

MODIFIED MCM-56, ITS PREPARATION AND USE

This invention relates to selectively modified MCM-56, to a method of its preparation and to its use as a sorbent and a catalyst component for conversion of organic compounds, in particular as a component of a catalytic cracking catalyst.

MCM-56 is a porous inorganic solid and is described in U.S. Patent No.

5 5,362,697. MCM-56 is an unusual material in that it exhibits features of both layered and zeolitic materials. Thus MCM-56 has layers which are microporous and contain cation-exchangeable acid sites. This leads to the presence of acid sites at two different locations; acid sites are located on the large external surface of MCM-56 and further acid sites are located within the internal pore structure of the layers. These further internal
10 acid sites are only accessible through the pore openings in the layers which are believed to be elliptical with dimensions of about 5.9 by 4.0 Angstrom.

According to the present invention, it has now been found that the catalytic and sorptive properties of MCM-56 can be significantly altered by selectively modifying the material so that the ratio of the number of active acid sites at its external surface to the
15 number of internal active acid sites is different, and preferably greater, than that of unmodified MCM-56. For example, MCM-56 modified so as to selectively increase the ratio of its external to internal acid activity has been found to result in an unexpected increase in the yield of high value liquid products, such as gasoline and distillate, and less bottoms fraction and coke, as compared to unmodified MCM-56, when used as an
20 additive to a conventional zeolite Y cracking catalyst.

In one aspect, therefore, the present invention resides in a layered composition of matter, MCM-56, which has an X-ray diffraction including the lines listed in Table II below and which has been selectively modified so that the ratio of the number of active acid sites at its external surface to the number of internal active acid sites is greater than
25 that of the unmodified material.

The layered MCM-56 material of the invention has an X-ray diffraction pattern which is distinguished by the combination of line positions and intensities from the patterns of other known as-synthesized or thermally treated materials as shown below in

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Table I (as synthesized) and Table II (calcined). In these tables, intensities are defined relative to the d-spacing line at 12.4 Angstroms.

TABLE I

MCM-56
(as-synthesized)

	Interplanar d-Spacing (A)	Relative Intensity
5		
10	12.4 $\pm$ 0.2	vs
	9.9 $\pm$ 0.3	m
	6.9 $\pm$ 0.1	w
	6.4 $\pm$ 0.3	w
	6.2 $\pm$ 0.1	w
15	3.57 $\pm$ 0.07	m-s
	3.44 $\pm$ 0.07	vs

TABLE II

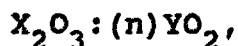
MCM-56
(as-calcined)

	Interplanar d-Spacing (A)	Relative Intensity
20		
25	12.4 $\pm$ 0.2	vs
	9.9 $\pm$ 0.3	m-s
	6.9 $\pm$ 0.1	w
	6.2 $\pm$ 0.1	s
30	3.55 $\pm$ 0.07	m-s
	3.42 $\pm$ 0.07	vs

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These X-ray diffraction data were collected with a Scintag diffraction system, equipped with a germanium solid state detector, using copper K-alpha radiation. The diffraction data were recorded by step-scanning at 0.02
5 degrees of two-theta, where theta is the Bragg angle, and a counting time of 10 seconds for each step. The interplanar spacings, d's, were calculated in Angstrom units (A), and the relative intensities of the lines, I/I_0 , is one-hundredth of the intensity of the strongest line, above
10 background, 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 (60-100), s = strong (40-60), m = medium (20-
15 40) and w = weak (0-20). It should be understood that diffraction data listed for this sample 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
20 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
25 content, framework composition, nature and degree of pore filling, and thermal and/or hydrothermal history.

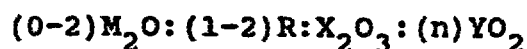
The layered material MCM-56 of this invention has a composition involving the molar relationship:



wherein X is a trivalent element, such as aluminum, boron, iron and/or gallium, preferably aluminum; Y is a tetravalent element such as silicon and/or germanium,
35 preferably silicon; and n is less than about 35, e.g. from about 5 to less than about 25, usually from about 10 to

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less than about 20, more usually from about 13 to about 18. In the as-synthesized form, the material has a formula, on an anhydrous basis and in terms of moles of oxides per n moles of YO_2 , as follows:



wherein M is an alkali or alkaline earth metal, and R is an organic moiety. The M and R components are associated with the material as a result of their presence during synthesis, and are easily removed by post-synthesis methods hereinafter more particularly described.

To the extent desired, the original alkali or alkaline earth, e.g. sodium, cations of the as-synthesized MCM-56 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 IIA, IIIA, IVA, IB, IIB, IIIB, IVB and VIII of the Periodic Table of the Elements.

In the calcined form, MCM-56 exhibits high surface area (greater than $300 \text{ m}^2/\text{gm}$) and unusually large sorption capacity for certain large molecules when compared to previously described materials such as calcined PSH-3, SSZ-25, MCM-22, and MCM-49. Thus calcined MCM-56 is characterised by a sorption capacity for 1,3,5-trimethylbutane of at least about $35 \mu\text{l}/\text{gram}$ and an initial uptake of 2,2-dimethylbutane of $15 \text{ mg}/\text{gram}$ in less than about 20 seconds.

MCM-56 can be prepared from a reaction mixture 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

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Y, e.g. silicon, directing agent (R), and water, said reaction mixture having a composition, in terms of mole ratios of oxides, within the following ranges:

	<u>Reactants</u>	<u>Useful</u>	<u>Preferred</u>
5	YO_2/X_2O_3	5 to 35	10 to 25
	H_2O/YO_2	10 to 70	16 to 40
	OH^-/YO_2	0.05 to 0.5	0.06 to 0.3
	M/YO_2	0.05 to 3.0	0.06 to 1.0
10	R/YO_2	0.1 to 1.0	0.3 to 0.5

The source of YO_2 should comprise predominantly solid YO_2 , for example at least about 30 wt.% solid YO_2 in order to obtain the crystal product of the invention. Where YO_2 is silica, the use of a silica source containing at least about 30 wt.% solid silica, e.g. Ultrasil (a precipitated, spray dried silica containing about 90 wt.% silica) or HiSil (a precipitated hydrated SiO_2 containing about 87 wt.% silica, about 6 wt.% free H_2O and about 4.5 wt.% bound H_2O of hydration and having a particle size of about 0.02 micron) favors crystalline MCM-56 formation from the above mixture under the synthesis conditions required. Preferably, therefore, the YO_2 , e.g. silica, source contains at least about 30 wt.% solid YO_2 , e.g. silica, and more preferably at least about 40 wt.% solid YO_2 , e.g. silica.

Directing agent R is selected from the group consisting of cycloalkylamine, azacycloalkane, diazacycloalkane, and mixtures thereof, alkyl comprising from 5 to 8 carbon atoms. Non-limiting examples of R include cyclopentylamine, cyclohexylamine, cycloheptylamine, hexamethyleneimine, heptamethyleneimine, homopiperazine, and combinations thereof, with hexamethyleneimine being particularly preferred.

Crystallization of the present layered material can be carried out under either static or stirred conditions in a

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suitable reactor vessel, such as for example polypropylene jars or teflon lined or stainless steel autoclaves, at a temperature of about 80°C to about 225°C. It is critical, however, in the synthesis of MCM-56 from the above reaction mixture to stop and quench the reaction prior to the onset of MCM-49 formation at the expense of MCM-56. One method for controlling the synthesis to produce the required MCM-56 is disclosed in U.S. Patent No. 5,362,697 and involves monitoring the X-ray diffraction pattern in the 8.8-11.2 Angstrom d-spacing range. MCM-56 is characterized by a broad band centered around d-spacing 9.9 Angstroms, whereas MCM-49 exhibits two resolved maxima at approximately 8.8-9.2 Angstroms and 10.8-11.2 Angstroms with a distinct depression between them. While the band in the 8.8-11.2 Angstrom d-spacing range for the synthesis mixture may have an asymmetric profile, for example with an inflection point, the emergence of a depression may be indicative of the onset of MCM-49 formation and the loss of MCM-56.

It should be realized that the reaction mixture components can be supplied by more than one source. The reaction mixture can be prepared either batchwise or continuously.

After synthesis is complete, the MCM-56 is separated from the reaction mixture and is then conveniently dehydrated and treated to remove the organic directing agent.

Dehydration is generally performed by heating to a temperature in the range of 200°C to about 370°C in an atmosphere such as air, nitrogen, etc. and at atmospheric, subatmospheric or superatmospheric pressures for between 30 minutes and 48 hours. Dehydration can also be performed at room temperature merely by placing the MCM-56 in a vacuum, but a longer time is required to obtain a sufficient amount of dehydration.

Removal of the organic directing agent is generally performed by heating at a temperature of at least about

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370°C for at least 1 minute and generally not longer than 20 hours. While subatmospheric 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 resultant MCM-56 is subjected to the selective modification procedure of the invention so as to alter the ratio of the surface acid activity of the material to its internal acid activity.

One suitable method for selective modification involves a multi-stage ion exchange procedure, in which the calcined MCM-56 is initially contacted with a catalytically inactive cation, which is capable of occupying all the exchange sites, both internal and external, of the MCM-56. Suitable cations have dimensions less than the pore windows of MCM-56, which have dimensions of 5.9x4 Angstrom, and include the sodium cation, the potassium cation and the cesium cation. The product is then back-exchanged with a bulky cation which replaces the cations on the external surface of the MCM-56 but which, by virtue of its size, is sterically hindered from entering the pore openings of the material. Suitable bulky cations have at least one dimension greater than 6 Angstrom and include the tetrapropylammonium (TPA⁺) cation, the tetraethylammonium (TEA⁺) cation and the tetrabutylammonium (TBA⁺) cation.

Another suitable method for selective modification involves coating the external surface of the MCM-56 with a catalytically active or inactive material, such as alumina or silica, so as to increase or decrease respectively the surface activity compared to the internal activity of the MCM-56.

A convenient method of measuring the surface acidity of MCM-56, exclusive of its internal acidity, is to determine its activity for the dealkylation of 1,3,5-tri-tertbutylbenzene (TTBB), a bulky molecule that can only react with the acid sites on the surface of the material.

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Dealkylation of TTBB is a facile, reproducible method for measuring surface acidity of catalysts. External surface activity can be measured exclusive of internal activity for zeolites with pore diameters up to and including faujasite. As a test reaction dealkylation of TTBB occurs at a constant temperature in the range of from about 25 to about 300°C, and preferably in the range of from about 200 to about 260°C.

The experimental conditions for the test used herein include a temperature of 200°C and atmospheric pressure. The dealkylation of TTBB is carried out in a glass reactor (18 cm x 1 cm OD) containing an 8 gm 14/30 mesh Vycor chip preheater followed by 0.1 gm catalyst powder mixed with Vycor chips. The reactor is heated to 200°C in 30 cc/gm nitrogen for 30 minutes to remove impurities from the catalyst sample. Ten gm/hr of TTBB dissolved in toluene (7% TTBB) is injected into the reactor. The feed vaporizes as it passes through the preheater and is vapor when passing over the catalyst sample. After equilibrium is reached the nitrogen is switched to 20 cc/min hydrogen. The test is then run for about 30 minutes and the reaction products are analyzed by gas chromatography.

The major dealkylation product is di-t-butylbenzene (DTBB). Further dealkylation to t-butylbenzene (TBB) and benzene (B) occurs but to a lesser extent. Conversion of TTBB is calculated on a molar carbon basis. Dealkylation product weight % are each multiplied by the appropriate carbon number ratio to convert to the equivalent amount of TTBB, i.e. DTBB x 18/14, TBB x 18/10 and B x 18/6. These values are then used in the following conversion equation where asterisks indicate adjustment to the equivalence.

$$\% \text{ TTBB Conversion} = \frac{\text{DTBB}^* + \text{TBB}^* + \text{B}^*}{\text{TTBB} + \text{DTBB}^* + \text{TBB}^* + \text{B}^*}$$

The coefficient of reaction, k_{TTBB} is then calculated

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on the assumption that that the conversion of TTBB is a first order reaction according to the equation:

$$k_{\text{TTBB}} = \frac{\text{Gas flow rate, cc/min} \times \ln(1 - \epsilon_{\text{TTBB}})}{60 \times \text{Catalyst volume, cc}}$$

where ϵ_{TTBB} is the fractional conversion of TTBB at 30 minutes on stream.

In the case of MCM-56, the TTBB conversion is accompanied by significant conversion of toluene by disproportionation into benzene and xylenes. The toluene conversion is calculated based on the weight % of toluene in the feed converted and, again assuming that the conversion is a first order reaction, k_{Toluene} is derived from:

$$k_{\text{Toluene}} = \frac{\text{Gas flow rate, cc/min} \times \ln(1 - \epsilon_{\text{Toluene}})}{60 \times \text{Catalyst volume, cc}}$$

where $\epsilon_{\text{Toluene}}$ is the fractional conversion of toluene at 30 minutes on stream.

A convenient method of measuring the overall acidity of MCM-56, inclusive of both its internal and external acidity, is the alpha test, which is described in U.S. Patent No. 3,354,078; in the Journal of Catalysis, Vol. 4, p. 527 (1965); Vol. 6, p. 278 (1966); and Vol. 61, p. 395 (1980), each incorporated herein by reference as to that description. The experimental conditions of the test used herein include a constant temperature of 538°C and a variable flow rate as described in detail in the Journal of Catalysis, Vol. 61, p. 395.

Thus the selective modification of the invention can be demonstrated by comparing the TTBB conversion and the alpha value of the MCM-56 before and after modification.

The modified MCM-56 material of this invention may be used as an adsorbent, such as for separating at least one

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component from a mixture of components in the vapor or liquid phase having differential sorption characteristics with respect to MCM-56. Therefore, at least one component can be partially or substantially totally separated from a mixture of components having differential sorption characteristics with respect to MCM-56 by contacting the mixture with the MCM-56 to selectively sorb the one component.

The modified MCM-56 material of this invention can also be used to catalyze a wide variety of chemical conversion processes including many of present commercial/industrial importance. When used as a catalyst, the modified MCM-56 material of the invention may be intimately combined with a hydrogenating component such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal such as platinum or palladium where a hydrogenation-dehydrogenation function is to be performed. Such component can be in the composition by way of cocrystallization, exchanged into the composition to the extent a Group IIIA element, e.g. aluminum, is in the structure, impregnated therein or intimately physically admixed therewith. Such component can be impregnated in or on to it such as, for example, by, in the case of platinum, treating the silicate with a solution containing a platinum metal-containing ion. Thus, suitable platinum compounds for this purpose include chloroplatinic acid, platinumous chloride and various compounds containing the platinum amine complex.

When used as a catalyst, it may be desirable to incorporate the modified MCM-56 of the invention 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

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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 MCM-56, i.e. combined therewith or present during synthesis of MCM-56, 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. Said 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 and/or oxide binders have been employed normally only for the purpose of improving the crush strength of the catalyst.

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, dickite, nacrite, or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification. Binders useful for compositing with the present MCM-56 layered material also include inorganic oxides, notably alumina.

In addition to the foregoing materials, the MCM-56 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

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compositions such as silica-alumina-thoria, silica-alumina-zirconia silica-alumina-magnesia and silica-magnesia-zirconia.

5 The relative proportions of finely divided MCM-56 material and inorganic oxide matrix vary widely, with the MCM-56 content ranging from about 1 to about 90 percent by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of about 2 to about 80 weight percent of the composite.

10 The modified MCM-56 produced according to the invention is particularly intended for use as an additive catalyst to a catalytic cracking catalyst. Conventional cracking catalysts comprise a primary cracking component, which may be amorphous, such as silica/alumina, but more
15 normally comprises a large pore crystalline zeolite, such as zeolite X, zeolite Y, REY or US-REY, ZSM-20 or zeolite L. In addition, to the large pore zeolite, such as zeolite Y, conventional cracking catalysts contain other components, notably a matrix for the zeolite. When a
20 matrix is used, the content of the large pore zeolite is conveniently about 5 to 50% by weight of the matrixed catalyst.

25 The modified MCM-56 according to the invention can be added to such a conventional cracking catalyst, either as a separate particle, typically bound with a separate matrix, or combined with the large pore zeolite as a single particle. The amount of modified MCM-56 present in the cracking catalyst can vary between 0.5% and 90% by weight, and preferably is between 2% and 45% by weight, of the
30 overall cracking catalyst.

Cracking catalysts containing the modified MCM-56 of the invention are useful in both fluid catalytic cracking (FCC) and Thermoform catalytic cracking (TCC). Such
35 processes typically operate at temperatures between 200°C and 700°C and under reduced or superatmospheric pressure.

Catalysts containing the modified MCM-56 of the

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invention can be used to crack a wide variety of heavy hydrocarbon feedstocks, such as petroleum fractions having an initial boiling point of 200°C, a 50% point of at least 260°C and an end point in excess of 315°C. Such hydrocarbon feedstocks include gas oils, residual oils, cycle stocks, whole and topped crudes and the heavy hydrocarbon fractions derived from the destructive hydrogenation of coal, tar, pitches asphalts and the like.

According to the invention, it has surprisingly been found that cracking of a petroleum feedstock with a catalyst MCM-56 which has been modified to increase the ratio of external activity to internal activity gives an improved gasoline yield/octane relationship, an improved coke selectivity and a higher combined gasoline and potential alkylate yield than an identical catalyst containing unmodified MCM-56.

Examples of other chemical conversion processes which are effectively catalyzed by the modified MCM-56 of the invention, by itself or in combination with one or more other catalytically active substances including other crystalline catalysts, include:

(1) alkylation of aromatic hydrocarbons, e.g. benzene, with long chain olefins, e.g. C₁₄ olefin, with reaction conditions including a temperature of from about 340°C to about 500°C, a pressure of from about atmospheric to about 200 atmospheres, 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;

(2) 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 a temperature of from about 10°C to about 125°C, a pressure of from about 1

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to about 30 atmospheres, and an aromatic hydrocarbon weight hourly space velocity (WHSV) of from 5 hr^{-1} to about 50 hr^{-1} ;

(3) alkylation of reformat containing substantial quantities of benzene and toluene with fuel gas containing C_5 olefins to provide, inter alia, mono- and dialkylates with reaction conditions including a temperature of from about 315°C to about 455°C , a pressure of from about 400 to about 800 psig, a WHSV-olefin of from about 0.4 hr^{-1} to about 0.8 hr^{-1} , a WHSV-reformat 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;

(4) 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 a temperature of from about 160°C to about 260°C and a pressure of from about 350 to 450 psig;

(5) alkylation of phenols with olefins or equivalent alcohols to provide long chain alkyl phenols with reaction conditions including a temperature of from about 200°C to about 250°C , a pressure of from about 200 to 300 psig and a total WHSV of from about 2 hr^{-1} to about 10 hr^{-1} ; and

(6) alkylation of isoalkanes, e.g. isobutane, with olefins, e.g. 2-butene, with reaction conditions including a temperature of from about -25°C to about 400°C , e.g., from 75°C to 200°C , a pressure of from below atmospheric to about 35000 kPa (5000 psig), e.g. from 100 to 7000 kPa (1 to 1000 psig), a weight hourly space velocity based on olefin of from about 0.01 hr^{-1} to about 100 hr^{-1} , e.g. from 0.1 hr^{-1} to 20 hr^{-1} , and a mole ratio of total isoalkane to total olefin of from about 1:2 to about 100:1, e.g. from 3:1 to 30:1.

In order to more fully illustrate the nature of the invention and the manner of practicing same, the following examples are presented.

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Example 1

This example demonstrates the preparation of the hydrogen form of MCM-56.

A sample of as-synthesized MCM-56 prepared as described in U.S. Patent No. 5,362,697 was ammonium exchanged and was dried at 250°F (120°C) overnight. The dried ammonium exchanged MCM-56 was first heated in flowing nitrogen at 900°F (480°C) for 3 hours to decompose the directing agent followed by calcining in flowing air at 1000°F (540°C) for 6 hours. The resulting MCM-56 sample was in the [H]-form and was designated as sample A. The properties of sample A are listed in Table III below.

Example 2

This example discloses the preparation of selective cation exchanged MCM-56.

529 g of sample A from Example 1 was slurried in 2650 ml of a 1 N NaCl solution for 2 hours. The sample was filtered and washed with deionized water. The filter cake was re-slurried in 2650 ml of 1 N NaCl solution for 2 hours, and was filtered and washed. The filtercake was dried at 250°F overnight. The dried MCM-56 sample was in the [Na]-form and was designated as sample B. The properties of sample B are listed in Table III below.

600 g of sample B was slurried in 6 liter of 35% tetrapropylammonium bromide ([TPA]Br) solution for 2 hours. The sample was filtered and washed with deionized water until no residual bromide was detected in the filtrate. The filtercake was re-slurried in another 6 liter of 35% tetrapropylammonium bromide solution for another 2 hours. After filtering and washing with deionized water, the filtered cake was dried at 250°F (120°C) overnight. The dried MCM-56 sample was in the [TPA]/[Na]-form and was designated as sample C. The properties of sample C are listed in Table III below.

The selective ion exchange process described above involved the use of a small cation, sodium [Na]⁺, to occupy

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all exchange (acid) sites in MCM-56. The sodium cations on the sample were then back exchanged with a bulky cation, tetrapropylammonium, $[\text{TPA}]^+$. Due to the bulky dimension of $[\text{TPA}]^+$ cation, it was selectively exchanged with the sodium cations located on the external surface of MCM-56. For those exchange (acid) sites located within the layer, they remained occupied with sodium because the $[\text{TPA}]^+$ cations were too large to access through the 10-ring pore openings of MCM-56 during the second exchange.

Example 3

This example discloses the preparation of alumina-coated MCM-56.

A 1852 g of sample A from Example 1 was slurried in 9 liters of 1 N ammonium nitrate solution for 1 hour. The slurry was filtered and washed with deionized water. The filter cake was dried at 250°F (120°C) overnight.

An alum solution was prepared by adding 112.5 g of deionized water to 1406 g of aluminum sulfate (8 wt.% Al_2O_3) solution. The density of the diluted alum solution is 1.38 g/ml. A sodium aluminate solution was prepared by adding 886 g of sodium aluminate (USALCO 45) to 39.8 g of caustic soda. The density of the sodium aluminate solution is 1.54 g/ml. A second sodium aluminate solution was also prepared using the same procedure.

The dried filtercake (845 g) was first slurried in deionized water, and the slurry was heated up to 120°F (50°C). After the temperature of the slurry equilibrated at 120°F (50°C), the alum solution and the first sodium aluminate solution were introduced to the slurry simultaneously by using two separate pumps. The pH of the slurry was maintained at pH 7.4 - 7.6 by adjusting the flow rate of the sodium aluminate solution. After completing the addition of the two solutions, the slurry was allowed to stir at 120°F (50°C) for an additional 10 minutes. The second sodium aluminate solution was then introduced to the

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slurry. The final pH of the slurry was allowed to stabilize at 9.8 - 10.0 at 120°F (50°C). The slurry was stirred at 120°F (50°C) for an additional 30 minutes, and was filtered and washed with hot deionized water. The filtercake was further washed with deionized water until the pH of the filtrate was below 9. The filtercake was dried at 250°F (120°C) overnight. The dried filter cake was ammonium exchanged and was calcined at 1000°F (540°C) for 3 hours. The calcined sample was the alumina-coated MCM-56 and was designated as sample D.

The properties of sample D are listed in Table III below.

Table III

Sample I.D.	A	B	C	D
	1	2	2	3
Example Form	[H]	[Na]	[TPA]/[Na]	Alumina-coated
SiO ₂ , wt%	84.8	82	70	49.2
Al ₂ O ₃ , wt%	8	9	6	39
Na, wt%	0.038	4.63	0.926	0.041
N, wt%	-	-	1.2	-
Ash, %	94.5	88.5	79.5	96
Alpha *	121	0.7	39	94
TTBB Test K_{TTBB}, s^{-1}	0.24	0.0	3.07	5.02
$K_{toluene}, s^{-1}$	0.95	N/a	0.08	0.06
n-C ₆ , wt% (@90°C)	5.03	3.49	4.89	2.57
Na/Al (atomic ratio)	0.01	1.14	0.27	< 0.01
(Na+N)/Al (atomic ratio)	-	-	1.0	-

* The alpha measurements were conducted on the samples after calcination at 1000°F (540°C). For sample C, it was first calcined in nitrogen at 900°F (480°C) to decompose the [TPA]⁺ cations followed by air calcining at 1000°F (540°C).

Table III shows that after sodium exchange, all exchange sites in MCM-56 (Sample B) were occupied by sodium cations, as indicated by a Na/Al ratio of 1.14. After the

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[TPA]Br exchange (Sample C), approximately 73% of the exchange sites were not occupied by sodium cations, as indicated by a Na/Al ratio of 0.27. The results of the alpha measurements were also consistent with the elemental analyses. As all the exchange (acid) sites were occupied with sodium cations, sample B exhibited insignificant alpha cracking activity. In contrast, sample C demonstrated an alpha value of 39, consistent with only part of the exchange (acid) sites still being occupied by sodium cations. For sample D, although the alpha value was only 94 (less than the alpha value of sample A), comparison of the n-C₆ uptake at 90°C of samples A and D indicates that the MCM-56 content of sample D was only about 51% by weight.

Table III also shows that the catalytic properties of sample A were dominated by the conversion of toluene which mostly occurred at the internal acid sites. The conversion of TTBB with sample A was an order of magnitude smaller than those of sample C and D. The conversion of TTBB in the presence of toluene demonstrated the unique catalytic properties of the modified MCM-56 of samples C and D. Both samples C and D showed a high TTBB conversion but with a minimum conversion of toluene, which is consistent with the internal acid sites being blocked by sodium or with the accessibility to the internal acid sites being limited by the alumina coating. Sample B exhibited no conversion of TTBB or toluene since all acid sites were occupied by sodium.

Example 4

This example demonstrates the preparation of rare earth exchanged USY.

A commercial USY, Z14US (Grace Davison), was ammonium exchanged. 4300 g of dried ammonium exchanged USY was slurried in 10.8 liter of deionized water. A rare earth chloride solution containing 844 g of RECl₃·7H₂O was added

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to the USY slurry. After completing the addition of the rare earth chloride solution, the slurry was stirred under ambient conditions overnight. The slurry was filtered and the filtercake was washed with deionized water until no chloride was detected in the filtrate. The filter cake was dried at 250°F (120°C) overnight and calcined at 1000°F (540°C) for 3 hours. This calcined sample was designated as sample E. Elemental analyses of sample E are listed below:

10	RE ₂ O ₃ , wt%	5.73
	Na, wt%	0.489
	Al ₂ O ₃ , wt%	22.1
	SiO ₂ , wt%	65.5
	Unit cell size Å	24.595
15	Ash, %	96.5

Example 5

Three catalysts, designated catalysts G, H and I, were formulated with 20% rare earth exchanged USY (sample E) and 20% unmodified or modified MCM-56 using samples A, C, and D respectively in a 25% silica/35% clay matrix according to the following procedure.

932 g of ball milled rare earth exchanged USY slurry (32.2% solid) was introduced to 1103 g of colloidal silica (Nalco 1034A). The zeolite-silica slurry was mixed for at least 3 minutes. A 1282 g of ball milled modified or unmodified MCM-56 slurry (23.4% solid) was added to the zeolite-silica mixture and mixed for at least 3 minutes. 875 g of kaolin clay (Thiele RC-32) was then added to the mixture. Additional deionized water was added for satisfactory operation of the spray dryer. The pH of the slurry was maintained at pH 3.5 - 3.75.

The slurry was spray dried in a Bowen Engineering 2' diameter spray dryer with an outlet temperature of 350°F (180°C). The collected fluid catalyst was washed with deionized water and filtered. The wet cake was dried at

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250°F (120°C) overnight. The dried product was first calcined in air at 1000°F (540°C) for 2 hours followed by steam deactivation at 1450°F (790°C) in 45% steam/55% air, 0 psig (100 kPa) for 10 hours before catalytic testing.

Table IV lists the properties of catalysts G, H and I.

Example 6

A further catalyst, designated catalyst F, was formulated with 20% rare earth exchanged USY (sample E) in a 25% silica-55% clay matrix according to the following procedure:

932 g of ball milled rare earth exchanged USY slurry (32.2% solid) was introduced to 1103 g of colloidal silica (Nalco 1034A). The zeolite-silica slurry was mixed for at least 3 minutes. 1323 g of kaolin clay (Thiele RC-32) was then added to the mixture. Additional deionized water was added for satisfactory operation of the spray dryer. The pH of the slurry was maintained at pH 3.5 - 3.75.

The slurry was spray dried in a Bowen Engineering 2' diameter spray dryer with an outlet temperature of 350°F (180°C). The collected fluid catalyst was washed with deionized water and filtered. The wet cake was dried at 250°F (120°C) overnight. The dried product was first calcined in air at 1000°F (540°C) for 2 hours followed by steam deactivation at 1450°F (790°C) in 45% steam/55% air, 0 psig (100 kPa) for 10 hours before catalytic testing. Table IV lists the properties of catalyst F.

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Table IV

	Catalyst Formulation	F	G	H	I
5	RE-USY, wt%	20	20	20	20
	MCM-56 sample type	None	Sample A	Sample C	Sample D
	Clay matrix, wt%	55	35	35	35
	Silica matrix, wt%	25	25	25	25
10	SiO ₂ , wt%	65.2	73.3	72.1	66.4
	Al ₂ O ₃ , wt%	28.3	21.3	21.3	27.5
	Na, wt%	0.10	0.12	0.32	0.11
	RE ₂ O ₃ , wt%	1.2	0.98	1.10	1.05
	Clay, wt%	55	35	35	35
15	Silica, wt%	25	25	25	25
	Surface area, m ² /g	134	185	197	163
	Ash, %	98.6	99.4	98.0	99.2

The results of the rare earth analyses on the four catalysts suggest that they have similar RE-USY content in each of the catalyst prepared. The results of the surface area measurements of the four steamed catalysts are consistent with the relative amount of MCM-56 in each of the catalyst.

Example 7

Each of the catalysts F, G, H, and I was evaluated in a fixed fluidized bed reactor using a Joliet sour heavy gas oil (JSHGO) as a petroleum feedstock. The properties of the feedstock are listed in Table V below:

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Table V

	Feed	JHSGO
	API gravity	19.7
	Pour Point, °F (°C)	95 (35)
5	Kinematic Viscosity at 100C, cs	7.95
	Molecular weight	369
	CCR, wt%	0.56
	Aromatics, wt%	55.3
	Saturates, wt%	44.7
10	Sulfur, wt%	2.6
	Total nitrogen, ppm	1500
	Basic nitrogen, ppm	490
	Ni, ppm	0.48
	V, ppm	0.29
15	Fe, ppm	1.2
	Initial boiling point, °F (°C)	497 (258)
	50% point, °F (°C)	826 (441)
	90% point, °F (°C)	1001 (583)

20 The reactor temperature was 960°F (515°C), and the oil delivery time was 1 minute. At a cat-to-oil ratio of 4, the activity ranking based on the volume percent conversion of fresh feed was as follows:

$$H < G \approx I < F$$

$$25 \quad 75 < 73.2 \approx 73.5 < 71.1$$

30 Comparing the activity of catalyst F with those of catalysts G, H, and I, the presence of unmodified or modified MCM-56 helped to increase the conversion of a RE-USY containing catalyst. It is also surprising to note that catalyst H was the most active among the four catalysts as part of the acid sites on MCM-56 were occupied by sodium (ref. Sample C, Example 2). The similar conversions observed for catalyst G and I suggest that the alumina coating on MCM-56 enhanced its activity, as there was only approximately 50% MCM-56 in the alumina-coated MCM-56 sample (ref. Sample D, Example 3).

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The yield pattern of catalysts F, G, H, and I at 70 vol.% conversion is given in Table VI below:

Table VI

Catalyst	F	G	H	I
Light gas, wt%	3.0	2.9	2.8	2.9
H ₂ , wt%	0.14	0.10	0.06	0.12
Total C ₃ , vol.%	7.9	11.1	9.6	9.4
C ₃ =/C ₃ , mol/mol	2.3	3.0	3.2	3.3
Total C ₄ , vol.%	13.7	18.0	15.1	16.1
C ₄ =/C ₄ , mol/mol	0.7	0.8	0.7	0.8
C ₅ ⁺ Gasoline, vol%	55.6	50.6	55.2	54.2
C ₅ ⁺ Gasoline, wt%	45.1	41.0	45.2	44.0
LCO, wt% (430-740°F)	26.4	26.7	26.4	26.6
HFO, wt% (740+°F)	6.3	6.2	6.3	6.2
Coke, wt%	6.2	5.7	4.5	5.0
RON, C ₅ ⁺ Gasoline	88.5	91.0	89.0	90.1
Isobutane/(C ₃ +C ₄) Olefins	0.60	0.54	0.54	0.49
Iso-C ₄ =/C ₄ =	0.19	0.29	0.27	0.26
(Gasoline+LCO)/(HFO+Coke)	5.7	5.7	6.6	6.3
Potential alkylate, % vol.	18.3	26.7	22.8	24.4
Gasoline + Potential alkylate, % vol.	73.9	77.3	77.9	78.6
ΔRON/ΔGasoline loss(vol%)	Base	0.5	1.3	1.1

The incorporation of unmodified or modified MCM-56 into a RE-USY containing catalyst improved the coke selectivity, the octane of the gasoline, and the LPG yield. However, the latter came at an expense of the gasoline yield loss.

The modification of MCM-56 by the selective cation exchange method and its incorporation in a RE-USY containing catalyst (Catalyst H) resulted in a reduction in the gasoline yield loss. Although the absolute gasoline octane gain was less than that observed for Catalyst G, the (ΔRON/ΔGasoline loss) ratio suggests that Catalyst H was more effective in increasing RON without a significant debit in gasoline yield. Table 5 shows that Catalyst G and H had (ΔRON/ Gasoline loss) ratios of 0.5 and 1.3, respectively.

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When alumina-coated MCM-56 was incorporated into a RE-USY containing catalyst (catalyst I), it offered similar benefits in the yield pattern of the cracked products to those of the catalyst containing the selective exchanged MCM-56 and RE-USY (catalyst H). Further-more, the former yielded a higher octane gasoline than that of catalyst H, and had the highest combined gasoline and potential alkylate yield among the four catalysts at about 50% less MCM-56 than catalysts G and H.

Both catalysts H and I exhibited better bottom upgrading capabilities than catalysts F and G, as determined by the (Gasoline+LCO)/(HFO+Coke) ratios. Therefore, using modified MCM-56 in the catalytic cracking of petroleum feedstock should produce more high value liquid products, such as gasoline and distillate, and less bottoms fraction and coke.

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CLAIMS:

1. A layered composition of matter, MCM-56, which has an X-ray diffraction including the lines listed in Table II below:

TABLE II

5	Interplanar d-Spacing	Relative Intensity
	(A)	
	12.4 $\pm$ 0.2	vs
	9.9 $\pm$ 0.3	m-s
	6.9 $\pm$ 0.1	w
10	6.2 $\pm$ 0.1	s
	3.55 $\pm$ 0.07	m-s
	3.42 $\pm$ 0.07	vs

and which has been selectively modified so that the ratio of the number of active acid sites at its external surface to the number of internal active acid sites is greater than that of the unmodified material.

2. The layered composition of matter of Claim 1 which has been selectively modified so as to render the internal acid sites substantially catalytically inactive.

3. The layered composition of matter of Claim 1 which has been selectively modified by the application of a coating of a catalytically active or inactive material to its external surface.

4. The layered composition of matter of Claim 3 wherein the coating comprises an inorganic oxide material.

5. The layered composition of matter of Claim 4 wherein the coating comprises silica or alumina.



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6. A catalyst composition comprising a large pore zeolite cracking catalyst and the layered composition of matter claimed in claim 1.

5 7. The catalyst composition of Claim 6 wherein the large pore zeolite is a zeolite Y.

8. The catalyst composition of Claim 6 comprising about 0.5 to 90% by weight of said layered composition of matter by weight of the catalyst composition.

10 9. A hydrocarbon conversion process comprising contacting a reaction stream comprising a hydrocarbon to be converted, under conversion conditions, with the layered composition of matter of claim 1.

15 10. The process of Claim 9 selected from catalytic cracking of a heavy hydrocarbon feedstock, alkylation of an aromatic feedstock with an olefin, and alkylation of isoparaffin with an olefin.

