

PROCESS OF MAKING ALKYLAROMATICS USING EMM-12

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 61/084,166, filed July 28, 2008 which is hereby incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present disclosure relates to a process for producing alkylaromatic compounds, especially mono-alkylaromatic compounds, for example ethylbenzene, cumene and sec-butylbenzene, using a molecular sieve composition designated as EMM-12 which is an MCM-22 family material having unique XRD features.

BACKGROUND OF THIS DISCLOSURE

[0003] Molecular sieve materials, both natural and synthetic, have been demonstrated in the past to have catalytic properties for various types of hydrocarbon conversion. Molecular sieves that find application in catalysis include any of the naturally occurring or synthetic crystalline molecular sieves. Examples of these zeolites include large pore zeolites, intermediate pore size zeolites, and small pore zeolites. These zeolites and their isotypes are described in "Atlas of Zeolite Framework Types", eds. W. H. Meier, D. H. Olson and Ch. Baerlocher, Elsevier, Fifth Edition, 2001, which is hereby incorporated by reference. A large pore zeolite generally has a pore size of at least about 7 Å and includes LTL, VFI, MAZ, FAU, OFF, *BEA, and MOR framework type zeolites (IUPAC Commission of Zeolite Nomenclature). Examples of large pore zeolites include mazzite, offretite, zeolite L, VPI-5, zeolite Y, zeolite X, omega, and Beta. An intermediate pore size zeolite generally has a pore size from about 5 Å to less than about 7 Å and includes, for example, MFI, MEL, EUO, MTT, MFS, AEL, AFO, HEU, FER, MWW, and TON framework type zeolites (IUPAC Commission of Zeolite Nomenclature). Examples of intermediate pore size zeolites include ZSM-5, ZSM-11, ZSM-22, MCM-22, silicalite 1, and silicalite 2. A small pore size zeolite has a pore size from about 3 Å to less than about 5.0 Å and includes, for example, CHA, ERI, KFI, LEV, SOD, and LTA framework type zeolites (IUPAC Commission of Zeolite Nomenclature). Examples of small pore zeolites include ZK-4, ZSM-2, SAPO-34, SAPO-35, ZK-14, SAPO-42, ZK-21, ZK-22, ZK-5, ZK-20, zeolite A, chabazite, zeolite T, gmelinite, ALPO-17, and clinoptilolite.

[0004] U.S. Patent No. 4,439,409 refers to a crystalline molecular sieve composition of matter named PSH-3 and its synthesis from a reaction mixture for hydrothermal reaction

containing hexamethyleneimine, an organic compound which acts as directing agent for synthesis of the MCM-56 (U.S. Patent No. 5,362,697). Hexamethyleneimine is also taught for use in synthesis of crystalline molecular sieves MCM-22 (U.S. Patent No. 4,954,325) and MCM-49 (U.S. Patent No. 5,236,575). A molecular sieve composition of matter referred to as zeolite SSZ-25 (U.S. Patent No. 4,826,667) is synthesized from a reaction mixture for hydrothermal reaction containing an adamantane quaternary ammonium ion. U.S. Patent No. 6,077,498 refers to a crystalline molecular sieve composition of matter named ITQ-1 and its synthesis from a reaction mixture for hydrothermal reaction containing one or a plurality of organic additives.

10 **[0005]** U.S. Patent Application No. 11/823,129 discloses a molecular sieve composition designated as EMM-10-P, having, in its as-synthesized form, an X-ray diffraction pattern including d-spacing maxima at 13.18 ± 0.25 and 12.33 ± 0.23 Angstroms, wherein the peak intensity of the d-spacing maximum at 13.18 ± 0.25 Angstroms is at least as great as 90% of the peak intensity of the d-spacing maximum at 12.33 ± 0.23 Angstroms. U.S. Patent Application No. 11/824,742 discloses a molecular sieve composition designated as EMM-10, in its ammonium exchanged form or in its calcined form, comprising unit cells with MWW topology, said crystalline molecular sieve is characterized by diffraction streaking from the unit cell arrangement in the c direction. The crystalline molecular sieve is further characterized by the arced hk0 patterns of electron diffraction pattern. The crystalline molecular sieve is further characterized by the streaks in the electron diffraction pattern along the c^* direction. U.S. Patent Application No. 11/827,953 discloses a crystalline MCM-22 family molecular sieve having, in its as-synthesized form, an X-ray diffraction pattern including a peak at d-spacing maximum of 12.33 ± 0.23 Angstroms, a distinguishable peak at a d-spacing maximum between 12.57 to about 14.17 Angstroms and a non-discrete peak at a d-spacing maximum between 8.8 to 11 Angstroms, wherein the peak intensity of the d-spacing maximum between 12.57 to about 14.17 Angstroms is less than 90% of the peak intensity of the d-spacing maximum at 12.33 ± 0.23 Angstroms.

[0006] The term “MCM-22 family material” (or “material of the MCM-22 family” or “molecular sieve of the MCM-22 family”), as used herein, includes:

- 30 (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”, Fifth edition, 2001, the entire content of

which is incorporated as reference;

- (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 cell thickness", preferably one c-unit cell thickness;
- 5 (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, or any combination thereof; or
- 10 (iv) molecular sieves made by any regular or random 2-dimensional or 3-dimensional combination of unit cells having the MWW framework topology.

[0007] 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. Materials belong to the MCM-22 family include 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 No. 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), EMM-10-P (described in U.S. Patent Application No. 11/823,129) and EMM-10 (described in U.S. Patent Application No. 11/824,742). The entire contents of the patents are incorporated herein by reference.

[0008] It is to be appreciated the MCM-22 family molecular sieves described above are distinguished from conventional large pore zeolite alkylation catalysts, such as mordenite, in that the MCM-22 materials have 12-ring surface pockets which do not communicate with the 10-ring internal pore system of the molecular sieve.

[0009] The zeolitic materials designated by the IZA-SC as being of the MWW topology are multi-layered materials which have two pore systems arising from the presence of both 10 and 12 membered rings. The Atlas of Zeolite Framework Types classes five differently named materials as having this same topology: MCM-22, ERB-1, ITQ-1, PSH-3, and SSZ-25.

5 [0010] The MCM-22 family molecular sieves have been found to be useful in a variety of hydrocarbon conversion processes. Examples of MCM-22 family molecular sieve are MCM-22, MCM-49, MCM-56, ITQ-1, PSH-3, SSZ-25, and ERB-1. Such molecular sieves are useful for alkylation of aromatic compounds. For example, U.S. Patent No. 6,936,744
10 comprising the step of contacting a polyalkylated aromatic compound with an alkylatable aromatic compound under at least partial liquid phase conditions and in the presence of a transalkylation catalyst to produce the mono-alkylaromatic compound, wherein the transalkylation catalyst comprises a mixture of at least two different crystalline molecular sieves, wherein each of the molecular sieves is selected from zeolite beta, zeolite Y,
15 mordenite and a material 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.

[0011] A report by J. Ruan, P. Wu, B. Slater, L. Wu, J. Xiao, Y. Liu, M. He, O. Terasaki at the 15 IZA Conference in Beijing in 2007 disclosed ISE-MWW and ISE-FER materials, the former made from MCM-22-P material as starting material. U.S. Patent Application
20 Publication 2005/0158238 to Tatsumi et al. disclosed MWW type zeolite substance. U.S. Patent Application Publication 2004/0092757 to Oguchi et al. disclosed crystalline MWW type titanosilicate catalyst. A report by W. Fan, P. Wu, S. Namba, and T. Tatsumi (J. Catalyst 243 (2006) 183-191) disclosed a new titanosilicate molecular sieve with the structure analogous to MWW-type lamellar precursor. J. Ruan, P. Wu B. Slater and O. Terasaki
25 disclosed detailed structure of Ti-YNU-1 (Angew. Chem. Int. Ed., 2005, 44, 6719) similar to ISE-MWW.

[0012] These closely related materials may further be distinguished by comparing XRD diffraction patterns for d-spacing maxima corresponding to (002), (100), (101) and (102) reflections for both as-synthesized and calcined materials. The d-spacing maximum
30 corresponding to (002) reflection is typically in the range from 14.17 to 12.57 Angstroms (~ 6.15 - 7.05 deg 2θ Cu $K\alpha$ radiation). The d-spacing maximum corresponding to (100) reflection is typically in the range from 12.1 to 12.56 Angstroms (~ 7.3 - 7.05 deg 2θ). The d-spacing maximum corresponding to (101) reflection is typically in the range from 10.14 to

12.0 Angstroms (8.7-7.35 deg 2- θ). The d-spacing maximum corresponding to (102) reflection is typically in the range from 8.66 to 10.13 Angstroms (10.2-8.7 deg 2- θ). The following table (Table 1) summarizes the differences between MCM-22, MCM-49, EMM-10, MCM-56 and the titanosilicate material reported by Tatsumi et al. based on the existence
 5 and/or the feature of XRD diffraction pattern for d-spacing maxima corresponding to (002), (100), (101) and (102) reflections for both as-synthesized and calcined materials.

Table 1

	As-synthesized				Calcined			
XRD	(002)	(100)	(101)	(102)	(002)	(100)	(101)	(102)
MCM-22	MCM-22-P				MCM-22			
	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
	All four peaks are resolved. A valley exists between (101) and (102), wherein the measured intensity corrected for background at the lowest point being less than 50 % of the point at the same XRD d-spacing on the line connecting maxima for (101) and (102).				Peak corresponding to (002) is not visible. All other three peaks are resolved. A valley exists between (101) and (102), wherein the measured intensity corrected for background at the lowest point being less than 50 % of the point at the same XRD d-spacing on the line connecting maxima for (101) and (102).			
EMM-10	EMM-10-P				EMM-10			
	Yes	Yes	Non-discrete		Yes	Yes	Non-discrete	
	Both (002) peak and (100) peak are resolved, wherein the peak intensity for (002) is at least as great as 90% of the peak intensity of the d-spacing maximum for (100). Further, peaks corresponding to (101) and (102) are non-discrete or exhibit a valley but with measured intensity corrected for background at the lowest point being not less than 50 % of the point at the same XRD d-spacing on the line connecting maxima for (101) and (102).				Peak corresponding to (002) is not visible. Peak corresponding to (100) is well resolved. And, peaks corresponding to (101) and (102) are non-discrete or exhibit a valley but with measured intensity corrected for background at the lowest point being not less than 50 % of the point at the same XRD d-spacing on the line connecting maxima for (101) and (102).			

	As-synthesized				Calcined			
	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
MCM-22 family material as disclosed in U.S. Patent App. No. 11/827,953	Peaks corresponding to (002) and (100) are well resolved And, peaks corresponding to (101) and (102) are non-discrete peaks at a d-spacing maximum between 8.8 to 11 Angstroms, wherein the peak intensity of the (002) is less than 90% of the peak intensity of the (100).				Peak corresponding to (002) is not visible. All other three peaks are resolved. A valley exists between (101) and (102), wherein the measured intensity corrected for background at the lowest point being less than 50 % of the point at the same XRD d-spacing on the line connecting maxima for (101) and (102).			
	MCM-49-P				MCM-49			
	No	Yes	Yes	Yes	No	Yes	Yes	Yes
MCM-49	Peak corresponding to (002) is not visible or as a shoulder peak. Peak corresponding to (100) is well resolved. And, peaks corresponding to (101) and (102) are resolved or exhibit a valley but with measured intensity corrected for background at the lowest point being not greater than 50 % of the point at the same XRD d-spacing on the line connecting maxima for (101) and (102).				Peak corresponding to (002) is not visible or as a shoulder peak. Peak corresponding to (100) is well resolved. And, peaks corresponding to (101) and (102) are resolved or exhibit a valley but with measured intensity corrected for background at the lowest point being not greater than 50 % of the point at the same XRD d-spacing on the line connecting maxima for (101) and (102).			
	MCM-56-P				MCM-56			
	No	Yes	non-discrete		No	Yes	non-discrete	
MCM-56	Peak corresponding to (002) is not visible. Peak corresponding to (100) is well resolved. Peaks corresponding to (101) and (102) are non-discrete scattering.				Peak corresponding to (002) is not visible. Peak corresponding to (100) is well resolved. Peaks corresponding to (101) and (102) are non-discrete or exhibit a valley but with measured intensity corrected for background at the lowest point being not less than 50 % of the point at the same XRD d-spacing on the line connecting			

		maxima for (101) and (102).						
MWW material	Precursor (US Patent Publication 20050158238, Fig. 4)				Calcined (US Patent Publication 20050158238 Fig. 2)			
	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
	All four peaks are resolved. A valley exists between (101) and (102), wherein the measured intensity corrected for background at the lowest point being less than 50 % of the point at the same XRD d-spacing on the line connecting maxima for (101) and (102).				Only three peaks are resolved. A valley exists between (101) and (102), wherein the measured intensity corrected for background at the lowest point being less than 50 % of the point at the same XRD d-spacing on the line connecting maxima for (101) and (102).			
Ti-MCM-22	Precursor (J. Catal., Table 1)				Calcined (US20050158238 Fig. 1)			
	Yes	Yes	Yes	Yes	Yes/No	Yes	Yes	Yes
	All four peaks reported for Si/Ti = 106.				All four peaks are resolved for Si/Ti higher than 70. Only three peaks for Si/Ti less than 70. A valley exists between (101) and (102), wherein the measured intensity corrected for background at the lowest point being less than 50 % of the point at the same XRD d-spacing on the line connecting maxima for (101) and (102).			

[0013] It is known that crystal morphology, size and aggregation/agglomeration, or new x-ray diffraction can affect catalyst behavior, especially regarding catalyst activity and stability.

[0014] The alkylaromatic compounds ethylbenzene and cumene, for example, are valuable commodity chemicals which are used industrially for the production of styrene monomer and co-production of phenol and acetone respectively. In fact, a common route for the production of phenol comprises a process which involves alkylation of benzene with propylene to produce cumene, followed by oxidation of the cumene to the corresponding hydroperoxide, and then cleavage of the hydroperoxide to produce equal molar amounts of phenol and acetone. Ethylbenzene may be produced by a number of different chemical

processes. One process which has achieved a significant degree of commercial success is the vapor phase alkylation of benzene with ethylene in the presence of a solid, acidic ZSM-5 zeolite catalyst. Examples of such ethylbenzene production processes are described in U.S. Patents Nos. 3,751,504 (Keown), 4,547,605 (Kresge) and 4,016,218 (Haag).

5 **[0015]** Another process which has achieved significant commercial success is the liquid phase process for producing ethylbenzene from benzene and ethylene since it operates at a lower temperature than the vapor phase counterpart and hence tends to result in lower yields of by-products. For example, U.S. Patent No. 4,891,458 (Innes) describes the liquid phase synthesis of ethylbenzene with zeolite Beta, whereas U.S. Patent No. 5,334,795 (Chu)
10 describes the use of MCM-22 in the liquid phase synthesis of ethylbenzene.

[0016] Cumene has for many years been produced commercially by the liquid phase alkylation of benzene with propylene over a Friedel-Crafts catalyst, particularly solid phosphoric acid or aluminum chloride. More recently, however, zeolite-based catalyst systems have been found to be more active and selective for propylation of benzene to
15 cumene. For example, U.S. Patent No. 4,992,606 (Kushnerick) describes the use of MCM-22 in the liquid phase alkylation of benzene with propylene.

[0017] Existing alkylation processes for producing alkylaromatic compounds, for example ethylbenzene and cumene, inherently produce polyalkylated species as well as the desired monoalkylated product. It is therefore normal to transalkylate the polyalkylated
20 species with additional aromatic feed, for example benzene, to produce additional monoalkylated product, for example ethylbenzene or cumene, either by recycling the polyalkylated species to the alkylation reactor or, more frequently, by feeding the polyalkylated species to a separate transalkylation reactor. Examples of catalysts which have been used in the alkylation of aromatic species, such as alkylation of benzene with ethylene
25 or propylene, and in the transalkylation of polyalkylated species, such as polyethylbenzenes and polyisopropylbenzenes, are listed in U.S. Patent No. 5,557,024 (Cheng) and include MCM-49, MCM-22, PSH-3, SSZ-25, zeolite X, zeolite Y, zeolite Beta, acid dealuminized mordenite and TEA-mordenite. Transalkylation over a small crystal (<0.5 micron) form of TEA-mordenite is also disclosed in U.S. Patent 6,984,764 (Roth et al).

30 **[0018]** Where the alkylation step is performed in the liquid phase, it is also desirable to conduct the transalkylation step under liquid phase conditions. However, by operating at relatively low temperatures, liquid phase processes impose increased requirements on the catalyst, particularly in the transalkylation step where the bulky polyalkylated species must

be converted to additional monoalkylated product without producing unwanted by-products. This has proven to be a significant problem in the case of cumene production where existing catalysts have either lacked the desired activity or have resulted in the production of significant quantities of by-products such as ethylbenzene and n-propylbenzene.

- 5 [0019] There is, therefore, a need for a new process of producing alkylaromatic compounds, especially mono-alkylaromatic compounds, with crystalline molecular sieve.

SUMMARY OF THIS DISCLOSURE

- 10 [0020] In some embodiments, this disclosure relates to an alkylation process of producing mono-alkylaromatic compounds using a catalyst comprising EMM-12 molecular sieve, wherein the EMM-12 molecular sieve has, in its as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks having a d-spacing maximum in the range of 14.17 to 12.57 Angstroms (~ 6.15 - 7.05 deg $2-\theta$ Cu $K\alpha$), a d-spacing maximum in the range of 12.1 to 12.56 Angstroms (~ 7.3 - 7.05 deg $2-\theta$ Cu $K\alpha$), and non-discrete scattering between about 8.66 to 12.0 Angstroms or exhibit a valley in between the peaks having a d-spacing maximum in the range of 10.14 to 12.0 Angstroms (8.7 - 7.35 deg $2-\theta$ Cu $K\alpha$) and a d-spacing maximum in the range from 8.66 to 10.13 Angstroms (10.2 - 8.7 deg $2-\theta$) but with measured intensity corrected for background at the lowest point being not less than 50 % of the point at the same XRD d-spacing on the line connecting maxima in the range of 10.14 to 12.0 Angstroms (8.7 - 7.35 deg $2-\theta$ Cu $K\alpha$) and in the range from 8.66 to 10.13 Angstroms (10.2 - 8.7 deg $2-\theta$ Cu $K\alpha$).

- 20 [0021] In other embodiments, this disclosure relates to an alkylation process of producing mono-alkylaromatic compounds using a catalyst comprising EMM-12 molecular sieve, wherein the EMM-12 molecular sieve has, in its as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks at d-spacing maxima at 13.5 ± 0.25 , 12.33 ± 0.23 , and non-discrete scattering between about 8.66 to 12.0 Angstroms or exhibit a valley in between the peaks at 11.05 ± 0.3 and 9.31 ± 0.3 Angstroms but with measured intensity corrected for background at the lowest point being not less than 50 % of the point at the same XRD d-spacing on the line connecting maxima at around 11.05 ± 0.18 and 9.31 ± 0.13 Angstroms.

- 25 [0022] In yet other embodiments, the mono-alkylaromatic compounds comprise at least one of ethylbenzene, cumene and sec-butylbenzene.

- 30 [0023] In yet other embodiments, the process of this disclosure comprises contacting an alkylating agent with an alkylatable aromatic compound in the presence of a catalyst comprising EMM-12 under alkylation conditions to form mono-alkylaromatic compounds.

[0024] These and other facets of the present invention shall become apparent from the following detailed description, Figures, and appended claims.

BRIEF DESCRIPTION OF THE FIGURE

[0025] Figure 1 shows the XRD pattern between 5 to 11 degree 2- θ of Example 1.

5 **DETAILED DESCRIPTION**

Introduction

[0026] All patents, patent applications, test procedures (such as ASTM methods, UL methods, and the like), priority documents, articles, publications, manuals, and other documents cited herein are fully incorporated by reference to the extent such disclosure is not
10 inconsistent with the present invention and for all jurisdictions in which such incorporation is permitted.

[0027] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. While the illustrative embodiments of the disclosure have been described with particularity, it will be understood that various
15 other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present disclosure, including all features which would
20 be treated as equivalents thereof by those skilled in the art to which the disclosure pertains.

[0028] As used in this specification, the term “framework type” is used in the sense described in the “Atlas of Zeolite Framework Types,” 2001.

[0029] As used herein, the numbering scheme for the Periodic Table Groups is used as in Chemical and Engineering News, 63(5), 27 (1985).

25 **X-Ray Powder Diffraction Pattern**

[0030] The interplanar spacings, d 's, were calculated in Angstrom units ($\text{\AA}$), and the relative intensities of the lines, I/I_0 , where the intensity of the strongest line above background, I_0 , is counted as 100, were derived with the use of a profile fitting routine (or second derivative algorithm). The intensities are uncorrected for Lorentz and polarization
30 effects. The relative intensities are given in terms of the symbols VS=very strong (greater than 60 to 100), S=strong (greater than 40 to 60), M=medium (greater than 20 to 40) and W=weak (0 to 20). It should be understood that diffraction data listed as single lines may consist of multiple overlapping lines which under certain conditions, such as differences in

crystallographic changes, may appear as resolved or partially resolved lines. Typically, crystallographic changes can include minor changes in unit cell parameters and/or a change in crystal symmetry, without a change in the structure. These minor effects, including changes in relative intensities, can also occur as a result of differences in cation content, framework composition, nature and degree of pore filling, and thermal and/or hydrothermal history. Other changes in diffraction patterns can be indicative of important differences between materials, which is the case for comparing MCM-22 with similar materials, e.g., MCM-49, MCM-56, and PSH-3.

[0031] The interplanar spacings, d's, were considered broad if they exhibited peak width of about 1.5° or more at half height determined as 50 % intensity value from the maximum to the baseline.

[0032] The term "XRD distinguishable peak" as used herein is defined as XRD peak with clearly defined peak maximum, which is at least two times of the average background noise level.

[0033] The term "non-discrete" peaks (also "unresolved" peaks) in XRD as used herein means peaks having a monotonic profile in-between them (successive points either consistently increasing (or staying even) or decreasing (or staying even) within noise).

[0034] The term "discrete" peaks (also "resolved" peaks) in XRD as used herein means XRD peak(s) which are not non-discrete (unresolved).

[0035] Figure 1 graphically demonstrates the XRD pattern between 5 to 11 degree 2-θ of the product of Example 1. The measured intensity corrected for background at the lowest point between d-spacing maxima in the range of 10.14 to 12.0 Angstroms and in the range from 8.66 to 10.13 Angstroms, represented as B, is the distance between the lowest point (point a) and the point (point b) on the line of the background correction line at the same XRD d-spacing of the lowest point (point a). The distance between the point b and the point (point c) on the line connecting d-spacing maxima in the range of 10.14 to 12.0 Angstroms and in the range from 8.66 to 10.13 Angstroms at the same XRD d-spacing of the lowest point is represented as A.

Composition Matter of EMM-12

[0036] In some embodiments, the composition matter of EMM-12 has, in as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks having a d-spacing maximum in the range of 14.17 to 12.57 Angstroms (~6.15-7.05 deg 2-θ Cu Kα), such as, at 13.5±0.25, a d-spacing maximum in the range of 12.1 to 12.56 Angstroms (~7.3-7.05 deg 2-

0), such as, 12.33 ± 0.23 , and non-discrete scattering between about 8.66 to 12.0 Angstroms or exhibit a valley in between the peaks having a d-spacing maximum in the range of 10.14 to 12.0 Angstroms ($8.7-7.35$ deg $2-\theta$), such as, at 11.05 ± 0.3 , and a d-spacing maximum in the range from 8.66 to 10.13 Angstroms ($10.2-8.7$ deg $2-\theta$), such as, at 9.31 ± 0.3 Angstroms, with
5 measured intensity corrected for background at the lowest point being not less than 50 % of the point at the same XRD d-spacing on the line connecting d-spacing maximum in the range of 10.14 to 12.0 Angstroms ($8.7-7.35$ deg $2-\theta$) and d-spacing maximum in the range from 8.66 to 10.13 Angstroms ($10.2-8.7$ deg $2-\theta$).

[0037] In some embodiments, the composition matter of EMM-12 has, in as-synthesized
10 form and in calcined form, an X-ray diffraction pattern including peaks at d-spacing maxima at 13.5 ± 0.25 , 12.33 ± 0.23 , and non-discrete scattering between about 8.85 to 11.05 Angstroms or exhibit a valley in between the peaks at 11.05 ± 0.3 and 9.31 ± 0.3 Angstroms but with measured intensity corrected for background at the lowest point being not less than 50 % of the point at the same XRD d-spacing on the line connecting maxima at around 11.05 ± 0.18
15 and 9.31 ± 0.13 Angstroms.

[0038] In further embodiments, the composition matter of EMM-12 further has, in as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks at d-spacing maxima at 3.57 ± 0.06 and 3.43 ± 0.06 Angstroms. In yet further embodiments, the composition matter of EMM-12 further has, in as-synthesized form and in calcined form, an
20 X-ray diffraction pattern including peak at d-spacing maximum at 6.9 ± 0.15 Angstroms. In yet further embodiments, the composition matter of EMM-12 further has, in as-synthesized form and in calcined form, an X-ray diffraction pattern including peak at d-spacing maximum at 3.96 ± 0.08 Angstroms.

[0039] In other embodiments, the composition matter of EMM-12 has, in as-synthesized
25 form and in calcined form, an X-ray diffraction pattern including peaks at d-spacing maxima and relative intensities at 13.5 ± 0.25 (M-VS), 12.33 ± 0.23 (M-VS), and non-discrete scattering between about 8.85 to 11.05 Angstroms (W-S) or exhibit a valley in between the peaks at 11.05 ± 0.18 (W-S) and 9.31 ± 0.13 (W-S) Angstroms but with measured intensity corrected for background at the lowest point being not less than 50 % of the point at the same XRD d-
30 spacing on the line connecting maxima at around 11.05 ± 0.18 and 9.31 ± 0.13 Angstroms.

Table 2

Interplanar d-Spacing (Å)	Relative Intensity, I/I _o x 100
14.17 > d > 12.57	M-VS
12.56 > d > 12.1	M-VS
12.0 > d > 10.14	W-S
10.13 > d > 8.66	W-S
6.9 ± 0.15	W-M, broad
3.96 ± 0.08	W-VS, broad
3.57 ± 0.06	W-M
3.43 ± 0.06	M-VS

[0040] In other embodiments, the composition matter of EMM-12 further has, in as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks at d-spacing maxima at 3.57 ± 0.06 (W-M) and 3.43 ± 0.06 (M-VS) Angstroms. In yet further
5 embodiments, the composition matter of EMM-12 further has, in as-synthesized form and in calcined form, an X-ray diffraction pattern including peak at d-spacing maximum at 6.9±0.15 Angstroms (W-M, broad). In yet further embodiments, the composition matter of EMM-12 further has, in as-synthesized form and in calcined form, an X-ray diffraction pattern
10 including peak at d-spacing maximum at 3.96 ± 0.08 Angstroms (W-VS, broad).

[0041] In some preferred embodiments, the X-ray diffraction pattern of the crystalline molecular sieve EMM-12 further has peaks at d-spacing maxima and intensities listed in Table 2.

[0042] In some embodiments, the X-ray diffraction pattern of the crystalline molecular sieve EMM-12 of this disclosure further includes a d-spacing maximum at 28±2 Angstroms.
15

[0043] In some embodiments, the EMM-12 exhibits an extraordinary high collidine number of greater than 150 μmoles/g, preferably greater than 200 μmoles/g, more preferably greater than 250 μmoles/g, even more preferably greater than 300 μmoles/g, and most preferably greater than 350 μmoles/g, compared for up to about 200 μmoles/g for EMM-10
20 and 120 μmoles/g for MCM-22.

Chemical Composition of as-synthesized EMM-12 and calcined EMM-12

[0044] The as-synthesized EMM-12 molecular sieve material of this disclosure may have a composition, in terms of mole ratios of oxides:

YO₂/X₂O₃ in the range of 10 to infinity or in the range of 10 to 50;
25 M/X₂O₃ in the range of 0.005-0.1; and
R/X₂O₃ in the range of 1-4.

[0045] The calcined EMM-12 molecular sieve material of this disclosure may be prepared by calcining as-synthesized EMM-12 under calcination conditions to remove at least the majority of the organic template R from the as-synthesized EMM-12.

Process of making EMM-12

5 [0046] In some embodiments, this disclosure relates to a method of manufacturing an as-synthesized crystalline molecular sieve EMM-12, the method comprising the steps of:

- (a) providing a mixture comprising EMM-10-P family composition and acidic composition, optionally a spacing agent;
- (b) treating the mixture at treatment conditions to form a product comprising as-synthesized EMM-12; and
- (c) recovering the acid treated crystalline molecular sieve.

[0047] In some preferred embodiments, the as-synthesized EMM-12 is made by a process comprising:

- (1) providing a mixture comprising EMM-10-P having Si/Al₂ in the range from 10-infinity, preferable from about 10 to 150, and acidic composition comprising at least one of nitric acid, sulfuric acid, hydrochloric acid; oxalic acid, wherein said acid has a concentration of less than or equal to 10 N, preferably less than 1N, optionally a spacing agent comprising at least one of dimethyldiethoxy silane, diethyldiethoxy silane, and tetraethyl silane (TEOS), preferable TEOS; and
- (2) treating the mixture of step (1) to treatment conditions, wherein the treatment conditions comprise a temperature in the range of 50-170°C for a time in the range of 1-24 hrs, optionally with a stirring speed in the range of 0-1000 RPM.

[0048] The mixture of step (a) comprises EMM-10-P family composition, acidic composition, and optionally a spacing agent, wherein the weight ratio of the solid content of the EMM-10-P family composition over the acidic composition and the weight ratio of the spacing agent over the solid content of the EMM-10-P family composition are listed in the following table (Table 3). Useful and preferred ranges of the treatment temperature and treatment time are also listed in Table 3.

Table 3

	<u>Useful range</u>	<u>Preferred range</u>	<u>Most preferred range</u>
<u>Solid content (wt)</u> Acidic composition	0.001-1000	0.01-100	0.1-10
<u>Spacing agent (wt)</u> Solid content (wt)	0-2	0-1	0.01-0.5
Acid concentration (N)	0.001-10	0.001-5	0.01-2
Temperature (°C)	25-250	50-200	90-170
Time (hr)	0.01-240	1-48	1-24

[0049] The following solid content over acidic composition weight ratios are useful lower limits: 0.001, 0.01, 0.05, 0.1, 0.5, 1, 5, 10, 50, 100 and 500. The following solid content over acidic composition weight ratios are useful upper limits: 0.01, 0.05, 0.1, 0.5, 1, 5, 10, 50, 100, 500 and 1000. The solid content over acidic composition weight ratio falls in a range between any one of the above-mentioned lower limits and any one of the above-mentioned upper limits, so long as the lower limit is less than or equal to the upper limit. The solid content over acidic composition weight ratio may be present in an amount ranging from 0.01 to 100 in one embodiment, alternatively 0.1 to 10, alternatively 0.1 to 5.

[0050] The following ratios are useful lower spacing agent over solid content weight ratio limits: 0, 0.001, 0.01, 0.05, 0.1, 0.5, 1, and 1.5. The following ratios are useful upper spacing agent over solid content weight ratio limits: 0.001, 0.01, 0.05, 0.1, 0.5, 1, 1.5, and 2. The spacing agent over solid content weight ratio falls in a range between any one of the above-mentioned lower spacing agent over solid content weight ratio limits and any one of the above-mentioned upper spacing agent over solid content weight ratio limits, so long as the lower spacing agent over solid content weight ratio limit is less than or equal to the upper spacing agent over solid content weight ratio limit. The spacing over solid content weight ratio may be present in an amount ranging from 0 to 2 in one embodiment, alternatively 0 to 1, and alternatively 0.1 to 0.5.

[0051] The following temperatures (°C) are useful lower treatment temperature limits: 25, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, and 200. The following temperatures (°C) are useful upper treatment temperature limits: 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, and 250. The treatment temperature (°C) falls in a range between any one of the above-mentioned lower treatment temperature limits and any one of the above-mentioned upper treatment temperature limits, so long as the lower treatment temperature limit is less than or equal to the upper treatment

temperature limit. The treatment temperature may be present in an amount ranging from 25°C to 250°C in one embodiment, alternatively 70°C to 200°C, and alternatively 90°C to 170°C.

[0052] The following times (hr) are useful lower time limits for treatment: 0.01, 1, 5, 10, 20, 30, 50, 100, and 150. The following time (hr) are useful upper time limits for treatment: 1, 5, 10, 20, 40, 50, 70, 100, 150, 200, and 240. The time (hr) for treatment falls in a range between any one of the above-mentioned lower time limits for treatment and any one of the above-mentioned upper time limits for treatment, so long as the lower time limit for treatment is less than or equal to the upper time limit for treatment. The time for treatment may be present in an amount ranging from 1 to 100 in one embodiment, alternatively 1 to 48, and alternatively 1 to 24.

(1) EMM-10-P family composition

[0053] EMM-10-P family composition as used herein comprises at least one of EMM-10-P composition disclosed in U.S. Patent Application No.11/823,129 (its entirety of which is enclosed herein by reference) and as-synthesized MCM-22 family molecular sieve composition disclosed in U.S. Patent Application No. 11/827,953 (its entirety of which is enclosed herein by reference).

[0054] The EMM-10-P composition relates to a crystalline molecular sieve, designated as EMM-10-P, having, in its as-synthesized form, an X-ray diffraction pattern including d-spacing maxima at 13.18 ± 0.25 and 12.33 ± 0.23 Angstroms, wherein the peak intensity of the d-spacing maximum at 13.18 ± 0.25 Angstroms is at least as great as 90% of the peak intensity of the d-spacing maximum at 12.33 ± 0.23 Angstroms. In addition, the X-ray diffraction pattern of the EMM-10-P molecular sieve further includes two XRD distinguishable peaks with d-spacing maxima at 11.06 ± 0.18 and 9.25 ± 0.13 Angstroms, wherein the peak intensity of the d-spacing maximum at 11.06 ± 0.18 Angstroms is at least as great as the peak intensity of the d-spacing maximum at 9.25 ± 0.13 Angstroms. Additionally, the peaks with d-spacing maxima at 11.06 ± 0.18 and 9.25 ± 0.13 Angstroms may be non-discrete peaks.

[0055] Further the EMM-10-P relates to a crystalline MCM-22 family molecular sieve that has a total surface area of greater than $450 \text{ m}^2/\text{g}$ as measured by the N_2 BET method, and preferably has a ratio of the external surface area over the total surface area of less than 0.15 after conversion into H-form by exchange with ammonium nitrate and calcination, wherein the external surface area is determined from a t-plot of the N_2 BET.

[0056] Additionally, the EMM-10-P relates to a MCM-22 family crystalline molecular sieve that has a morphology of tabular habit, wherein at least 50 wt% of the crystalline

molecular sieve have a crystal diameter greater than 1 μm as measured by the SEM, preferably greater than 2 μm as measured by the SEM, preferably at least 50 wt% of the crystalline molecular sieve have a crystal thickness of about 0.025 μm as measured by the SEM.

- 5 **[0057]** U.S. Patent Application No. 11/827,953, its entirety of which is enclosed herein by reference, discloses a novel crystalline MCM-22 family molecular sieve having, in its as-synthesized form, an X-ray diffraction pattern including a peak at d-spacing maximum of 12.33 $\pm$ 0.23 Angstroms, a distinguishable peak at a d-spacing maximum between 12.57 to about 14.17 Angstroms and a non-discrete peak at a d-spacing maximum between 8.8 to 11
10 Angstroms, wherein the peak intensity of the d-spacing maximum between 12.57 to about 14.17 Angstroms is less than 90% of the peak intensity of the d-spacing maximum at 12.33 $\pm$ 0.23 Angstroms.

[0058] The EMM-10-P as disclosed in U.S. Patent Application No. 11/827,953, may be made by crystallizing a mixture having a composition in molar ratio listed in Table 4.

15

Table 4

Reactants	Useful	Preferred
YO ₂ / X ₂ O ₃	10 to infinity	15-55
H ₂ O/ YO ₂	1 to 10000	5-35
OH ⁻ / YO ₂ *	0.001-0.39	0.1-0.35
OH ⁻ / YO ₂ **	0.001-0.59	0.1-0.5
M/YO ₂	0.001-2	0.1-1
R/YO ₂	0.001-2	0.01-0.5
Seed***	0-25 wt%	1-5 wt%
R	Me ₆ -diquat-5 salt(s)	Me ₆ -diquat-5 salt(s)

[0059] After crystallization, the EMM-10-P product has a composition in molar ratio listed in Table 5.

Table 5

Reactants	Useful	Preferred
YO ₂ / X ₂ O ₃	10 to infinity	
M/ X ₂ O ₃	0.005-0.1	
R/ X ₂ O ₃	1-4	
R	Me ₆ -diquat-5 salt(s)	Me ₆ -diquat-5 salt(s)

20

[0060] U.S. Patent Application No. 11/827,953, its entirety of which is enclosed herein by reference, discloses a novel crystalline MCM-22 family molecular sieve. The as-synthesized composition disclosed in U.S. Patent Application No. 11/827,953 is a novel crystalline MCM-22 family molecular sieve having, in its as-synthesized form, an X-ray diffraction pattern including a peak at d-spacing maximum of 12.33 ± 0.23 Angstroms, a distinguishable peak at a d-spacing maximum between 12.57 to about 14.17 Angstroms and a non-discrete peak at a d-spacing maximum between 8.8 to 11 Angstroms, wherein the peak intensity of the d-spacing maximum between 12.57 to about 14.17 Angstroms is less than 90% of the peak intensity of the d-spacing maximum at 12.33 ± 0.23 Angstroms. The as-synthesized composition of U.S. Patent Application No. 11/827,953 may further comprises XRD peaks at d-spacing maxima at 3.57 ± 0.06 and 3.43 ± 0.06 Angstroms and/or a d-spacing maximum at 28 ± 1 Angstroms.

[0061] Furthermore, the X-ray diffraction pattern of the as-synthesized composition of U.S. Patent Application No. 11/827,953 includes values and relative intensities substantially as shown in Table 6:

Table 6

Interplanar d-Spacing (Å)	Relative Intensity, $I/I_0 \times 100$
$14.17 > d > 12.57$	M-VS
12.33 ± 0.23	M-VS
11.1 to 8.8	W-S
4.41 ± 0.1	W-M, broad
3.96 ± 0.08	W-VS, broad
3.57 ± 0.06	W-M
3.43 ± 0.06	M-VS

[0062] The solid content of an EMM-10-P family composition used in the weight ratio of the solid content of the EMM-10-P family composition over the acidic composition and the weight ratio of the spacing agent over the solid content of the EMM-10-P family composition is calculated by the total weight of tetravalent element oxide and trivalent element oxide in an EMM-10-P family composition.

(2) Acidic compositions

[0063] The acidic composition useful for this disclosure comprises an acidic solute and a solvent. The acidic solute comprises at least one of inorganic acid, such as, nitric acid hydrochloric acid and sulfuric acid, and organic acid, such as, oxalic acid and acetic acid, or any combination of inorganic acid and organic acid. Preferably, the acidic solute is nitric acid.

The solvent comprises at least one of water, methanol, ethanol, acetone and dimethylsulfone (DMSO).

[0064] The acid concentration of the acidic composition is in the range of 0.001 to 10. The following acid concentrations are useful lower limits: 0.001, 0.01, 0.05, 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, and 9. The following acid concentrations are useful upper limits: 0.01, 0.05, 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10. The acid concentration falls in a range between any one of the above-mentioned lower limits and any one of the above-mentioned upper limits, so long as the lower limit is less than or equal to the upper limit. The acid concentration may be present in an amount ranging from 0.001 to 5 in one embodiment, alternatively 0.01 to 4, and alternatively 0.1 to 2.

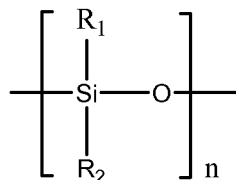
[0065] The weight of acidic composition as used in the solid content over acidic composition weight ratios is calculated based on the total weight of acidic solute and solvent.

(3) Optional spacing agent

[0066] Optionally, the acidic treatment step also comprises a spacing agent. The spacing agent useful is any agent capable of providing a silicon moiety that can stabilize the precursor in expanded form (i.e. having the distinct (002) peak at 13.5 ± 0.25 in both as-synthesized and calcined forms).

[0067] Examples of compounds for spacing include organo-compounds of a tetravalent element, a trivalent element, and/or pentavalent compounds, such as, organosilicon compound, organogermanium compound, orgnotitanium compounds, organoboron compounds, organoaluminum compound, and organophorphous compound. The organosilicon silicon compounds may comprise a polysiloxane include silicones, a siloxane, and a silane including disilanes and alkoxysilanes.

[0068] Silicone compounds that can be used in the present invention include the following:

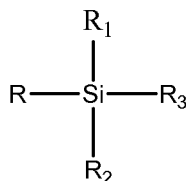


wherein R_1 is hydrogen, fluoride, hydroxy, alkyl, aralkyl, alkaryl or fluoro-alkyl. The hydrocarbon substituents generally contain from 1 to about 10 carbon atoms and preferably are methyl or ethyl groups. R_2 is selected from the same group as R_1 , and n is an integer of at least 2 and generally in the range of 2 to about 1000. The molecular weight of the silicone

compound employed is generally between about 80 to about 20,000 and preferably about 150 to about 10,000. Representative silicone compounds include dimethylsilicone, diethylsilicone, phenylmethylsilicone, methyl hydrogensilicone, ethylhydrogensilicone, phenylhydrogensilicone, fluoropropylsilicone, ethyltrifluoropropylsilicone, tetrachlorophenyl methyl methylethylsilicone, phenylethylsilicone, diphenylsilicone, methyltrisilicone, tetrachlorophenylethyl silicone, methylvinylsilicone and ethylvinylsilicone. The silicone compound need not be linear but may be cyclic as for example hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, hexaphenyl cyclotrisiloxane and octaphenylcyclotetrasiloxane. Mixtures of these compounds may also be used as well as silicones with other functional groups.

[0069] Useful siloxanes and polysiloxanes include as non-limiting example hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethyl cyclopentasiloxane, hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, hexaethylcyclotrisiloxane, octaethylcyclo tetrasiloxane, hexaphenylcyclotrisiloxane and octaphenylcyclo-tetrasiloxane.

[0070] Useful silanes, disilanes, or alkoxysilanes include organic substituted silanes having the general formula:



wherein R is a reactive group such as hydrogen, alkoxy, halogen, carboxy, amino, acetamide, trialkylsilyloxy, R₁, R₂ and R₃ can be the same as R or can be an organic radical which may include alkyl of from 1 to about 40 carbon atoms, alkyl or aryl carboxylic acid wherein the organic portion of alkyl contains 1 to about 30 carbon atoms and the aryl group contains about 6 to about 24 carbons which may be further substituted, alkylaryl and arylalkyl groups containing about 7 to about 30 carbon atoms. Preferably, the alkyl group for an alkyl silane is between about 1 and about 4 carbon atoms in chain length. Mixtures may also be used.

[0071] The silanes or disilanes include, as non-limiting examples, dimethylphenylsilane, phenyltrimethylsilane, triethylsilane and hexamethyldisilane. Useful alkoxysilanes are those with at least one silicon-hydrogen bond.

Alkylation Process

[0072] The term “aromatic” in reference to the alkylatable aromatic compounds which may be useful as feedstock herein is to be understood in accordance with its art-recognized scope. This includes alkyl substituted and unsubstituted mono- and polynuclear compounds.

5 Compounds of an aromatic character that possess a heteroatom may also be useful provided sufficient catalytic activity is maintained under the reaction conditions selected.

[0073] Substituted aromatic compounds that 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, and/or
10 other groups that do not interfere with the alkylation reaction.

[0074] Suitable aromatic compounds include benzene, naphthalene, anthracene, naphthacene, perylene, coronene, and phenanthrene, with benzene being preferred.

[0075] Generally the alkyl groups that may be present as substituents on the aromatic compound contain from 1 to about 22 carbon atoms and usually from about 1 to 8 carbon
15 atoms, and most usually from about 1 to 4 carbon atoms.

[0076] Suitable alkyl substituted aromatic compounds include toluene, xylene, isopropylbenzene, n-propylbenzene, alpha-methylnaphthalene, ethylbenzene, mesitylene, durene, cymenes, butylbenzene, pseudocumene, o-diethylbenzene, m-diethylbenzene, p-diethylbenzene, isoamylbenzene, isohexylbenzene, pentaethylbenzene, pentamethylbenzene;
20 1,2,3,4- 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; dimethylnaphthalenes; ethylnaphthalene; 2,3-dimethylantracene; 9-ethylantracene; 2-methylantracene; o-methylantracene; 9,10-dimethylphenanthrene; and 3-methyl-phenanthrene. Higher molecular weight alkylaromatic
25 compounds can also be used as starting materials and include aromatic organics such as are produced by the alkylation of aromatic organics 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 high boiling fraction in which the
30 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 n-propyl benzene and xylenes respectively. These by-products made in such instances may be less than about 100 wppm.

[0077] Reformate containing a mixture of benzene, toluene and/or xylene constitutes a particularly useful feed for the alkylation process of this disclosure.

[0078] The alkylating agents that may be useful in the process of this disclosure generally include any aliphatic or aromatic organic compound having one or more available alkylating aliphatic groups capable of reaction with the alkylatable aromatic compound, preferably with the alkylating group possessing from 1 to 5 carbon atoms. Examples of suitable alkylating agents are olefins such as ethylene, propylene, the butenes such as, for example, 1-butene, 2-butene or isobutylene, and the pentenes; 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, and n-valeraldehyde; and alkyl halides such as methyl chloride, ethyl chloride, the propyl chlorides, the butyl chlorides, and the pentyl chlorides, alkylaromatic compounds, such as, trimethylbenzenes, di-ethylbenzenes, triethylbenzenes, and so forth. Mixtures of these compounds may also be useful, such as, for example, propylene and propanol mixtures.

[0079] Mixtures of light olefins are useful as alkylating agents in the alkylation process of this disclosure. 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 off-gas containing ethylene, propylene, etc., naphtha cracker off-gas containing light olefins, refinery FCC propane/propylene streams, etc., are useful alkylating agents. For example, a typical FCC light olefin stream possesses the following composition:

	<u>Wt. %</u>	<u>Mole %</u>
Ethane	3.3	5.1
Ethylene	0.7	1.2
Propane	4.5	15.3
25 Propylene	42.5	46.8
Isobutane	12.9	10.3
n-Butane	3.3	2.6
Butenes	22.1	18.32
Pentanes	0.7	0.4

[0080] Reaction products that may be obtained from the process of the present disclosure include ethylbenzene from the reaction of benzene with ethylene, cumene from the reaction of benzene with propylene, ethyltoluene from the reaction of toluene with ethylene, cymenes from the reaction of toluene with propylene, and sec-butylbenzene from the reaction of benzene and n-butenes. Particularly preferred process mechanisms of the disclosure relate to

the production of cumene by the alkylation of benzene with propylene and production of ethylbenzene by the alkylation of benzene with ethylene.

[0081] The reactants can be partially or completely in the liquid phase and can be neat, i.e. free from intentional admixture or dilution with other material, or they can be brought
5 into contact with the catalyst composition with the aid of carrier gases or diluents such as, for example, hydrogen, methane and/or nitrogen.

[0082] The alkylation process of this disclosure may be conducted such that the organic reactants, i.e., the alkylatable aromatic compound and the alkylating agent, are brought into contact with the presently required catalyst in a suitable reaction zone under effective
10 alkylation conditions. Such conditions include a temperature of from about 0°C to about 500°C, preferably from about 10°C to about 260°C, a pressure of from about 20 to about 25000 kPa-a, preferably from about 100 to about 5500 kPa-a, a molar ratio of alkylatable aromatic compound to alkylating agent of from about 0.1:1 to about 50:1, preferably from about 0.5:1 to about 10:1, and a feed weight hourly space velocity (WHSV) based on the
15 alkylating agent of from about 0.1 to 500 hr⁻¹, preferably from about 0.1 to about 100 hr⁻¹.

[0083] When benzene is alkylated with ethylene to produce ethylbenzene, the alkylation reaction is preferably carried out in the liquid phase under conditions including a temperature of from about 150°C to about 300°C, more preferably from about 170°C to about 260°C; a pressure up to about 20400 kPa-a, more preferably from about 2000 kPa-a to about 5500 kPa-
20 a; a weight hourly space velocity (WHSV) based on the ethylene alkylating agent of from about 0.1 to about 20 hr⁻¹, more preferably from about 0.5 to about 6 hr⁻¹; and a ratio of benzene to ethylene in the alkylation reaction zone of from about 0.5:1 to about 100:1 molar, preferably 0.5:1 to 50:1 molar, more preferably from about 1:1 to about 30:1 molar, most preferably from about 1:1 to about 10:1 molar.

[0084] When benzene is alkylated with propylene to produce cumene, the reaction may also take place under liquid phase conditions including a temperature of up to about 250°C, preferably up to about 150°C, e.g., from about 10°C to about 125°C; a pressure of about 25000 kPa-a or less, e.g., from about 100 to about 3000 kPa-a; a weight hourly space velocity (WHSV) based on propylene alkylating agent of from about 0.1 hr⁻¹ to about 250 hr⁻¹,
25 preferably from about 1 hr⁻¹ to about 50 hr⁻¹; and a ratio of benzene to propylene in the alkylation reaction zone of from about 0.5:1 to about 100:1 molar, preferably 0.5:1 to 50:1 molar, more preferably from about 1:1 to about 30:1 molar, most preferably from about 1:1 to about 10:1 molar.
30

[0085] When benzene is alkylated with a butene to produce sec-butylbenzene, the reaction may also take place under liquid phase conditions including a temperature of up to about 250°C, preferably up to about 150°C, e.g., from about 10°C to about 125°C; a pressure of about 25000 kPa-a or less, e.g., from about 1 to about 3000 kPa-a; a weight hourly space velocity (WHSV) based on the butene alkylating agent of from about 0.1 hr⁻¹ to about 250 hr⁻¹, preferably from about 1 hr⁻¹ to about 50 hr⁻¹; and a ratio of benzene to butene in the alkylation reaction zone of from about 0.5:1 to about 100:1 molar, preferably 0.5:1 to 50:1 molar, more preferably from about 1:1 to about 30:1 molar, most preferably from about 1:1 to about 10:1 molar.

10 [0086] A summary of the molecular sieves and/or zeolites, in terms of production, modification and characterization of molecular sieves, is described in the book "Molecular Sieves - Principles of Synthesis and Identification"; (R. Szostak, Blackie Academic & Professional, London, 1998, Second Edition). In addition to molecular sieves, amorphous materials, chiefly silica, aluminum silicate and aluminum oxide, have been used as adsorbents and catalyst supports. A number of long-known forming techniques, like spray drying, pilling, pelletizing and extrusion, have been and are being used to produce macrostructures in the form of, for example, spherical particles, extrudates, pellets and Tablets of both micropores and other types of porous materials for use in catalysis, adsorption and ion exchange. A summary of these techniques is described in "Catalyst Manufacture," A. B. Stiles and T. A. Koch, Marcel Dekker, New York, 1995.

20 [0087] To the extent desired, the original metal cations of the as-synthesized material can be replaced in accordance with techniques well known in the art, at least in part, by ion exchange with other cations. Preferred replacing cations include metal ions, hydrogen ions, hydrogen precursor, e.g., ammonium, ions and mixtures thereof. Particularly preferred cations are those which tailor the catalytic activity for certain hydrocarbon conversion reactions. These include hydrogen, rare earth metals and metals of Groups 1-17, preferably Groups 2-12 of the Periodic Table of the Elements.

30 [0088] The EMM-12 crystalline molecular sieve of this disclosure should be generally dehydrated, at least partially. This can be done by heating to a temperature in the range of e.g., 200°C to 595°C in an atmosphere such as air or nitrogen, and at atmospheric, sub-atmospheric or super-atmospheric pressures for e.g., between 30 minutes and 48 hours. The degree of dehydration is measured by the percentage of weight loss relative to the total weight loss of a molecular sieve sample at 595°C under flowing dry nitrogen (less than 0.001

kPa partial pressure of water vapor) for 48 hours. Dehydration can also be performed at room temperature (~25°C) merely by placing the silicate in a vacuum, but a longer time is required to obtain a sufficient amount of dehydration.

[0089] The EMM-12 crystalline molecular sieve of this disclosure especially in its metal, hydrogen and ammonium forms can be beneficially converted to another form by thermal treatment. This thermal treatment is generally performed by heating one of these forms at a temperature of at least 370°C for at least one minute and generally not longer than 1000 hours. While sub-atmospheric pressure can be employed for the thermal treatment, atmospheric pressure is desired for reasons of convenience. The thermal treatment can be performed at a temperature up to about 925°C. The thermal treated product is particularly useful in the catalysis of certain hydrocarbon conversion reactions. The thermally treated product, especially in its metal, hydrogen and ammonium forms, is particularly useful in the catalysis of certain organic, e.g., hydrocarbon, conversion reactions. Non-limiting examples of such reactions include those described in U.S. Patent Nos. 4,954,325; 4,973,784; 4,992,611; 4,956,514; 4,962,250; 4,982,033; 4,962,257; 4,962,256; 4,992,606; 4,954,663; 4,992,615; 4,983,276; 4,982,040; 4,962,239; 4,968,402; 5,000,839; 5,001,296; 4,986,894; 5,001,295; 5,001,283; 5,012,033; 5,019,670; 5,019,665; 5,019,664; and 5,013,422, each incorporated herein by reference as to the description of the catalytic reactions.

[0090] The EMM-12 crystalline molecular sieve of this disclosure can be shaped into a wide variety of particle sizes. Generally speaking, the particles can be in the form of a powder, a granule, or a molded product, such as an extrudate. In cases where the catalyst is molded, such as by extrusion, the crystals can be extruded before drying or partially dried and then extruded.

[0091] It is desired to incorporate the EMM-12 molecular sieve with another material resistant to the temperatures and other conditions employed in alkylation processes. Such materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and/or metal oxides such as alumina. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Use of a material in conjunction with the EMM-12 molecular sieve, i.e. combined therewith or present during synthesis of the EMM-12 molecular sieve, which is active, tends to change the conversion and/or selectivity of the catalyst. Inactive materials suitably serve as diluents to control the amount of conversion in a given process so that products can be obtained economically and orderly without employing

other means for controlling the rate of reaction. These materials may be incorporated into naturally occurring clays, e.g., bentonite and kaolin, to improve the crush strength of the catalyst under commercial operating conditions. The materials, i.e. clays, oxides, etc., function as binders for the catalyst. It is desirable to provide a catalyst having good crush strength because in commercial use it is desirable to prevent the catalyst from breaking down into powder-like materials. These clay binders have been employed normally only for the purpose of improving the crush strength of the catalyst.

[0092] Naturally occurring clays which can be composited with the EMM-12 molecular sieve include the montmorillonite and kaolin family, which families include the subbentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dictite, narcite, or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, treatment or chemical modification. Binders useful for compositing with the present crystal also include inorganic oxides, notably alumina.

[0093] In addition to the foregoing materials, the EMM-12 molecular sieve can be composited with a porous matrix material such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia silica-alumina-magnesia and silica-magnesia-zirconia.

[0094] The relative proportions of finely divided EMM-12 crystalline molecular sieve and inorganic oxide matrix vary widely, with the crystal content ranging from about 1 to about 99 percent by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of about 20 to about 80 wt% of the composite.

[0095] The following examples reflect embodiments of the invention and are by no means intended to be limiting of the scope of the invention.

Experiments

Powder X-ray Diffraction

[0096] Powder x-ray data were obtained on a Bruker D4 instrument in Bragg-Brentano geometry with monochromatic Cu K α radiation. The pattern used for structural characterization extended from 1.2 to 80° in 2 θ . Intensities for Rietveld refinement were extracted from the continuous scans.

Surface areas

[0097] The overall surface area of a molecular sieve may be measured by the Brunauer-Emmett-Teller (BET) method using adsorption-desorption of nitrogen (temperature of liquid nitrogen, 77 K). The internal surface area may be calculated using t-plot of the Brunauer-Emmett-Teller (BET) measurement. The external surface area is calculated by subtracting the internal surface area from the overall surface area measured by the Brunauer-Emmett-Teller (BET) measurement.

Collidine number measurement

[0098] The collidine number of a molecular sieve may be measured by TGA. A sample is dried at 200°C to constant weight (weight change less than $\pm 1\%$ for the period of 1 hour). The weight of the dried sample, the sorbate, is then measured. The sorbent, 2,4,6-collidine, is delivered by a sparger maintained at 3 Torr collidine partial pressure and carried over the sample by nitrogen passed 200 ml/min for 60 min. The collidine number is expressed as micromoles of adsorbed per gram of the sorbate.

Example 1: Preparation of EMM-12

[0099] A sample of EMM-10-P (1.5 g) made according to Example 1 of U.S. Patent Application No.11/823,129 was added to the mixture of 30 g of 1 M nitric acid and 0.3 g of diethoxydimethylsilane. The reaction was carried out in a teflon container sealed in a Parr™ bomb in the oven at 170°C for 24 hrs. The solid product of EMM-12 was isolated by filtration, washed and dried at 120°C.

[00100] The XRD pattern of the solid product of EMM-12 is characterized as comprising a doublet at between 12.45 and 13.60 Angstroms, corresponding to $6.5\text{-}7.1^\circ 2\theta$ (Cu K α) and non-discrete scattering between 8.85 to 11.05 Angstroms, the $8\text{-}10^\circ 2\theta$ (Cu K α) region or exhibit a valley in between the peaks at 11.05 ± 0.18 and 9.31 ± 0.13 Angstroms but with measured intensity corrected for background at the lowest point being not less than 50 % of the point at the same XRD d-spacing on the line connecting maxima at around 11.05 ± 0.18 and 9.31 ± 0.13 Angstroms.

[00101] The calcined product of EMM-12 has high surface area of 523 m²/g and extraordinary enhancement of collidine adsorption of 321 $\mu\text{moles/g}$.

Benzene

[00102] Benzene was obtained from a commercial source. The benzene was passed through a pretreatment vessel containing equal parts (by volume) molecular sieve 13X, molecular sieve 4A, Engelhard F-24 Clay, and Selexsorb CD (in order from inlet to outlet),

and then through a pretreatment vessel containing MCM-22 catalyst. All feed pretreatment materials were dried in a 260°C oven for 12 hours before using.

Propylene

[00103] Propylene was obtained from a commercial specialty gases source and was
5 polymer grade.

Ethylene

[00104] Ethylene was obtained from a commercial specialty gases source and was polymer grade.

Nitrogen

10 [00105] Nitrogen was ultra high purity grade and obtained from a commercial specialty gases source.

Example 2

[00106] A 65 wt.% EMM-12 calcined of Example 1 and 35 wt.% alumina catalyst was prepared. This catalyst was tested for benzene alkylation with propylene to form cumene.

15 Feed Pretreatment

[00107] The experiment was conducted in a fixed bed 3/8" OD tubular reactor in a downflow configuration with an 1/8" internal thermocouple. The reactor furnace was controlled in isothermal mode. Two grams of catalyst sized to 14/20 mesh was loaded into the 3/8" reactor. Experiment was conducted with catalyst loaded into the 3/8" reactor. The
20 catalyst bed was axially centered in the middle furnace zone. The catalyst was packed with inert sand to fill the interstitial void spaces. Reaction conditions were 130°C, 2169 kPa-a and the benzene/propylene molar ratio was 3/1. Weight hourly space velocity was 1 hr⁻¹ on a propylene basis.

[00108] At reactor start-up, the reactor was brought to reaction pressure of 2169 kPa-a
25 with the ultra high purity nitrogen, and heated to reaction temperature of 150°C prior to introducing the benzene feed for 24 hours. The catalyst was allowed to equilibrate for 1 day prior to introducing the propylene to achieve steady state before data was collected. The reactor was cooled to 130°C under benzene flow and then propylene was introduced. Products were collected and analyzed for 13 days on-stream. Results shows that
30 Diisopropylbenzene (DIPB) over cumene (isopropylbenzene, IPB) molar ratios of the products fall in the range of 10% to 14%.

Example 3

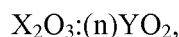
[00109] One gram of pellet of 65 wt.% EMM-12 and 35 wt.% Versal 300 alumina (commercially available from UOP) was used for benzene alkylation with ethylene to form ethylbenzene. The catalyst was calcined for 2 hours at 538°C

- 5 [00110] Benzene alkylation with ethylene was conducted by charging a fixed weight of catalyst to a well-mixed Parr autoclave reactor along with a mixture comprising benzene and ethylene (benzene/ethylene ratio of 3.5 molar). The reaction was carried out at 220°C and 3893 KPa-a (550 psig) for 4 hours. A small sample of the product was withdrawn at regular intervals and analyzed by gas chromatography. The catalyst performance was assessed by a
- 10 kinetic activity rate constant and diethylbenzene/ethylbenzene weight ratio after 4 hours. The EMM-12 catalyst has an activity of $2 \text{ (hr.gmole/cc)}^{-1}$ and a selectivity of 5.3 measured by diethylbenzene/ethylbenzene weight ratio.

Claims

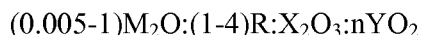
We claim:

1. A process for manufacturing a mono-alkylaromatic compound, said process comprising contacting a feedstock comprising an alkylatable aromatic compound and an alkylating agent under alkylation reaction conditions with a catalyst comprising a molecular sieve having, in its as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks having a d-spacing maximum in the range of 14.17 to 12.57 Angstroms, a d-spacing maximum in the range of 12.1 to 12.56 Angstroms, and non-discrete scattering between about 8.85 to 11.05 Angstroms or exhibit a valley in between the peaks having a d-spacing maximum in the range of 10.14 to 12.0 Angstroms and a d-spacing maximum in the range from 8.66 to 10.13 Angstroms with measured intensity corrected for background at the lowest point being not less than 50% of the point at the same XRD d-spacing on the line connecting maxima in the range of 10.14 to 12.0 Angstroms and in the range from 8.66 to 10.13 Angstroms.
2. The process of claim 1, wherein said molecular sieve further has, in its as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks at 6.9 ± 0.15 , 3.57 ± 0.07 and 3.42 ± 0.07 Angstroms.
3. The process of claim 1 or 2, wherein said molecular sieve has a composition involving the molar relationship:



wherein X is a trivalent element comprises at least one of aluminum, boron, iron and gallium, Y is a tetravalent element comprises at least one of silicon and germanium, and n is at least about 10.

4. The process of claim 3, wherein said molecular sieve, in the as-synthesized form, has a formula, on an anhydrous basis and in terms of moles of oxides per n moles of YO_2 , as follows:



wherein M is an alkali or alkaline earth metal, and R is an organic moiety.

5. The process of claim 3 or 4, wherein said n is from about 10 to about 150.
6. The process of any one of claims 3 to 5, wherein X is aluminum and Y is silicon.
7. The process sieve of any preceding claim, wherein said molecular sieve has a collidine adsorption capacity of at least 150 $\mu\text{moles/g}$.

8. The process of any preceding claim, wherein said alkylatable aromatic compound is selected from the group consisting of benzene, naphthalene, anthracene, naphthacene, perylene, coronene, phenanthrene, xylene, n-propylbenzene, alpha-methylnaphthalene, o-diethylbenzene, m-diethylbenzene, p-diethylbenzene, pentaethylbenzene, pentamethylbenzene; 1,2,3,4- 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; dimethylnaphthalenes; ethylnaphthalene; 2,3-dimethylantracene; 9-ethylantracene; 2-methylantracene; o-methylantracene; 9,10-dimethylphenanthrene; 3-methyl-phenanthrene and mixtures thereof.
9. The process of any preceding claim, wherein said alkylatable aromatic compound comprises at least one of benzene and naphthalene.
10. The process of any preceding claim, wherein said alkylating agent is selected from the group consisting of olefins, alcohols, aldehydes, alkyl halides and mixtures thereof.
11. The process of any preceding claim, wherein said alkylating agent comprises at least one of ethylene, propylene and butenes.
12. The process of any preceding claim, wherein said alkylation reaction conditions include a temperature of from about 0°C to about 500°C, a pressure of from about 0.2 to about 25000 kPa-a, a molar ratio of alkylatable aromatic compound to alkylating agent of from about 0.1:1 to about 50:1, and a feed weight hourly space velocity (WHSV) based on the alkylating agent of from about 0.1 to 500 hr⁻¹.
13. The process of any one of claims 1-7, wherein said alkylatable aromatic compound comprises benzene, said alkylating agent comprises ethylene, said mono-alkylaromatic compound comprises ethylbenzene, said alkylation reaction conditions include a temperature of from about 150°C to about 300°C, a pressure of from about 2000 to about 5500 kPa-a, a molar ratio of alkylatable aromatic compound to alkylating agent of from about 0.5:1 to about 50:1, and a feed weight hourly space velocity (WHSV) based on the alkylating agent of from about 0.1 to 20 hr⁻¹.
14. The process of any one of claims 1-7, wherein said alkylatable aromatic compound comprises benzene, said alkylating agent comprises propylene, said mono-alkylaromatic compound comprises cumene, said alkylation reaction conditions include a temperature of from about 10°C to about 250°C, a pressure of from about 100 to about 3000 kPa-a, a molar ratio of alkylatable aromatic compound to alkylating

agent of from about 0.5:1 to about 50:1, and a feed weight hourly space velocity (WHSV) based on the alkylating agent of from about 0.1 to 250 hr⁻¹.

15. The process of any one of claims 1-7, wherein said alkylatable aromatic compound comprises benzene, said alkylating agent comprises butylene, said mono-alkylaromatic compound comprises sec-butylbenzene, said alkylation reaction conditions include a temperature of from about 10°C to about 250°C, a pressure of from about 1 to about 3000 kPa-a, a molar ratio of alkylatable aromatic compound to alkylating agent of from about 0.5:1 to about 50:1, and a feed weight hourly space velocity (WHSV) based on the alkylating agent of from about 0.1 to 250 hr⁻¹.
16. A process for manufacturing a mono-alkylaromatic compound, said process comprising contacting a feedstock comprising an alkylatable aromatic compound and an alkylating agent under alkylation reaction conditions with a catalyst comprising EMM-12.