylated aromatic product.

19 As an example, zeolite Y catalyst powder is mixed with mordenite zeolite
20 catalyst powder to obtain a final ratio of 85:15 in the final Zeolite Catalyst
21 Composition.

22 Zeolite Catalyst Composition 1 is prepared by the following method:

23 Loss-on-ignition (LOI) is determined for samples of commercially available
24 zeolite Y (CBV 760® and CBV 600®) and mordenite zeolite (CBV 90A®)
25 available from Zeolyst International by heating the samples to 538°C for
26 1 hour. The LOI obtained provides the percent volatiles in the zeolite Y and

1 mordenite zeolite batches being used. The LOI of a commercial sample of
2 Versal® hydrated aluminum oxide available from Sasol is also obtained by
3 heating the samples to 538°C for 1 hour. Next, based on the results obtained
4 from the LOI of the zeolite Y, mordenite zeolite and the alumina powders the
5 amount of alumina powder is weighed out to obtain 80% (volatile-free basis)
6 zeolite content of the composite consists of 85% zeolite Y and 15% mordenite
7 zeolite on a volatile-free basis.

8 The three dry powders are added to a Baker Perkins mixer and dry mixed for
9 4 minutes. The amount of concentrated (70.7%) nitric acid to give
10 0.7 weight % (based on 100% nitric acid) of the dry weight of the zeolite and
11 the alumina powders is calculated. This amount of 70.7% nitric acid was
12 weighed out and dissolved in deionized water.

13 The total amount of water and 70.7% nitric acid needed to obtain a final
14 concentration of approximately 50% total volatiles is calculated as follows.
15 Volatiles in the Y zeolite, mordenite zeolite and alumina powders is
16 calculated. Nitric acid solution is considered to be 100% volatiles. Thus, the
17 amount of deionized water that must be added is the difference between the
18 final concentration of volatiles of 50% minus the total volatiles in the three
19 powders.

20 Deionized water is added over a period of 5 minutes to the powders in the
21 mixer using a peristaltic pump. The mixer is then stopped so that the walls of
22 the mixer can be scraped down. Mixing is then resumed and the solution of
23 nitric acid in water is added over 5 minutes using the peristaltic pump. At the
24 end of acid addition, mixing is continued for a total time of 40 minutes, with
25 occasional holds to allow for scraping the sides of the mixer. At the end of the
26 mixing period, the percent volatiles are measured. Additional amounts of
27 deionized water is added until the mixture appears extrudable and the percent
28 volatiles are again measured.

1 The wet mixture is extruded through 1.27 millimeters, asymmetric quadrilobe
2 die inserts, in a Bonnot extruder. The wet long cylindrical strands are dried at
3 121°C for 8 hours. The long cylindrical strands are then broken to give
4 extrudates with length to diameter ratio of 2:6. The extrudates are sieved and
5 the portion larger than 1.0 millimeter is retained.

6 The extrudates are then calcined in a muffle furnace using the following
7 temperature program:

8 The extrudates are heated to 593°C over two hours, then held at 593°C for
9 1/2 hour and next cooled to 204°C. A total weight of the extrudates is
10 obtained.

11 Mercury Intrusion Porosimetry is used to characterize the extrudates. A peak
12 macropore diameter in angstroms and a cumulative pore volume at diameters
13 less than 300 angstroms is obtained from the Mercury Intrusion Porosimetry
14 data.

15 The Zeolite Catalyst Composition is charged to a pilot plant reactor used for
16 the alkylation of aromatic hydrocarbons. The reaction effluent of this reactor
17 has greater than or equal to 99% conversion of the olefin feed stream. When
18 benzene is used as the aromatic hydrocarbon and the alkylation reaction is
19 conducted using the Zeolite Catalyst Composition, there is a much higher
20 attachment of the alkyl chain to the aromatic ring at the 2-position along the
21 alkyl chain in the alkylated benzene than when the zeolite Y catalyst
22 composite is used alone in the alkylation reaction.

23 Excess benzene is removed by distillation, stripping or any other suitable
24 means and the alkylated benzene is sulfonated using sulfonation procedures
25 well known in the art. The alkyl benzene sulfonic acid is further carbonated
26 with an alkaline earth metal and carbon dioxide.

1 Example 2

2 Preparation of Zeolite Y Catalyst Composite

3 Zeolite Y Catalyst Composite was prepared are described above in
4 Example 1 using zeolite Y CBV 760® available from Zeolyst International.

5 Example 3

6 Preparation of Mordenite Zeolite Catalyst Composite

7 Mordenite Zeolite Catalyst Composite was prepared are described above in
8 Example 1 using mordenite zeolite CBV 90A® available from Zeolyst
9 International.

10 Example 4

11 Preparation of Zeolite Catalyst Composition 2

12 Zeolite Catalyst Composition 2 is prepared by mixing Zeolite Y Catalyst
13 Composite and Mordenite Zeolite Catalyst Composite prepared in Examples 2
14 and 3. The Zeolite Y Catalyst Composite and Mordenite Zeolite Catalyst
15 Composite are mixed in any proportion based on the desired alkylated
16 aromatic product. As an example, Zeolite Y Catalyst Composite is mixed with
17 Mordenite Zeolite Catalyst Composite to obtain a final ratio of 85:15 in the
18 Zeolite Catalyst Composition 2.

19 The resulting Zeolite Catalyst Composition 2 is charged to a pilot plant reactor
20 for the alkylation of aromatic hydrocarbons as described below in Example 5.

21 Example 5

22 Preparation of alkylbenzene compositions using zeolite Y catalyst composite

23 Typically, alkylation of aromatic hydrocarbons with normal alpha olefins,
24 partially-branched-chain isomerized olefins and branched-chain olefins was
25 carried out as described below:

1 A fixed bed reactor constructed from 15.54 millimeters Schedule 160 stainless
2 steel pipe was used for this alkylation test. Pressure in the reactor was
3 maintained by an appropriate back pressure valve. The reactor and heaters
4 were constructed so that adiabatic temperature control could be maintained
5 during the course of alkylation runs. A 192 gram bed of 850 micrometer to
6 2 millimeters Alundum particles was packed in the bottom of the reactor to
7 provide a pre-heat zone. Next, 100 grams of a zeolite Y catalyst composite
8 similar to the zeolite Y catalyst composite prepared in Example 2 above was
9 charged to the fixed bed reactor. The reactor was gently vibrated during
10 loading to give a maximum packed bulk density of catalyst in the reactor.
11 Finally, void spaces in the catalyst bed were filled with 351 grams
12 150 micrometers Alundum particles as interstitial packing.

13
14 The reactor was then closed, sealed, and pressure tested under nitrogen.
15 Next, the alkylation catalyst was dehydrated during 15 hours at 200°C under a
16 20 liters per hour flow of nitrogen measured at ambient temperature and
17 pressure and then cooled to 100°C under nitrogen. Benzene was then
18 introduced into the catalytic bed in an up-flow manner at a flow rate of
19 195 grams per hour. Temperature (under adiabatic temperature control) was
20 increased to a start-of-run temperature of 182°C (measured just before the
21 catalyst bed) and the pressure was increased to 14.6 atmospheres.

22
23 When temperature and pressure had lined out at desired start-of-run
24 conditions of 182°C and 14.6 atmospheres, a feed mixture, consisting of
25 benzene and C₂₀₋₂₄ NAO at a molar ratio of 10:1 and dried over activated
26 alumina, was introduced in an up-flow manner. As the feed reached the
27 catalyst in the reactor, reaction began to occur and internal catalyst bed
28 temperatures increased above the inlet temperature. After about 8 hours
29 on-stream, the reactor exotherm was 20°C. At 26 hours on-stream, the olefin
30 conversion in the product was 99.1%. The run was stopped after 408 hours
31 on-stream, although the run could have continued. At this time, the olefin
32 conversion was 99.45%.

1 Alkylated aromatic hydrocarbon products containing excess benzene were
2 collected during the course of the run. After distillation to remove excess
3 aromatic hydrocarbon, analysis showed that greater than 99% conversion of
4 olefin was achieved during the course of the run.

5 A fixed bed reactor was constructed from 15.54 millimeters Schedule 160
6 stainless steel pipe. Pressure in the reactor was maintained by an
7 appropriate back pressure valve. The reactor and heaters were constructed
8 so that adiabatic temperature control could be maintained during the course of
9 alkylation runs. A small amount of 850 micrometer to 2 millimeters
10 acid-washed Alundum was packed in the bottom of the reactor to provide a
11 pre-heat zone. Next, 100 grams of whole alkylation extrudate catalyst was
12 charged to the fixed bed reactor. Finally, void spaces in the catalyst bed were
13 filled with 150 micrometers acid-washed Alundum interstitial packing. The
14 zeolite Y or the mordenite zeolite alkylation catalyst was then dehydrated for
15 at least 8 hours at 200°C under a flow of nitrogen gas and then cooled to
16 ambient temperature under nitrogen gas. Benzene was then introduced into
17 the catalytic bed in an up-flow manner. Temperature (isothermal temperature
18 control) and pressure were increased at start of run conditions. Normal
19 operating pressure was 11.91 atmospheres. The initial temperature of
20 approximately 150°C was chosen so that the temperature in the catalytic bed
21 increased under adiabatic temperature control to about 160°C to about 175°C.
22 When temperature and pressure had lined out at desired start-of-run
23 conditions, the reactor system was switched to adiabatic temperature control.
24 A dried feed mixture, consisting of olefin and benzene, was introduced in an
25 up-flow manner. The benzene to olefin molar ratio was 10:1. As the reaction
26 began to occur, temperature increased in the catalyst bed above the inlet
27 temperature.

28

29 Alkylated benzene product containing excess benzene was collected during
30 the course of the run. After distillation to remove excess benzene, analysis
31 showed that greater than 99% conversion of olefin was achieved during the
32 course of the run.

1

2

3

6

21

29

1 benzene and C₂₀₋₂₄ NAO at a molar ratio of 15:1 and dried over activated
2 alumina, was introduced in an up-flow manner at 200 grams per hour. As the
3 feed reached the catalyst in the reactor, reaction began to occur and internal
4 catalyst bed temperatures increased above the inlet temperature. After about
5 8 hours on-stream, the reactor exotherm was 20°C. In the first 57 hours
6 on-stream, the olefin conversion decreased from 100% to 98.8% (Run
7 Period 1). At this point, the catalyst bed was flushed with benzene at
8 200 grams per hour during 18 hours. Following the benzene flush, the
9 benzene and olefin feed flow was resumed. Inlet temperature was increased
10 to 162°C at 57 run hours. Feed was continued until 351 run hours (Run
11 Period 2 from 57 to 351 run hours). Olefin conversion was initially 98.9%
12 during Run Period 2 but declined to 98.1% at 321 run hours and further to
13 95.3% at 351 run hours. A second benzene flush was performed at 351 run
14 hours during 17 hours. After the second benzene flush, feed flow was
15 resumed again to start Run Period 3. Feed was continued until 550 run
16 hours. Olefin conversion was initially 98.5% but declined to 98.3% at 519 run
17 hours and to 97.0% at 550 run hours. A third benzene flush was done during
18 a weekend. Feed flow was resumed after the third benzene flush to begin
19 Run Period 4. At the beginning of Run Period 4, olefin conversion was 98.8%
20 and at 942 run hours the olefin conversion was 98.4%. The run was stopped
21 after 942 hours on-stream but could have continued longer.

22

23 Alkylated aromatic hydrocarbon products containing excess benzene were
24 collected during the course of the run. After distillation to remove excess
25 aromatic hydrocarbon, analysis showed that greater than 97% conversion of
26 olefin was achieved during most of the course of the run.

27

28

Example 7

29

Preparation of alkylbenzene sulfonic acids

30

A mixture of 85 weight % of the alkylated benzene prepared using the

31

zeolite Y catalyst and 15 weight % of the alkylated benzene prepared using

1 mordenite zeolite catalyst as in Examples 5 and 6 above was sulfonated by a
2 concurrent stream of sulfur trioxide (SO_3) and air with in a tubular reactor
3 (2 meters long, 1 centimeter inside diameter) in a down flow mode using the
4 following conditions:

5

6 Reactor temperature was 60°C , SO_3 flow rate was 73 grams per hour, and
7 alkylate flow rate was 327 grams per hour at a SO_3 to alkylate molar ratio of
8 1.05. The SO_3 was generated by passing a mixture of oxygen and sulfur
9 dioxide (SO_2) through a catalytic furnace containing vanadium oxide (V_2O_5).

10

11 The resulting crude alkylbenzene sulfonic acid had the following properties
12 based on the total weight of the product: weight % of HSO_3 was 15.61 % and
13 weight % of H_2SO_4 was 0.53.

14

15 The crude alkylbenzene sulfonic acid (1665 grams) was diluted with 83 grams
16 of 100 Neutral diluent oil and placed in a 4 liter four-neck glass reactor fitted
17 with a stainless steel mechanical agitator rotating at about 300 rpm, a
18 condenser and a gas inlet tube (2 millimeters inside diameter) located just
19 above the agitator blades for the introduction of nitrogen. The contents of the
20 reactor were placed under vacuum (40 millimeters Hg) and the reactor was
21 heated to 110°C with stirring and nitrogen was bubbled through the mixture at
22 about 30 liters per hour for about 30 minutes until the weight % of H_2SO_4 is
23 less than about 0.3 weight %. This material is the final alkylbenzene sulfonic
24 acid.

25

26 The final alkylbenzene sulfonic acid had the following properties based on the
27 total weight of the product: weight % of HSO_3 was 14.95 and weight % of
28 H_2SO_4 was 0.17.

29

Example 7

Preparation of alkylbenzene sulfonates

To a 5 liter four-neck glass reactor equipped with heating and cooling capability and fitted with a stainless steel mechanical agitator rotating at between 300 and 350 rpm, a gas inlet tube (2 millimeters inside diameter) located just above the agitator blades for the addition of CO₂, a distillation column and condenser under nitrogen gas was charged 129.4 grams of centrate.

The centrate was a mixture of the sludge fractions previously produced during the purification of high TBN carbonated, overbased synthetic sulfonates by centrifugation and decantation and was added to the reaction mixture of this example for recycling the contents of the centrate. The centrate had a TBN of 197 and contained approximately 73 grams of xylene solvent, 12 grams active calcium sulfonate, 9 grams calcium hydroxide and calcium carbonate, 8 grams of carbon dioxide, and 23 grams of 100 Neutral diluent oil.

Next, 40 grams of methanol, 207 grams of xylene solvent, 296.5 grams (0.59 mole) of the alkylbenzene sulfonic acid (HSO₃ was 14.95 weight % based on the total weight of the reaction mixture) from Example 6 above was charged to the reactor over 15 minutes at room temperature. A slurry of 160 grams (2.16 mole) of calcium hydroxide, 362 grams of xylene solvent and 94.2 grams of methanol was added to the reactor and the contents of the reactor were cooled to 25°C. Subsequently, 33 grams (0.79 mole) of CO₂ was added to the reactor through the gas inlet tube over 39 minutes while the temperature of the reactor increased to about 32°C. A second slurry composed of 160 grams (2.16 mole) of calcium hydroxide, 384 grams xylene solvent, and 131 grams of methanol was then added to the reactor concurrently with 0.9 grams of CO₂ over about 1 minute. Then 92 grams of CO₂ was added to the reactor over 64 minutes while the temperature of the reactor was increased from about 30°C to about 41°C. A third slurry

1 composed of 82 grams of oxide and 298 grams of xylene solvent was then
2 charged to the reactor concurrently with 1.4 grams of CO₂ over about
3 1 minute. Next, 55 grams (1.25 mole) of CO₂ was added to the reactor over
4 approximately 60 minutes while keeping the reactor temperature at
5 approximately 38°C.
6

7 The water and methanol were then distilled from the reactor by first heating
8 the reactor to 65°C over about 40 minutes at atmospheric pressure and then
9 to 93°C over about 60 minutes at atmospheric pressure and then finally to
10 130°C over about 30 minutes at atmospheric pressure. The temperature of
11 the reactor was then decreased to 110°C over about 60 minutes at
12 atmospheric pressure and next then cooled to approximately 30°C and
13 475.7 grams of 600 Neutral diluent oil was added to the reactor followed by
14 413 grams of xylene solvent. The sediment in the product was then removed
15 by centrifugation. The xylene solvent in the product was distilled by heating
16 the product to 204°C over approximately 45 minutes at 30 millimeters Hg
17 vacuum and holding the product at 204°C and 30 millimeters Hg vacuum for
18 10 minutes. The vacuum was replaced with nitrogen gas and the contents
19 allowed to cool to room temperature to obtain the overbased sulfonate having
20 the following properties based on the total weight of the product:
21

22 The weight % of calcium was 16.2, TBN was 429, weight % of sulfur was
23 1.70, weight % of calcium sulfonate was 0.94, and viscosity was 111 cSt at
24 100°C.

1 **CLAIMS:**

2 1. A process for preparing an alkylated aromatic composition comprising:

3

4 (a) contacting at least one aromatic hydrocarbon with at least one
5 olefin under alkylation conditions in the presence of a zeolite
6 catalyst having a macropore structure comprising zeolite Y, and
7 wherein the peak macropore diameter of the catalyst, measured
8 by ASTM Test No. D 4284-03, is less than or equal to about
9 2000 angstroms and the cumulative pore volume of the catalyst
10 at pore diameters less than or equal to about 500 angstroms,
11 measured by ASTM Test No. D 4284-03, is less than or equal to
12 about 0.30 milliliters per gram to form a first alkylated aromatic
13 hydrocarbon product;

14

15 (b) contacting at least one aromatic hydrocarbon with at least one
16 olefin under alkylation conditions in the presence of a zeolite
17 catalyst having a macropore structure comprising mordenite
18 zeolite having a silica to alumina molar ratio of about 50:1 to
19 about 105:1, and wherein the peak macropore diameter of the
20 catalyst, measured by ASTM Test No. D 4284-03, is less than or
21 equal to about 900 angstroms and the cumulative pore volume of
22 the catalyst at pore diameters less than or equal to about
23 500 angstroms, measured by ASTM Test No. D 4284-03, is less
24 than or equal to about 0.30 milliliters per gram to form a second
25 alkylated aromatic hydrocarbon product; and

26

27 (c) combining the first alkylated aromatic hydrocarbon product and
28 the second alkylated aromatic hydrocarbon product to form the
29 alkylated aromatic composition;

30

31 wherein steps (a) and (b) can be conducted in any order.

- 1
- 2 2. The process of claim 1 wherein step (b) further comprises the
- 3 reactivation of the deactivated zeolite catalyst with an aromatic
- 4 hydrocarbon flush.
- 5
- 6 3. The process of claim 2 further comprising sulfonating the alkylated
- 7 aromatic composition to form an alkylated aromatic sulfonic acid.
- 8
- 9 4. The process of claim 3 further comprising reacting the alkylated
- 10 aromatic sulfonic acid with an alkaline earth metal and carbon dioxide
- 11 to produce a carbonated, overbased alkylated aromatic sulfonate.
- 12
- 13 5. The process of claim 2 wherein the first alkylated aromatic
- 14 hydrocarbon product in the alkylated aromatic composition is in the
- 15 range of about 40 percent to about 99 percent based on the total
- 16 alkylated aromatic composition.
- 17
- 18 6. The process of claim 5 wherein the first alkylated aromatic
- 19 hydrocarbon product in the alkylated aromatic composition is in the
- 20 range of about 50 percent to about 90 percent based on the total
- 21 alkylated aromatic composition.
- 22
- 23 7. The process of claim 6 wherein the first alkylated aromatic
- 24 hydrocarbon product in the alkylated aromatic composition is in the
- 25 range of about 70 percent to about 80 percent based on the total
- 26 alkylated aromatic composition.
- 27
- 28 8. The process of any one of claims 2 to 7, wherein the olefin in step (a)
- 29 and step (b) is independently an alpha olefin, an isomerized olefin, a
- 30 branched-chain olefin, or mixtures thereof.

- 1 9. The process of claim 8 wherein the alpha olefin or isomerized olefin
2 has from about 6 carbon atoms to about 40 carbon atoms.
3
- 4 10. The process of claim 9 wherein the alpha olefin or isomerized olefin
5 has from about 20 carbon atoms to about 40 carbon atoms.
6
- 7 11. The process of claim 8 wherein the branched-chain olefin has from
8 about 6 carbon atoms to about 70 carbon atoms.
9
- 10 12. The process of claim 11 wherein the branched-chain olefin has from
11 about 8 carbon atoms to about 50 carbon atoms.
12
- 13 13. The process of claim 12 wherein the branched-chain olefin has from
14 about 12 carbon atoms to about 18 carbon atoms.
15
- 16 14. The process of any one of claims 2 to 7, wherein the olefin in step (a)
17 or step (b) is independently a partially-branched-chain isomerized
18 olefin, and wherein the olefin has from about 6 carbon atoms to about
19 40 carbon atoms.
20
- 21 15. The process of claim 14 wherein the partially-branched-chain
22 isomerized olefin has from about 20 carbon atoms to about 40 carbon
23 atoms.
24
- 25 16. The process of any one of claims 2 to 15, wherein the aromatic
26 hydrocarbon in step (a) and step (b) is independently toluene or
27 benzene.
28
- 29 17. The process of any one of claims 2 to 16, wherein the cumulative pore
30 volume of the zeolite catalysts at pore diameters less than or equal to
31 about 400 angstroms in steps (a) and (b) are less than or equal to
32 about 0.30 milliliters per gram.

- 1
- 2 18. The process of claim 17 wherein the cumulative pore volume of the
- 3 zeolite catalysts at pore diameters less than or equal to about
- 4 300 angstroms in steps (a) and (b) are less than or equal to about
- 5 0.25 milliliters per gram.
- 6
- 7 19. The process of claim 18 wherein the cumulative pore volume of the
- 8 zeolite catalysts at pore diameters less than or equal to about
- 9 300 angstroms in steps (a) and (b) are less than or equal to about
- 10 0.20 milliliters per gram.
- 11
- 12 20. The process of claim 19 wherein the cumulative pore volume of the
- 13 zeolite catalysts at pore diameters less than or equal to about
- 14 400 angstroms in steps (a) and (b) are in the range of about
- 15 0.05 milliliters per gram to about 0.18 milliliters per gram.
- 16
- 17 21. The process of claim 20 wherein the cumulative pore volume of the
- 18 zeolite catalysts at pore diameters less than or equal to about
- 19 300 angstroms in steps (a) and (b) are in the range of about
- 20 0.08 milliliters per gram to about 0.16 milliliters per gram.
- 21
- 22 22. The process of any one of claims 2 to 21, wherein in step (a) the peak
- 23 macropore diameter of the zeolite Y catalyst is in the range of about
- 24 700 angstroms to about 1800 angstroms.
- 25
- 26 23. The process of claim 22 wherein in step (a) the peak macropore
- 27 diameter of the zeolite catalyst is in the range of about 750 angstroms
- 28 to about 1600 angstroms.
- 29
- 30 24. The process of claim 23 wherein in step (a) the peak macropore
- 31 diameter of the zeolite catalyst is in the range of about 800 angstroms
- to about 1400 angstroms.

- 1
- 2 25. The process of any one of claims 2 to 21, wherein in step (b) the peak
3 macropore diameter of the mordenite zeolite catalyst is in the range of
4 about 400 angstroms to about 800 angstroms.
5
- 6 26. The process of claim 25 wherein in step (b) the peak macropore
7 diameter of the mordenite zeolite catalyst is in the range of about
8 400 angstroms to about 700 angstroms.
9
- 10 27. The process of claim 26 wherein in step (b) the peak macropore
11 diameter of the mordenite zeolite catalyst is in the range of about
12 450 angstroms to about 600 angstroms.
13
- 14 28. The process of any one of claims 2 to 27, wherein in step (a) the
15 zeolite Y catalyst has a silica to alumina ratio of about 5:1 to about
16 100:1.
17
- 18 29. The process of claim 28 wherein in step (a) the zeolite Y catalyst has a
19 silica to alumina ratio of about 30:1 to about 90:1.
20
- 21 30. The process of claim 29 wherein in step (a) the zeolite Y catalyst has a
22 silica to alumina ratio of about 60:1 to about 80:1.
23
- 24 31. The process of any one of claims 1 to 30 wherein in step (b) the mordenite
25 zeolite catalyst has a silica to alumina ratio of about 60:1 to about 80:1.
26
- 27 32. The process of any one of claims 2 to 31, wherein the zeolite Y in step
28 (a) and the mordenite zeolite in step (b) contain a binder.
29
- 30 33. The process of claim 32 wherein the binder in the zeolite Y in step (a)
31 and the binder in the mordenite zeolite in step (b) is alumina.

- 1
- 2 34. The process of any one of claims 2 to 33, wherein the zeolite Y in step
- 3 (a) and the mordenite zeolite in step (b) are in the form of a tablet.
- 4
- 5 35. A process for preparing an alkylated aromatic composition comprising
- 6 contacting at least one aromatic hydrocarbon with at least one olefin in
- 7 the presence of a zeolite catalyst having a macropore structure
- 8 comprising zeolite Y and mordenite zeolite, wherein the mordenite
- 9 zeolite has a silica to alumina molar ratio of about 50:1 to about 105:1,
- 10 and wherein the peak macropore diameter of the catalyst, measured
- 11 by ASTM Test No. D 4284-03, is less than or equal to about
- 12 2000 angstroms and the cumulative pore volume of the catalyst at
- 13 pore diameters less than or equal to about 500 angstroms, measured
- 14 by ASTM Test No. D 4284-03, is less than or equal to about 0.30
- 15 milliliters per gram.
- 16 36. The process of claim 35 wherein the cumulative pore volume of the
- 17 zeolite catalyst at pore diameters less than or equal to about
- 18 400 angstroms is less than or equal to about 0.30 milliliters per gram.
- 19
- 20 37. The process of claim 36 wherein the cumulative pore volume zeolite
- 21 catalyst at pore diameters less than or equal to about 300 angstroms
- 22 is less than or equal to about 0.25 milliliters per gram.
- 23
- 24 38. The process of claim 37 wherein the cumulative pore volume zeolite
- 25 catalyst at pore diameters less than or equal to about 300 angstroms
- 26 is less than or equal to about 0.20 milliliters per gram.
- 27
- 28 39. The process of claim 38 wherein the cumulative pore volume of the
- 29 zeolite catalyst at pore diameters less than or equal to about
- 30 400 angstroms is in the range of about 0.05 milliliters per gram to
- 31 about 0.18 milliliters per gram.

- 1
2 40. The process of claim 39 wherein the cumulative pore volume of the
3 zeolite catalyst at pore diameters less than or equal to about
4 300 angstroms is in the range of about 0.08 milliliters per gram to
5 about 0.16 milliliters per gram.
6
7 41. The process of any one of claims 35 to 40, wherein the peak
8 macropore diameter of the zeolite catalyst is in the range of about 400
9 angstroms to about 1500 angstroms.
10
11 42. The process of claim 41 wherein the peak macropore diameter of the
12 zeolite catalyst is in the range of about 500 angstroms to about
13 1300 angstroms.
14
15 43. The process of claim 42 wherein the peak macropore diameter of the
16 zeolite catalyst is in the range of about 600 angstroms to about
17 1100 angstroms.
18
19 44. The process of claim 43 wherein the peak macropore diameter of the
20 zeolite catalyst is in the range of about 750 angstroms to about
21 900 angstroms.
22
23 45. The process of any one of claims 35 to 44, wherein the zeolite Y has a
24 silica to alumina molar ratio of about 5:1 to about 100:1 and the
25 mordenite zeolite has a silica to alumina molar ratio of about 50:1 to
26 about 105:1.
27
28 46. The process of claim 45 wherein the zeolite Y has a silica to alumina
29 molar ratio of about 30:1 to about 90:1.
30

- 1 47. The process of claim 46 wherein the zeolite Y and the mordenite
2 zeolite independently have a silica to alumina molar ratio of about 60:1
3 to about 80:1.
4
- 5 48. The process of any one of claims 35 to 47, wherein the zeolite catalyst
6 contains a binder.
7
- 8 49. The process of claim 48 wherein the binder is alumina.
9
- 10 50. The process of any one of claims 35 to 49, wherein the zeolite catalyst
11 is in the form of a tablet.
12
- 13 51. A zeolite catalyst composition having a macropore structure
14 comprising:
15
- 16 (a) zeolite Y; and
17
- 18 (b) mordenite zeolite having a silica to alumina molar ratio of about
19 50:1 to about 105:1;
20
- 21 wherein the peak macropore diameter of the catalyst composition,
22 measured by ASTM Test No. D 4284-03, is less than about
23 2000 angstroms and the cumulative pore volume of the catalyst at
24 pore diameters less than or equal to about 500 angstroms, measured
25 by ASTM Test No. D 4284-03, is less than or equal to about 0.30
26 milliliters per gram.
27
- 28 52. The zeolite catalyst composition of claim 51 wherein the cumulative
29 pore volume at pore diameters less than or equal to about
30 400 angstroms is less than or equal to about 0.30 milliliters per gram.
31

- 1 53. The zeolite catalyst composition of claim 52 wherein the cumulative
2 pore volume of the zeolite catalyst composition at pore diameters less
3 than or equal to about 300 angstroms is less than or equal to about
4 0.25 milliliters per gram.
5
- 6 54. The zeolite catalyst composition of claim 53 wherein the cumulative
7 pore volume of the zeolite catalyst composition at pore diameters less
8 than or equal to about 300 angstroms is less than or equal to about
9 0.20 milliliters per gram.
10
- 11 55. The zeolite catalyst composition of claim 54 wherein the cumulative
12 pore volume of the zeolite catalyst composition at pore diameters less
13 than or equal to about 400 angstroms is in the range of about 0.05
14 milliliters per gram to about 0.18 milliliters per gram.
15
- 16 56. The zeolite catalyst composition of claim 55 wherein the cumulative
17 pore volume of the zeolite catalyst composition at pore diameters less
18 than or equal to about 300 angstroms is in the range of about 0.08
19 milliliters per gram to about 0.16 milliliters per gram.
20
- 21 57. The zeolite catalyst composition of any one of claims 51 to 56, wherein
22 the peak macropore diameter of the zeolite catalyst composition is in
23 the range of about 400 angstroms to about 1500 angstroms.
24
- 25 58. The zeolite catalyst composition of claim 57 wherein the peak
26 macropore diameter of the zeolite catalyst composition is in the range
27 of about 500 angstroms to about 1300 angstroms.
28
- 29 59. The zeolite catalyst composition of claim 58 wherein the peak
30 macropore diameter of the zeolite catalyst composition is in the range
31 of about 600 angstroms to about 1100 angstroms.
32

- 1 60. The zeolite catalyst composition of claim 59 wherein the peak
2 macropore diameter of the zeolite catalyst composition is in the range
3 of about 750 angstroms to about 900 angstroms.
4
- 5 61. The zeolite catalyst composition of any one of claims 51 to 60, wherein
6 the zeolite Y in (a) has a silica to alumina molar ratio of about 5:1 to
7 about 100:1.
8
- 9 62. The zeolite catalyst composition of claim 61 wherein the zeolite Y in
10 (a) has a silica to alumina molar ratio of about 30:1 to about 90:1.
11
- 12 63. The zeolite catalyst composition of claim 62 wherein the zeolite Y in
13 (a) has a silica to alumina molar ratio of about 60:1 to about 80:1.
14
- 15 64. The zeolite catalyst composition of any one of claims 51 to 63, wherein
16 the mordenite zeolite in (b) has a silica to alumina molar ratio of about
17 50:1 to about 105:1.
18
- 19 65. The zeolite catalyst composition of claim 64 wherein the mordenite
20 zeolite in (b) has a silica to alumina molar ratio of about 60:1 to about
21 80:1.
22
- 23 66. The zeolite catalyst composition of any one of claims 51 to 65, wherein
24 the zeolite catalyst composition contains a binder.
25
- 26 67. The zeolite catalyst composition of claim 66 wherein the binder is
27 alumina.
28
- 29 68. The zeolite catalyst composition of any one of claims 51 to 67, wherein
30 the zeolite catalyst composition is in the form of a tablet.
31