A NOVEL MOLECULAR SIEVE COMPOSITION EMM-13, A METHOD OF MAKING AND A PROCESS OF USING THE SAME

FIELD OF THE INVENTION

[0001] The present disclosure relates to a novel molecular sieve composition designated as EMM-13, a method of making and a process of using the same. In particular, this disclosure relates to a novel molecular sieve composition designated as EMM-13 which is an MCM-22 family material having unique XRD features.

BACKGROUND OF THIS DISCLOSURE

[0002] 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 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.

[0003] 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.

[0004] U.S. Patent Application No. 11/823,129 discloses a novel 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 novel 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 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 11.0 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.

[0005] 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:

(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;

(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

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

[0006] 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. Pat. No. 4,954,325), PSH-3 (described in U.S. Pat. No. 4,439,409), SSZ-25 (described in U.S. Pat. No. 4,826,667), ERB-1 (described in European Patent No. 0293032), ITQ-1 (described in U.S. Pat. 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. Pat. No. 5,250,277), MCM-49 (described in U.S. Pat. No. 5,236,575) and MCM-56 (described in U.S. Pat. No. 5,362,697). The entire contents of the patents are incorporated herein by reference.

[0007] 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.

[0008] 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.

[0009] 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 discloses a process for producing a monoalkylated aromatic compound, particularly cumene, 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 monoalkylated aromatic compound, wherein the transalkylation catalyst comprises a mixture at least two different crystalline molecular sieves, wherein each of the molecular sieves is selected from zeolite beta, zeolite Y, 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.

[0010] 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 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 disclosed detailed structure of Ti-YNU-1 (Angew. Chem. Int. Ed., 2005, 44, 6719) similar to ISE-MWW. Another report by P. Wu, J. Ruan, L. Wang, L. Wu, Y. Wang, Y. Liu, W. Fan. M. He, O. Terasaki and T. Tatsumi disclosed a methodology for synthesizing crystalline aluminosilicates with expanded pore windows through molecular alkoxysilylation of zeolitic lamellar precursors (J. Am. Chem. Soc. 2008, 130, 8178-8187).

[0011] These closely related material may further be distinguished by comparing XRD diffraction pattern for d-spacing maxima corresponding to (002), (100), (101) and (102) reflections for both as-synthesized and calcined materials. The d-spacing maximum corresponding to (002) reflection is typically in the range from 14.17 to 12.57 Angstroms

(~6.15-7.05 deg 2-θ Cu Kα). 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 2-θ Cu Kα). 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 Cu Kα). 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 Cu Kα). The following table (Table 1) summarized the differences between MCM-22, MCM-49, EMM-10, MCM-56 and the titanosilicate material reported by Tatsumi et al. based on the existence 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				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			

	less than 50 % of the point at the same XRD d-spacing on the line connecting maxima for (101) and (102).				connecting maxima for (101) and (102).			
MCM-22 family material as disclosed in U.S. Patent App. No. 11/827,953	As-synthesized				Calcined			
	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
	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	MCM-49-P				MCM-49			
	No	Yes	Yes	Yes	No	Yes	Yes	Yes
	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	MCM-56-P				MCM-56			
	No	Yes	non-discrete		No	Yes	non-discrete	
	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 (US20050158238, Fig. 4)				Calcined (US20050158238 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).			

[0012] 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. There is, therefore, a need for novel crystalline molecular sieve compositions and method of making such novel crystalline molecular sieve compositions.

SUMMARY OF THIS DISCLOSURE

[0013] In some embodiments, this disclosure relates to an EMM-13 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 (~6.15-7.05 deg 2-θ), a d-spacing maximum in the range of 12.1 to 12.56 Angstroms (~7.3-7.05 deg 2-θ), a d-spacing maximum in the range of 10.14 to 12.0 Angstroms (8.7-7.35 deg 2-

θ), and a d-spacing maximum in the range from 8.66 to 10.13 Angstroms (10.2-8.7 deg 2-θ); wherein said peaks having d-spacing maximum in the range of 10.14 to 12.0 Angstroms (8.7-7.35 deg 2-θ) and d-spacing maximum in the range from 8.66 to 10.13 Angstroms (10.2-8.7 deg 2-θ) exhibit a valley in between, wherein the measured intensity corrected for background at the lowest point of said valley is less than 50 % of the intensity point at the same XRD d-spacing on the line connecting said peaks having d-spacing maxima in the range of 10.14 to 12.0 Angstroms (8.7-7.35 deg 2-θ) and in the range from 8.66 to 10.13 Angstroms (10.2-8.7 deg 2-θ); wherein said EMM-13 molecular sieve has less than 1.6 wt.% Ti.

[0014] In some embodiments, this disclosure relates to an EMM-13 molecular sieve having, in its as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks at d-spacing maxima at 13.18±0.25, 12.33±0.23, 11.06±0.18 and 9.25±0.13 Angstroms, wherein said peaks at 11.06±0.18 and 9.25±0.13 Angstroms exhibit a valley in between the 11.06±0.18 and 9.25±0.13 Angstroms but with measured intensity corrected for background at the lowest point being less than 50 % of the intensity point at the same XRD d-spacing on the line connecting d-spacing maxima at 11.06±0.18 and 9.25±0.13 Angstroms; wherein said EMM-13 molecular sieve has less than 1.6 wt.% Ti.

[0015] In other embodiments, this disclosure relates to a method of manufacturing an as-synthesized crystalline molecular sieve EMM-13, the method comprising the steps of:

(a) providing a mixture comprising MCM-22-P, acidic composition, and optionally a spacing agent; and

(b) treating the mixture at treatment conditions to form a product comprising as-synthesized EMM-13, wherein the treatment conditions comprise a temperature in the range of from 50°C to 200°C, and a crystallization time from about 1 hour to 400 hours; and

(c) recovering the crystalline molecular sieve.

[0016] In other embodiments, the as-synthesized crystalline molecular sieve EMM-13 is further calcined under calcination conditions to form calcined EMM-13, wherein the calcination conditions comprise a temperature in the range of 300 to 700°C for a time in the range of 1 min to 500 hours.

[0017] In some aspects, the EMM-13 molecular sieve further comprises, in its as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks at 3.57±0.07 and 3.42±0.07 Angstroms.

[0018] In other aspects, the EMM-13 molecular sieve further comprises, in its as-synthesized form and in calcined form, an X-ray diffraction pattern including peak at 6.9±0.15.

[0019] In yet other aspects, the EMM-13 calcined molecular sieve has a composition involving the molar relationship:

$$X_2O_3:(n)YO_2,$$

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. In the as-synthesized form the EMM-13 molecular sieve has a formula, on an anhydrous basis and in terms of moles of oxides per n moles of YO_2, as follows:

$$(0.005\text{-}1)M_2O:(1\text{-}4)R:X_2O_3:nYO_2$$

wherein M is an alkali or alkaline earth metal, and R is an organic moiety. In a preferred embodiment, n is from about 10 to about 150, more preferably from about 30 to about 60. In some preferred embodiment, X is aluminum and Y is silicon.

[0020] In some embodiments, the EMM-13 calcined molecular sieve has a collidine adsorption capacity at least 150 μmoles/g, preferably at least 250 μmoles/g.

[0021] These and other facets of the present invention shall become apparent from the following detailed description, Figures, and appended claims.

BRIEF DESCRIPTION OF THE FIGURES

[0022] Figure 1 shows the XRD pattern between 5 to 11 degree 2-θ of Example 1.

[0023] Figure 2 shows XRD patterns (shown in degrees 2θ) for as-synthesized and calcined products of Examples 1 and 3a.

[0024] Figure 3 shows XRD patterns (shown in degrees 2θ) MCM-22-P samples with different Si/Al acid-treated without the presence of the silylating agent. Top MCM-22-P with Si/Al_2 ~24/1 (Example 2); Bottom – EMM-13 as-synthesized of Example 3b.

[0025] Figure 4 shows electron diffraction patterns from EMM-13 calcined of Example 3a, a. (hk0), b. (00ℓ) and c. lattice image (edge view).

[0026] Figure 5 shows three-dimensional plot of reciprocal lattice constructed from an electron diffraction tilt series of a single microcrystal (Example 3a).

[0027] Figure 6 shows structure solution from MICE - final model compared to density profile (after origin shift). a. [001]; b. [110]; c. [-110].

[0028] Figure 7 shows experimental powder x-ray pattern from EMM-13 calcined of Example 3a.

[0029] Figure 8 shows powder pattern calculated from just expanded, pillared MCM-22 framework.

[0030] Figure 9 shows model for EMM-13 calcined - perspective view and solid view showing interface atoms.

[0031] Figure 10 shows final Rietveld fit of model to experimental powder pattern with linkage oxygen, Rwp=0.0973 and RF^2 =0.1071.

[0032] Figure 11 shows ^{29}Si NMR of MCM-22-P (Example 1) and its EMM-13 as-synthesized and EMM-13 calcined (Example 3a).

[0033] Figure 12 shows ^{13}C CPMAS NMR of MCM-22-P (Example 1) and its EMM-13 as-synthesized and EMM-13 calcined (Example 3a).

[0034] Figure 13 shows ^{27}Al MAS NMR of MCM-22-P (Example 1) and its EMM-13 as-synthesized and EMM-13 calcined (Example 3a).

[0035] Figure 14 shows ^{1}H MAS NMR of EMM-13 calcined (Example 3a).

[0036] Figure 15(a,b) shows XRD patterns (shown in degrees 2θ) of EMM-13 as-synthesized and EMM-13 calcined of Examples 6-16.

DETAILED DESCRIPTION

Introduction

[0037] 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 inconsistent with the present invention and for all jurisdictions in which such incorporation is permitted.

[0038] 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 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 be treated as equivalents thereof by those skilled in the art to which the disclosure pertains.

[0039] As used in this specification, the term "framework type" is used in the sense described in the "Atlas of Zeolite Framework Types," 2001.

[0040] As used herein, the numbering scheme for the Periodic Table Groups is used as in Chemical and Engineering News, 63(5), 27 (1985).

X-Ray Powder Diffraction Pattern

[0041] The interplanar spacings, d's, were calculated in Angstrom units (Å), and the relative intensities of the lines, I/I_o, where the intensity of the strongest line above background, I_o, 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 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.

[0042] 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 peak maximum to the baseline.

[0043] 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.

[0044] 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).

[0045] The term "discrete" peaks (also "resolved" peaks) in XRD as used herein means XRD peak(s) which are not non-discrete (unresolved).

[0046] 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-13

[0047] EMM-13 is a new MCM-22 family material with unprecedented XRD pattern indicating expanded structure and increased access to the interlayer region. It shows a unique distinctive combination of XRD features in the calcined form comprising peaks having a d-spacing maximum in the range of 14.17 to 12.57 Angstroms (~6.15-7.05 deg 2-θ), a d-spacing maximum in the range of 12.1 to 12.56 Angstroms (~7.3-7.05 deg 2-θ), a d-spacing maximum in the range of 10.14 to 12.0 Angstroms (8.7-7.35 deg 2-θ), and a d-spacing maximum in the range from 8.66 to 10.13 Angstroms (10.2-8.7 deg 2-θ); wherein said peaks having d-spacing maximum in the range of 10.14 to 12.0 Angstroms (8.7-7.35 deg 2-θ) and d-spacing maximum in the range from 8.66 to 10.13 Angstroms (10.2-8.7 deg 2-θ) exhibit a valley in between, wherein the measured intensity corrected for background at the lowest point of said valley is less than 50 % of the intensity point at the same XRD d-spacing on the line connecting said peaks having d-spacing maxima in the range of 10.14 to 12.0 Angstroms (8.7-7.35 deg 2-θ) and in the range from 8.66 to 10.13 Angstroms (10.2-8.7 deg 2-θ); wherein said EMM-13 molecular sieve has less than 1.6 wt.% Ti.

[0048] In some embodiments, the composition matter of EMM-13 has, in as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks at d-spacing maxima at 13.5±0.5, 12.33±0.23, and exhibit a valley in between the peaks at 11.05±0.2 and 9.31±0.2 Angstroms with 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 d-spacing maxima at around 11.05±0.2 and 9.31±0.2 Angstroms, wherein said EMM-13 molecular sieve has less than 1.6 wt.% Ti.

[0049] In further embodiments, the composition matter of EMM-13 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-13 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. In yet further embodiments, the composition matter of EMM-13 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.

[0050] In other embodiments, the composition matter of EMM-13 has, in as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks at d-spacing maxima and relative intensities at 13.5±0.5 (M-VS), 12.33±0.23(M-VS), and exhibit a valley in between the peaks at 11.05±0.2 (W-S) and 9.31±0.2 (W-S) Angstroms but with 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 d-spacing maxima at around 11.05±0.2 and 9.31±0.2 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

[0051] In other embodiments, the composition matter of EMM-13 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 embodiments, the composition matter of EMM-13 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-13 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 (W-VS, broad).

[0052] In some preferred embodiments, the X-ray diffraction pattern of the crystalline molecular sieve EMM-13 further has peaks at d-spacing maxima and intensities listed in Table 2.

[0053] In some embodiments, the X-ray diffraction pattern of the crystalline molecular sieve of this disclosure further includes a d-spacing maximum at 28±1 Angstroms.

[0054] In other embodiments, the composition matter of EMM-13 may be defined by its crystal structure. The crystal structure of EMM-13 may be defined by its unit cell, which is the smallest structural unit containing all the structural elements of the material. The unit cell of EMM-13 has P6/mmm space group and atomic coordinates of tetrahedral atoms (T) and oxygen atoms listed in Table 3 and with unit cell dimensions of a = 14.198(2) and c = 27.647(7) Å, wherein said EMM-13 molecular sieve has less than 1.6 wt.% Ti. Since the tetrahedral atoms may move about due to other crystal forces (presence of inorganic or organic species, for example), a range of ±0.05 nm is implied for each coordinate position.

Table 3

Atom	x/a	y/b	z/c	Uiso	occ.
T1	0.6667	0.3333	0.1126(2)	0.00649	1.0
T2	0.4652(5)	0.2326(3)	0.1754(3)		
T3	0.3901(5)	0.0	0.1897(4)		
T4	0.6667	0.3333	0.2403(4)		
T5	0.6667	0.3333	0.3575(4)		
T6	0.3894(5)	0.0	0.3050(4)		
T7	0.4215(5)	0.2108(2)	0.3593(3)		
T8	0.2502(5)	0.1251(3)	0.4450(2)		
T9	0.6667	0.3333	0.0		
O10	0.6667	0.3333	0.0562(1)	0.010	1.0
O11	0.5420(3)	0.2710(1)	0.1282(2)		
O12	0.3876(5)	0.1037(2)	0.1681(4)		
O13	0.5408(3)	0.2704(2)	0.2230(3)		
O14	0.6667	0.3333	0.2991(4)		
O15	0.3725(2)	0.0	0.2473(3)		
O16	0.5	0.0	0.176(1)		
O17	0.5	0.0	0.318(1)		
O18	0.3951(6)	0.1062(3)	0.3279(3)		
O19	0.5453(3)	0.2727(1)	0.3786(4)		
O20	0.3519(7)	0.1759(4)	0.4087(3)		
O21	0.1806(5)	0.0	0.4320(3)		
O22	0.2928(8)	0.1464(4)	0.5		
Extra-framework:					
T23	0.4499	0.1812	0.0686	0.025	0.355
T24	0.2477	0.1232	0.0360	0.025	0.160
Approximate					
O25	0.663	0.452	0.0	0.025	0.099

[0055] In Table 3, x/a, y/b, z/c are the fractional coordinates of the atoms in the unit cell referred to the unit cell axes a = b, c. Uiso is the isotropic temperature factor for each atom in $Å^2$. The quantity 'occ' is the occupancy factor for each atom, i.e., if less than 1.0, there is a statistical distribution of atoms or vacancies at each locus in the crystal.

[0056] In some embodiments, the EMM-13 calcined exhibits an extraordinary high collidine number 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 to about 120-200 μmoles/g for EMM-10 and 120 μmoles/g for MCM-22. Not intended to be limited by any theory, we believe that the EMM-13 calcined has c-unit cell parameter fixed in the expanded form as the precursor when calcined.

Chemical Composition of as-synthesized EMM-13 and calcined EMM-13

[0057] The as-synthesized EMM-13 molecular sieve material of this disclosure may be prepared from an MCM-22-P precursor, which can be obtained from a reaction mixture for hydrothermal reaction containing sources of alkali or alkaline earth metal (M), e.g., sodium or potassium, cation, an oxide of trivalent element X, e.g., aluminum, an oxide of tetravalent element Y, e.g., silicon, an organic (R) directing agent, hereinafter more particularly described, and water, the reaction mixture for hydrothermal reaction having a composition, in terms of mole ratios of oxides:

YO_2/X_2O_3 in the range of 10 to infinity or in the range of 10 to 50;

M/X_2O_3 in the range of 0.005-5.0; and

R/X_2O_3 in the range of 0.01-10.

[0058] The calcined EMM-13 molecular sieve material of this disclosure may be prepared by calcining as-synthesized EMM-13 under calcination conditions to remove at least the majority of the organic template R from the as-synthesized EMM-13.

[0059] The as-synthesized or calcined EMM-13 molecular sieve material has less than 1.6 wt.% titanium, preferably less than 1 wt,%, more preferably less than 0.5 wt.%, and most preferably less than 0.1 wt.% of titanium.

Process of making EMM-13

[0060] In some embodiments, this disclosure relates to a method of manufacturing an as-synthesized crystalline molecular sieve EMM-13, the method comprising the steps of:

(a) providing a mixture comprising MCM-22-P and acidic composition, optionally a spacing agent; and

(b) treating the mixture at treatment conditions to form a product comprising as-synthesized EMM-13; and

(c) recovering the acid treated crystalline molecular sieve.

[0061] In some preferred embodiments, the as-synthesized EMM-13 is made by a process comprising:

(1) providing a mixture comprising MCM-22-P having Si/Al_2 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 50-250°C for a time in the range of 1-24 hrs, optionally with a stirring speed in the range of 0-1000 RPM.

[0062] The mixture of step (a) comprises MCM-22-P, acidic composition, and optionally a spacing agent, wherein the weight ratio of the solid content of the MCM-22-P over the acidic composition and the weight ratio of the spacing agent over the solid content of the MCM-22-P are listed in Table 4. The treatment conditions of step (b) include treatment temperature, treatment time. Useful and preferred ranges of the treatment temperature and treatment time are listed in Table 4.

Table 4

	Useful range	Preferred range	Most preferred range
Solid content (wt) / Acidic composition	0.001-1000	0.01-100	0.1-10
Spacing agent (wt) / 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

[0063] 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.

[0064] 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.

[0065] 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.

[0066] The following times (hr) are useful lower time limits for treatment: 0.01, 1, 5, 10, 20, 30, 50, 100, and 150. The following times (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) MCM-22-P

[0067] The MCM-22-P product is disclosed in US Patent No. 4,954,325. The entirety of which is incorporated herein by reference.

[0068] The MCM-22-P as disclosed by US Patent No. 4,954,325, may be made by crystallizing a mixture having a composition in molar ratio listed in Table 5.

Table 5

Reactants	Useful	Preferred
YO_2/ X_2O_3	10 to infinity	15-55
H_2O/ 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	HMI	HMI

[0069] After crystallization, the MCM-22-P product has a composition in molar ratio listed in Table 6.

Table 6

Reactants	Useful	Preferred
YO_2/ X_2O_3	10 to infinity	10-150
M/ X_2O_3	0.005-0.1	
R/ X_2O_3	1-4	
R	HMI	

(2) Acidic composition

[0070] 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).

[0071] 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.

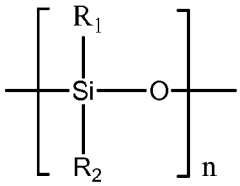
[0072] The weight of acidic composition as used in the solid content over acidic composition weight ratios is calculated based on the total weight of acidic solute and solvent.

(3) Spacing agent

[0073] Optionally, the acidic treatment step also comprises a spacing agent. The spacing agent useful is any agent capable of providing a 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). For example, the spacing agent may be a silylating agent which is capable of providing a silicon moiety that can stabilize the precursor in expanded form.

[0074] Examples of compounds for spacing include organo-compounds of a tetravalent element, a trivalent element, and/or a pentavalent compounds, such as, organosilicon compound, organogermanium compound, orgnaotitanium 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.

[0075] Silicone compounds that can be used in the present invention include the following:

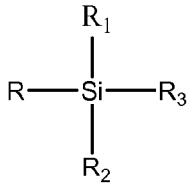


wherein R_1 is hydrogen, fluoride, hydroxy, alkyl, aralkyl, alkaryl or fluoro-alkyl. The hydrocarbon substituents generally contain from 1 to about 10 carbon atoms and preferably are methyl or ethyl groups. R_2 is selected from the same group as R_1, and n is an integer at least 2 and generally in the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

[0076] Useful siloxanes and polysiloxanes include as non-limiting example hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, hexamethyldisiloxane, octamethytrisiloxane, decamethyltetrasiloxane, hexaethylcyclotrisiloxane, octaethylcyclotetrasiloxane, hexaphenylcyclotrisiloxane and octaphenylcyclo-tetrasiloxane.

[0077] 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, trialkylsilyoxy, R_1, R_2 and R_3 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.

[0078] The silanes or disilanes include, as non-limiting examples, dimethylphenylsilane, phenytrimethylsilane, triethylsilane and hexamethyldislane. Useful alkoxysilanes are those with at least one silicon-hydrogen bond.

Catalysis and Adsorption

[0079] 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.

[0080] 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.

[0081] The EMM-13 crystalline molecular sieve of this disclosure when employed either as an adsorbent or as a catalyst in an organic compound conversion process 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.

[0082] The EMM-13 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 at least 370°C for at least 1 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.

[0083] The EMM-13 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.

[0084] The EMM-13 crystalline molecular sieve of this disclosure may be used as adsorbent, such as for separating at least one component from a mixture of components in the vapor or liquid phase having differential sorption characteristics with respect to the EMM-13 crystalline molecular sieve(s) of this disclosure. Therefore, at least one component can be partially or substantially totally separated from a mixture of components having differential sorption characteristics with respect to the EMM-13 crystalline molecular sieve(s) of this disclosure by contacting the mixture with the EMM-13 crystalline molecular sieve(s) of this disclosure to selectively sorb the one component.

[0085] The EMM-13 crystalline molecular sieve of this disclosure is useful as catalyst in a wide range of processes, including separation processes and hydrocarbon conversion processes. Specific examples of hydrocarbon conversion processes which are effectively catalyzed by the EMM-13 crystalline molecular sieve(s) of this disclosure by itself or in combination with one or more other catalytically active substances including other crystalline catalysts, include the following:

(i) alkylation of aromatic hydrocarbons, e.g., benzene, with long chain olefins, e.g., C_{14} olefin, with reaction conditions including, individually or in any combination, a temperature of from about 340°C to about 500°C, a pressure of from about 101 to about

20200 kPa-a (absolute), a weight hourly space velocity of from about 2 hr^{-1} to about 2000 hr^{-1} and an aromatic hydrocarbon/olefin mole ratio of from about 1/1 to about 20/1, to provide long chain alkyl aromatics which can be subsequently sulfonated to provide synthetic detergents;

(ii) alkylation of aromatic hydrocarbons with gaseous olefins to provide short chain alkyl aromatic compounds, e.g., the alkylation of benzene with propylene to provide cumene, with reaction conditions including, individually or in any combination, a temperature of from about 10°C to about 125°C, a pressure of from about 101 to about 3030 kPa-a, and an aromatic hydrocarbon weight hourly space velocity (WHSV) of from 5 hr^{-1} to about 50 hr^{-1};

(iii) alkylation of reformate containing substantial quantities of benzene and toluene with fuel gas containing C_5 olefins to provide, *inter alia*, mono- and di-alkylates with reaction conditions including, individually or in any combination, a temperature of from about 315°C to about 455°C, a pressure of from about 3000 to about 6000 kPa-a, a WHSV-olefin of from about 0.4 hr^{-1} to about 0.8 hr^{-1}, a WHSV-reformate of from about 1 hr^{-1} to about 2 hr^{-1} and a gas recycle of from about 1.5 to 2.5 vol/vol fuel gas feed;

(iv) alkylation of aromatic hydrocarbons, e.g., benzene, toluene, xylene and naphthalene, with long chain olefins, e.g., C_{14} olefin, to provide alkylated aromatic lube base stocks with reaction conditions including, individually or in any combination, a temperature of from about 160°C to about 260°C and a pressure of from about 2600 to 3500 kPa-a;

(v) alkylation of phenols with olefins or equivalent alcohols to provide long chain alkyl phenols with reaction conditions including, individually or in any combination, a temperature of from about 200°C to about 250°C, a pressure of from about 1500 to 2300 kPa-a and a total WHSV of from about 2 hr^{-1} to about 10 hr^{-1};

(vi) conversion of light paraffins to olefins and aromatics with reaction conditions including, individually or in any combination, a temperature of from about 425°C to about 760°C and a pressure of from about 170 to about 15000 kPa-a;

(vii) conversion of light olefins to gasoline, distillate and lube range hydrocarbons with reaction conditions including, individually or in any combination, a temperature of from about 175°C to about 375°C and a pressure of from about 800 to about 15000 kPa-a;

(viii) two-stage hydrocracking for upgrading hydrocarbon streams having initial boiling points above about 260°C. to premium distillate and gasoline boiling range products in a first stage using the MCM-22 family molecular sieve of this disclosure in combination

with a Groups 8-10 metal as catalyst with effluent therefrom being reaction in a second stage using zeolite Beta, also in combination with a Groups 8-10 metal, as catalyst, the reaction conditions including, individually or in any combination, a temperature of from about 340°C to about 455°C, a pressure of from about 3000 to about 18000 kPa-a, a hydrogen circulation of from about 176 to about 1760 liter/liter and a liquid hourly space velocity (LHSV) of from about 0.1 to 10 h^{-1};

(ix) a combination hydrocracking/dewaxing process in the presence of the MCM-22 family molecular sieve of this disclosure and a hydrogenation component as catalyst, or a mixture of such catalyst and zeolite Beta, with reaction conditions including, individually or in any combination, a temperature of from about 350°C to about 400°C, a pressure of from about 10000 to about 11000 kPa-a, an LHSV of from about 0.4 to about 0.6 and a hydrogen circulation of from about 528 to about 880 liter/liter;

(x) reaction of alcohols with olefins to provide mixed ethers, e.g., the reaction of methanol with isobutene and/or isopentene to provide methyl-t-butyl ether (MTBE) and/or t-amyl methyl ether (TAM) with conversion conditions including, individually or in any combination, a temperature of from about 20°C to about 200°C, a pressure of from 200 to about 20000 kPa-a, a WHSV (gram-olefin per hour gram-zeolite) of from about 0.1 hr^{-1} to about 200 hr^{-1} and an alcohol to olefin molar feed ratio of from about 0.1/1 to about 5/1;

(xi) toluene disproportionation with C_9+ aromatics as co-feed with reaction conditions including, individually or in any combination, a temperature of from about 315°C to about 595°C, a pressure of from about 101 to about 7200 kPa-a, a hydrogen/hydrocarbon mole ratio of from about 0 (no added hydrogen) to about 10 and a WHSV of from about 0.1 hr^{-1} to about 30 hr^{-1};

(xii) preparation of the pharmaceutically-active compound 2-(4-isobutylphenyl) propionic acid, i.e. ibuprofen, by reacting isobutyl benzene with propylene oxide to provide the intermediate 2-(4-isobutylphenyl) propanol followed by oxidation of the alcohol to the corresponding carboxylic acid;

(xiii) use as an acid-binding agent in the reaction of amines with heterocyclic fiber-reactive components in preparation of dyes to prepare practically salt-free reactive dye-containing solution, as in German Patent No. DE 3,625,693, incorporated entirely herein by reference;

(xiv) as the absorbent for separating 2,6-toluene diisocyanate (2,6-TDI) from isomers if TDI as in U.S. Patent No. 4,721,807, incorporated entirely herein by reference, whereby a feed mixture comprising 2,6-TDI and 2,4-TDI is contacted with the present MCM-22 family molecular sieve which has been cation-exchanged with K ions to absorb the 2,6-TDI, followed by recovering the 2,6-TDI by desorption with desorbent material comprising toluene;

(xv) as the absorbent for separating 2,4-TDI from its isomers as in U.S. Patent No. 4,721,806, incorporated entirely herein by reference, whereby a feed mixture comprising 2,4-TDI and 2,6-TDI is contact with the present MCM-22 family molecular sieve which has been cation-exchanged with Na, Ca Li and/or Mg ions to absorb the 2,4-TDI, followed by recovering the 2,4-TDI by desorption with desorbent material comprising toluene;

(xvi) in a process for decreasing the durene content of a 90-200°C+ bottoms fraction obtained from the catalytic conversion of methanol to gasoline which comprises contacting the durene-containing bottoms fraction with hydrogen over a catalyst of the present MCM-22 family molecular sieve with a hydrogenation metal, at conditions including, individually or in any combination, a temperature of from about 230°C to about 425°C and a pressure of from about 457 to about 22000 kPa-a;

(xvii) in a processes for co-producing phenol and ketones that proceed through benzene alkylation, followed by formation of the alkylbenzene hydroperoxide and cleavage of the alkylbenzene hydroperoxide into phenol and ketone, e.g., benzene and propylene to phenol and acetone, benzene and C_4 olefins to phenol and methyl ethyl ketone, such as those described for example in international application PCT/EP2005/008557, which can be followed by conversion of phenol and acetone to bis-phenol-A as described in international application PCT/EP2005/008554, benzene to phenol and cyclohexanone, or benzene and ethylene to phenol and methyl ethyl ketone, as described for example in PCT/EP2005/008551;

(xviii) in a process of benzene alkylation reactions where selectivity to the monoalkylbenzene is required, e.g., selectively sec-butylbenzene from benzene and C_4 olefin feeds that are rich in linear butenes, as described in international application PCT/EP2005/008557, preferably, this conversion is carried out by co-feeding benzene and the C_4 olefin feed with the catalyst of the present invention, at a temperature of about 60°C to about 260°C, for example of about 100°C to 200°C, a

pressure of 7000 kPa-a or less, and a feed weight hourly space velocity (WHSV) based on C_4 alkylating agent of from about 0.1 to 50 h^{-1} and a molar ratio of benzene to C_4 alkylating agent from about 1 to about 50; and

(xix) in a process for transalkylation, such as, for example, polyalkylbenzene transalkylation.

[0086] In the case of many catalysts, it is desired to incorporate the new crystal with another material resistant to the temperatures and other conditions employed in organic conversion 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 new crystal, i.e. combined therewith or present during synthesis of the new crystal, which is active, tends to change the conversion and/or selectivity of the catalyst in certain organic conversion processes. 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.

[0087] Naturally occurring clays which can be composited with the new crystal 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.

[0088] In addition to the foregoing materials, the new crystal 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.

[0089] The relative proportions of finely divided EMM-13 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.

[0090] 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

[0091] Powder x-ray data were obtained on a Bruker D4 instrument in Bragg-Brentano geometry with monochromatic Cu Kα radiation; the pattern used for structural characterization extended from 1.2 to 80° in 2θ. Intensities for Rietveld refinement were extracted from the continuous scans. Indexing of powder patterns were carried out with the tool in the MDI Inc. program JADE.

[0092] Indexing of powder patterns were carried out with the tool in the MDI Inc. program JADE. After construction of a trial model (facilitated by the structure building module in Cerius^2 (Accelrys, Inc.)), its fit to the powder diffraction profile was made via Rietveld refinements with the program GSAS as described in A. C. Larsson & R. B. von Dreele, *General Structure Analysis System, GSAS*, Los Alamos National Laboratory, Los Alamos, NM, 1994. Sometimes the framework would be optimized geometrically with the program DLS as described in Ch. Baerlocher, A. Hepp, & W. M. Meier, *Distance Least Squares Refinement Program, DLS-76*. ETH, Zürich, 1977. Electron density maps generated with GSAS could be used to locate additional atoms in the unit cell, tested first with Cerius^2 models to ensure that there would be no collision with framework atoms. Care was taken during refinements to avoid unusual bonding geometries. For the framework, this was partially ensured by imposing a restraint to the Si-O bond distances (1.61 ± 0.03 Å) and O-O tetrahedral distances (2.65 ± 0.06 Å). A weighting function for the framework refinement was gradually relaxed but, after each refinement step, the chemical reasonableness of the bonding geometry was ascertained. In addition to unit cell parameters, background and zero shift, profile functions were also refined to improve the model fit but it was sometimes seen that the usual R-values did not necessarily denote a close match of the model to the experimental intensity curve. In several cases, adjustments were made for preferred orientation, expected for Bragg-Brentano data from a platy crystal assembly according to R. A. Young, in: *The Rietveld Method* (R. A. Young, ed.). Oxford Univ. Press, Oxford, 1995, p. 11.

Surface areas

[0093] 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 (ZSA, m^2/g) may be calculated using t-plot of the Brunauer-Emmett-Teller (BET) measurement. The external surface area (ZSA, m^2/g) is calculated by subtracting the internal surface area from the overall surface area measured by the Brunauer-Emmett-Teller (BET) measurement. Micro-pore volume (M-pore in cm^3/g) is determined by nitrogen adsorption/desorption (nitrogen isotherm).

Collidine number measurement

[0094] 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 ±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 at 0.3 ml/hr via a gas tight syringe 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.

Electron Microscopy and Diffraction

[0095] Selected area electron diffraction experiments were carried out at 300 kV with an FEI/Philips CM-30 electron microscope using a selected area diameter of 0.25 μm. In some cases, three-dimensional tilts were made around a defined reciprocal lattice to map out a 3-D reciprocal lattice. Bright field electron micrographs were obtained at 32,240 x direct magnification. The field-limiting aperture passed diffraction information out to $d^* = 0.08$ $Å^{-1}$. All exposures were recorded on Kodak Biomax MS film.

[0096] For preliminary intensity data collection, diffraction films were digitized on a flat bed scanner and, after their indexing, the intensities of individual spots were estimated with the program ELD according to X. D. Zou, Yu. Sukharev & S. Hovmöller, Ultramicroscopy 53 (1994) 271 within the CRISP as described in S. Hovmöller, Ultramicroscopy 41 (1992) 121) package. Symmetry-related reflections were averaged and no Lorentz correction was applied to the derived structure factor magnitudes. In some cases it was difficult to obtain suitable peak integration with ELD. In this case, films were scanned on a flat bed Joyce Loebl Mk. III microdensitometer and the peak areas used as an estimate of their intensities. For merging data into a three-dimensional set, common reflections from separate zones were used for scaling one set to the other as discussed in D. L. Dorset, *Structural Electron Crystallography*. Plenum, NY, 1995.

[0097] For electron diffraction studies, structure factor calculations were carried out with the Fortran program SF and one-dimensional electrostatic potential distributions were obtained with the Fortran program ZPOT after phase approximates from a known structure were provided.

[0098] Three-dimensional tilts around defined unit cell reciprocal axes (generally a*) were plotted to give an undistorted view of the three-dimensional reciprocal lattice. Using the usual gold powder standard for calibration, the dimensions of the complete unit cell could be measured. From systematic absences in these plots, the unit cell symmetry could also be estimated according to Th. Hahn (ed.), *International Tables for Crystallography. Volume A. Space-Group Symmetry*. Kluwer, Dordrecht, 1995.

[0099] Structures were found from a 3-D dataset using maximum entropy and likelihood with the program MICE according to C. J. Gilmore, K. Shankland, & G. Bricogne, Proc. Roy. Soc. London 442 (1993) 97. It is useful to utilize a typical zeolite density histogram as described in Ch. Baerlocher, L. B.McCusker & L. Palatinus, Z. Krist. 222 (2007) 47 to further discriminate among trial structural solutions culled by a maximum likelihood figure of merit according to C. J. Gilmore, G. Bricogne & C. Bannister, Acta Cryst. A46 (1990) 297. Instead of full factorial phase permutation of identified reflections, a Nordström-Robinson error correcting code according to C. J. Gilmore, W. Dong, & G. Bricogne, Acta Cryst. A55 (1999) 70 was used to speed up the calculation.

NMR experimental procedures

[00100] All of the solid-state NMR measurements were made at room temperature. The ^{27}Al, ^{29}Si MAS and ^{29}Si CPMAS NMR spectra were recorded on a Varian *InfinityPlus*500 spectrometer operating at 11.7T (^{1}H 499.2 MHz) corresponding to 130 and 99 MHz Larmor frequencies for ^{27}Al and ^{29}Si, respectively. ^{29}Si MAS (Bloch decay) and CPMAS NMR were recorded using a 7.5-mm Varian probe at spinning speeds of 4- and 3.5-kHz, respectively. ^{29}Si MAS data were recorded with ^{1}H decoupling during data acquisition, 4 μs π/2 pulses, a 60s pulse delay, and 600 scans were collected. ^{29}Si CPMAS data were recorded with ^{1}H decoupling during data acquisition, 4 μs π/2 pulses, 3.5ms contact time, a 3s pulse delay, and 1440 - 4000 scans were collected. ^{27}Al MAS (Bloch decay) NMR spectra were recorded using a 4-mm Varian probe at spinning speeds of 10-kHz with ^{1}H dipolar decoupling during data acquisition, 1.2 μs π/6 pulses, a 0.3s pulse delay and 2400 - 4000 scans were collected. The ^{13}C CPMAS NMR spectra were recorded using a 5-mm Varian probe at spinning speeds of 4-kHz on a Chemagnetics CMX-200 operating at 4.7T (^{1}H 199.9 MHz), corresponding to a

^{13}C Larmor frequency of 50.3 MHz. ^{13}C CPMAS data were recorded with ^{1}H decoupling during data acquisition, 3.5 μs π/2 pulses, 3.5ms contact time, a 2s pulse delay, and 3200 - 8000 scans were collected. ^{1}H MAS NMR spectra were recorded on a 9.4 T Varian *InfinityPlus* 400 spectrometer corresponding to a ^{1}H Larmor frequency of 399.4MHz. ^{1}H MAS (Bloch decay) data were recorded using a 4-mm Varian probe at spinning speeds of 10-kHz with 4 μs π/2 pulses, a 30s pulse delay, and 32 scans were collected.

Materials and synthesis

Example 1: Synthesis of MCM-22-P with Si/Al2 ~ 60

[00101] The synthesis mixture was prepared with 184 g of water, 1.5 g of Usalco 45, 22 g of 10 % NaOH, 17 g of hexamethyleneimine and 23 g of Ultrasil. It was reacted at 150°C with 100 RPM in a 300 ml autoclave. Product composition and structural porosity characteristics are listed in Table 7.

Example 2: Synthesis of MCM-22-P with Si/Al2 ~ 23

[00102] The synthesis was analogous to Example 1, US Patent 4,954,325. Product composition and structural porosity characteristics are listed in Table 7.

Example 3a: Acid treatment of MCM-22-P (Example 1) with silane to produce EMM-13 as-synthesized and EMM-13 calcined

[00103] Mixing 30 grams of 1 M HNO_3 solution (obtained by mixing 3 g of concentrated acid with 27 g of water) with 0.3 g of spacing agent (silylating agent) dimethyldiethoxy silane, and followed with adding 3 g of as-synthesized MCM-22-P sample of Example 1. The mixture was reacted at 170°C for 24 hrs. The product was filtered, washed with water and dried. The as-treated material was identified by XRD as EMM-13 as-synthesized. The as-treated material was further calcined in air at 540°C for 4 hrs. The calcined material of example 3a was identified by XRD as EMM-13 calcined. Product composition and structural porosity characteristics are listed in Table 7.

Example 3b: Acid treatment of MCM-22-P (Example 1) to produce EMM-13 as-synthesized and EMM-13 calcined

[00104] Mixing 30 grams of 1 M HNO_3 solution (obtained by mixing 3 g of concentrated acid with 27 g of water), and followed with adding 3 g of as-synthesized MCM-22-P sample of Example 1. The mixture was reacted at 170°C for 24 hrs. The product was filtered, washed with water and dried. The as-treated material was identified by XRD as EMM-13 as-synthesized. The as-treated material was further calcined in air at 540°C for 4 hrs. The

calcined material of example 3b was identified by XRD as EMM-13 calcined. Product composition and structural porosity characteristics are listed in Table 7.

Example 3c: Acid treatment of MCM-22-P (Example 1) with silica to produce EMM-13 as-synthesized and EMM-13 calcined

[00105] Mixing 30 grams of 1 M HNO_3 solution (obtained by mixing 3 g of concentrated acid with 27 g of water) with 0.3 g of fumed silica (Cab-o-Sil), and followed with adding 3 g of as-synthesized MCM-22-P sample of Example 1. The mixture was reacted at 170°C for 24 hrs. The product was filtered, washed with water and dried. The as-treated material was identified by XRD as EMM-13 as-synthesized. The as-treated material was further calcined in air at 540°C for 4 hrs. The calcined material of example 3c was identified by XRD as EMM-13 calcined. Product composition and structural porosity characteristics are listed in Table 7.

Example 4a: Acid treatment of MCM-22-P (Example 2) with silane to produce MCM-22-P and MCM-22

[00106] Mixing 30 grams of 1 M HNO_3 solution (obtained by mixing 3 g of concentrated acid with 27 g of water) with 0.3 g of spacing agent (silylating agent) dimethyldiethoxy silane, and followed with adding 3 g of as-synthesized MCM-22-P sample of Example 2. The mixture was reacted at 170°C for 24 hrs. The product was filtered, washed with water and dried. The as-treated material was identified by XRD as MCM-22-P. The as-treated material was further calcined in air at 540°C for 4 hrs. The calcined material of example 4a was identified by XRD as MCM-22. Product composition and structural porosity characteristics are listed in Table 7.

Example 4b: Acid treatment of MCM-22-P (Example 1) to produce MCM-22

[00107] Mixing 30 grams of 1 M HNO_3 solution (obtained by mixing 3 g of concentrated acid with 27 g of water), and followed with adding 3 g of as-synthesized MCM-22-P sample of Example 2. The mixture was reacted at 170°C for 24 hrs. The product was filtered, washed with water and dried. The as-treated material was identified by XRD as MCM-22-P. The as-treated material was further calcined in air at 540°C for 4 hrs. The calcined material of example 4b was identified by XRD as MCM-22. Product composition and structural porosity characteristics are listed in Table 7.

Table 7

Example	1	3a	3b	3c	2	4a	4b
Synthesis conditions							
Si/Al_2	87				29.9		
Si+Al	8.7				13.9		
OH/Si	0.18				0.17		
R/Si	0.49				0.35		
T (C)	150				150		
Time (hr)	76				60-70		
Acid treatment conditions							
T (°C)		170	170	170		170	170
Time (hr)		24	24	24		24	24
Product Characterization and Properties							
XRD	MCM-22-P + trace ZSM-12	EMM-13 as-synthesized	EMM-13 as-synthesized	EMM-13 as-synthesized	MCM-22-P	MCM-22-P	MCM-22-P
Al_2O_3	2.3	2.16	2.1				4.88
Na	0.4	0.0339	0.267				0.0789
SiO_2	78.9	85.3	78.7				76
Si/Al_2	58.32	67.13	63.71				26.48
Product Characterization and Properties after Calcination in Air at 540°C for 4 hrs							
XRD	MCM-22	EMM-13	EMM-13	EMM-13	MCM-22	MCM-22	MCM-22
BET	410	485	463	396		436	472
ZSA	378	456	404	327		329	362
MSA	32	29	58	68		107	110
M-pore	0.152	0.18	0.16	0.13		0.13	0.15
Collidine		214	153		124		

Results and Discussion for Examples 1-4

[00108] The clear evidence of the EMM-13 as-synthesized structure was observed upon comparison of the XRD's of as-synthesized and calcined products of Examples 3a, 3b, 3c with the XRD's of as-synthesized and calcined products of Examples 1, especially in the lower angle region 6-10° 2θ (Cu Kα) in Figure 2. The four peak pattern of the former is retained after calcination for Examples 3a, 3b and 3c, while the first peak at 6.5° 2θ (Cu Kα) clearly disappears upon calcination for Example 1. Not intended to be bound by any theory, we believe that this is the result of unit cell contraction from 27 Å to ~ 25 Å causing the shift of this (002) peak and merging with the one at 7.1°. We believe that the preservation of the interlayer spacing demonstrated by XRD indicates insertion of an additional thermally stable

moiety, most likely incorporating Si atoms. Both ED and NMR results are consistent with this theory.

[00109] As shown in Table 7, the calcined product, EMM-13, reveals enhanced BET surface area and microporous volume compared to its MCM-22 parent.

[00110] With high Al MCM-22-P of Example 2, the treatment results in collapse to the 25 Å c-unit cell material in the acidic medium even prior to calcination as evidenced by the XRD shown in Figure 3. Also the EMM-13 as-synthesized and EMM-13 calcined may be made even without addition of the spacing agent (silylating agent).

[00111] The treatment causes that edge-views of layer stacking are commonly visible. This is illustrated in Figure 4. Views onto crystal plates can also be found to obtain characteristic hk0 electron diffraction patterns. Low resolution lattice images reveal a regular stacking of layers (Figure 4). Measured cell dimensions from electron diffraction patterns are a = 14.14 ± 0.14Å, c = 27.42 ± 0.32Å. Three-dimensional plots of the reciprocal lattice from tilt diffraction series of a single microcrystal (Figure 5) support the c = 27.1 Å spacing. The allowed reflection classes are consistent with space group P6/mmm (C4).

[00112] Measured hk0 intensities in patterns similar to the one depicted in Figure 5 reveal the strong resemblance to other members of the MWW family of zeolites in the [001] projection. Analysis of the 3-D crystal structure from 151 unique hk*l* electron diffraction amplitudes reveals the inclusion of the MCM-22 layer within this structure (Figure 6).

[00113] Application of a powder indexing program to the x-ray diffraction pattern (Figure 7) again identifies a hexagonal space group, e. g. P6/mmm, where a = 14.166, c = 27.533 Å. With the presence of MCM-22 layers in this structure identified by electron diffraction, a model was constructed where the -O- link of MCM-22 was replaced by -O-Si-O-, also using the expanded c-axis length. The model was optimized geometrically and energetically by a DLS refinement before the subsequent Rietveld refinement.

[00114] The calculated powder diffraction pattern for the initial EMM-13 calcined model (Figure 8) reveals that the predicted intensity for the peak near $2\theta = 3.0°$ is larger than observed. After optimization of the fit of the expanded layer structure model to the experimental powder data, an electron density map was calculated within GSAS to seek additional atomic positions. Two positions were found within the interface with the expanded -O-Si-O- link. These were included as Si atoms but refinements on atomic occupancy revealed that they either exist as such in reduced quantity or are, in fact, other atomic species. With these additional atoms and after framework refinement, Rwp = 0.0977, $RF^2 = 0.1080$.

Unit cell dimensions were refined as: a = 14.198(2), c = 27.647(7) Å and the atomic coordinates developed as in Table 3. The structural model is shown in Figure 9. The fit of the model to the observed intensity profile is reasonable (Figure 10), although there is some difficulty modeling the profile functions for large peaks below $2\theta = 10°$.

[00115] Shown in Figure 11 are the ^{29}Si MAS (Bloch decay) NMR spectra of MCM-22-P (top), EMM-13 as-synthesized (middle) and EMM-13 calcined (bottom). Close comparison of these spectra, as seen in the inset overlay, show that silylation of MCM-22-P to form EMM-13 as-synthesized results in significant loss of intensity in the δ_{Si} = -90 to -102 ppm region which is indicative of loss in silanols due to reaction of the dimethyldiethoxy silane with the surface. Subsequent calcination to form EMM-13 calcined results in an increase in spectral intensity in the δ_{Si} = -100 to -110 ppm region that might be associated with and is consistent with the formation of interlayer Si-O-Si linkages. The reaction of the dimethyldiethoxy silane with the surface is confirmed in the corresponding ^{29}Si CPMAS NMR spectra (Figure 12) where resonances associated with surface dimethylsilyl species in the δ_{Si} = -10 to -20 ppm region are detected in EMM-13 as-synthesized. Since the CP experiment is selective to Si nuclei in close proximity to H (e.g. surface hydroxyls, surface organosilyls, or occluded SDA) the data also confirm the corresponding loss in surface silanols as seen in the loss of intensity in the δ_{Si} = -90 to -102 ppm region for EMM-13 as-synthesized relative to MCM-22-P. The presence of surface bound dimethylsilyl species in EMM-13 as-synthesized is also confirmed in the ^{13}C CPMAS NMR spectrum (Figure 13) where a resonance associated with methylsilyl is detected ($\delta_C \sim 0$ ppm) in addition to the resonances from the hexamethyleneimine (HMI) SDA.

[00116] Shown in Figure 14 are the ^{27}Al MAS (Bloch decay) NMR spectra of MCM-22-P (top), EMM-13 as-synthesized (middle) and EMM-13 calcined (bottom). Close comparison of these spectra indicate that, perhaps as expected, there is little change in the average local Al tetrahedral environment upon silylation of MCM-22-P. As is typically seen for MCM-22, subsequent calcination of EMM-13 as-synthesized results in the formation of non-framework octahedral Al.

[00117] The ^{1}H MAS NMR spectrum of EMM-13 calcined shown in Figure 15 indicates the presence ~ 0.56 mmole/g of Brönsted acidity. Assuming these are all associated with T_d Al, this H^+ content corresponds to 2.8 wt% T_d Al_2O_3. The SiOH content of 0.62 mmole/g is consistent with what is typically detected in MCM-22/-49 materials.

Example 5: Synthesis of 40/1 MCM-22-P

[00118] The preparation was carried out like above but with a gel having the following molar ratio of reactants: silica/alumina = 54/1, OH/Si = 0.15, water/Si = 35, R/Si = 0.58. The mixture was heated at 170°C for 70 hrs and product isolated by standard methods.

Examples 6-16: Synthesis EMM-13 with 40/1 MCM-22-P

[00119] Examples 6-16 were conducted by mixing concentrated acid with water to form acid solution according to Table 8. Various amount of spacing agent (silylating agent) dimethyldiethoxy silane, were added followed by as-synthesized MCM-22-P sample of Example 5 according to Table 8. The mixtures were reacted at treatment conditions including a treatment temperature and time according to Table 8. The products were filtered, washed with water and dried. Calcination of the products was carried out in air at 540°C for 4 hrs. The as-treated materials were further calcined in air at 540°C for 4 hrs. The calcined materials of Example 6-16 were identified by XRD (Figure 16) as EMM-13 (except #12).

Table 8

	Amount, grams							Surface area, m^2/g			Collidine
Example number	Water	Conc. HNO3	40/1 Si/Al2 MCM-22-P	Silane	Time, hours	Temp., °C		Tortal BET	Zeolite ZSA	Mesopore, MSA	µmole/g
Parent	40/1 Si/Al2 MCM-22-P							521	478	43	44
6	9.5	0.5	0.4	0.02	24	170		568	485	83	350
7	7.25	2.75	1.7	0.21	17	145		600	540	60	244
8	9.5	0.5	3	0.02	10	170		615	544	71	262
9	5	5	0.4	0.02	10	120		642	573	69	195
10	5	5	0.4	0.4	10	170		492	462	30	134
11	9.5	0.5	3	0.4	10	120		623	565	58	327
12	5	5	3	0.02	24	120		556	480	76	89
13	9.5	0.5	0.4	0.4	24	120		533	499	34	266
14	5	5	3	0.4	24	170		675	609	66	311
15	7.25	2.75	1.7	0.21	17	145		609	547	62	245
16	8.62	1.38	3	0.5	17	90		642	588	55	212

Example 17

[00120] Three 65 wt.% EMM-13 calcined of Example 3a and 35 wt% alumina catalyst were prepared. These three catalysts were tested for benzene alkylation with propylene to form cumene.

Feed Pretreatment

Benzene

[00121] 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

Propylene was obtained from a commercial specialty gases source and were polymer grade.

Nitrogen

Nitrogen was ultra high purity grade and obtained from a commercial specialty gases source.

Test Sequence for Cumene Manufacture in a Fixed Bed Test

[00122] 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. The 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.

[00123] At reactor start-up, the reactor was brought to reaction pressure of 2169 kPa-a 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 Diisopropylbenzene (DIPB) over cumene (isopropylbenzene, IPB) molar ratios of the products fall in the range of 12% to 18%.

CLAIMS:

We claim:

1. A molecular sieve comprising a framework of tetrahedral atoms bridged by oxygen atoms, the tetrahedral atom framework being defined by a unit cell with atomic coordinates in nanometers shown in the following table:

Atom	x/a	y/b	z/c	Uiso	occ.
T1	0.6667	0.3333	0.1126(2)	0.00649	1.0
T2	0.4652(5)	0.2326(3)	0.1754(3)		
T3	0.3901(5)	0.0	0.1897(4)		
T4	0.6667	0.3333	0.2403(4)		
T5	0.6667	0.3333	0.3575(4)		
T6	0.3894(5)	0.0	0.3050(4)		
T7	0.4215(5)	0.2108(2)	0.3593(3)		
T8	0.2502(5)	0.1251(3)	0.4450(2)		
T9	0.6667	0.3333	0.0		
O10	0.6667	0.3333	0.0562(1)	0.010	1.0
O11	0.5420(3)	0.2710(1)	0.1282(2)		
O12	0.3876(5)	0.1037(2)	0.1681(4)		
O13	0.5408(3)	0.2704(2)	0.2230(3)		
O14	0.6667	0.3333	0.2991(4)		
O15	0.3725(2)	0.0	0.2473(3)		
O16	0.5	0.0	0.176(1)		
O17	0.5	0.0	0.318(1)		
O18	0.3951(6)	0.1062(3)	0.3279(3)		
O19	0.5453(3)	0.2727(1)	0.3786(4)		
O20	0.3519(7)	0.1759(4)	0.4087(3)		
O21	0.1806(5)	0.0	0.4320(3)		
O22	0.2928(8)	0.1464(4)	0.5		
Extra-framework:					
T23	0.4499	0.1812	0.0686	0.025	0.355
T24	0.2477	0.1232	0.0360	0.025	0.160
Approximate					
O25	0.663	0.452	0.0	0.025	0.099

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2. The molecular sieve of claim 1, having a composition involving the molar relationship:

$$X_2O_3:(n)YO_2,$$

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 30.

3. The molecular sieve of claim 2, in the as-synthesized form, having a formula, on an anhydrous basis and in terms of moles of oxides per n moles of YO_2, as follows:

$$(0.005\text{-}1)M_2O:(1\text{-}4)R:X_2O_3:nYO_2$$

wherein M is an alkali or alkaline earth metal, n is at least about 30 and R is an organic moiety.

4. The molecular sieve of claim 2 or 3, wherein said n is from about 30 to about 150.

5. The molecular sieve of claim 2 or 3, wherein said n is from about 30 to about 60.

6. The molecular sieve of any one of claims 2 to 5, wherein X is aluminum and Y is silicon.

7. The molecular sieve of any preceding claim, comprising less than 1 wt.% Ti.

8. The molecular sieve of any preceding claim, having a collidine adsorption capacity at least 150 μmoles/g.

9. The molecular sieve of any preceding claim, having a collidine adsorption capacity at least 200 μmoles/g.

10. The molecular sieve of any one of claims 1-6 having, in its as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks at d-spacing maxima at 13.18±0.25, 12.33±0.23, 11.05±0.2 and 9.31±0.2 Angstroms, wherein said peaks at d-spacing maxima at 11.05±0.2 and 9.31±0.2 Angstroms exhibit a valley in between and the measured intensity corrected for background at the lowest point of said valley is less than 50 % of the intensity point at the same XRD d-spacing on the line connecting d-spacing maxima at 11.05±0.2 and 9.31±0.2 Angstroms, said EMM-13 molecular sieve has less than 1.6 wt.% Ti.

11. The molecular sieve of claim 10, further having, in its as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks at 3.57±0.07 and 3.42±0.07 Angstroms.

12. The molecular sieve of claim 10 or 11, further having, in its as-synthesized form and in calcined form, an X-ray diffraction pattern including peak at 6.9±0.15 Angstroms.

13. A molecular sieve having, in its as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks at d-spacing maxima at 13.18±0.25, 12.33±0.23, 11.05±0.2 and 9.31±0.2 Angstroms, wherein said peaks at d-spacing maxima at 11.05±0.2 and 9.31±0.2 Angstroms exhibit a valley in between and the measured intensity corrected for background at the lowest point of said valley is less than 50 % of the intensity point at the same XRD d-spacing on the line connecting d-spacing maxima at 11.05±0.2 and 9.31±0.2 Angstroms, said EMM-13 molecular sieve has less than 1.6 wt.% Ti.

14. The molecular sieve of claim 13, further having, in its as-synthesized form and in calcined form, an X-ray diffraction pattern including peaks at 3.57±0.07 and 3.42±0.07 Angstroms.

15. The molecular sieve of claim 13 or 14, further having, in its as-synthesized form and in calcined form, an X-ray diffraction pattern including peak at 6.9±0.15 Angstroms.

16. The molecular sieve of any one of claims 13-15, having a composition involving the molar relationship:

$$X_2O_3:(n)YO_2,$$

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 30.

17. The molecular sieve of any one of claims 13-16, in the as-synthesized form, having a formula, on an anhydrous basis and in terms of moles of oxides per n moles of YO_2, as follows:

$$(0.005\text{-}1)M_2O:(1\text{-}4)R:X_2O_3:nYO_2$$

wherein M is an alkali or alkaline earth metal, n is at least about 30 and R is an organic moiety.

18. The molecular sieve of claim 16 or 17, wherein said n is from about 30 to about 150.

19. The molecular sieve of claim 16 or 17, wherein said n is from about 30 to about 60.

20. The molecular sieve of any one of claims 16 to 19, wherein X is aluminum and Y is silicon.

21. The molecular sieve of any preceding claim, comprising less than 1 wt.% Ti.

22. The molecular sieve of any one of claims 13-21, having a collidine adsorption capacity at least 150 μmoles/g.

23. The molecular sieve of any one of claims 13-22, having a collidine adsorption capacity at least 200 μmoles/g.

24. The molecular sieve of any one of claims 13-23, further comprising a framework of tetrahedral atoms bridged by oxygen atoms, the tetrahedral atom framework being defined by a unit cell with atomic coordinates in nanometers shown in Table 3, wherein each coordinate position may vary within ±0.05 nanometer.

25. A method of manufacturing an as-synthesized crystalline molecular sieve EMM-13, the method comprising the steps of:

(a) providing a mixture comprising MCM-22-P, and an acidic material having a concentration of less than or equal to 10 N, optionally spacing agent;

(b) treating the mixture at treatment conditions to form a product comprising as-synthesized EMM-13, wherein the treatment conditions comprise a treatment temperature in the range of from 50°C to 250°C, and a treatment time from about 0.01 hour to 240 hours; and

(c) recovering the as-synthesized crystalline molecular sieve EMM-13.

26. A method of manufacturing a calcined crystalline molecular sieve EMM-13, the method comprising the step of calcining said as-synthesized crystalline molecular sieve EMM-13 of claim 25 under calcining conditions.

27. A hydrocarbon conversion process comprising the step of contacting a hydrocarbon feedstock with said crystalline molecular sieve EMM-13 of claims 1-24 under hydrocarbon conversion conditions.