

1 PREPARATION OF Y ZEOLITE

2 Field of the Invention

3 The present invention relates to a process for producing crystalline aluminosilicate
4 Y zeolite from a reaction mixture which contains only sufficient water to form Y zeolite.

5 Background

6 Prior art methods of preparing crystalline Y zeolite typically produce finely divided
7 crystals which must be separated from an excess of liquid in which the zeolite is crystallized.
8 The liquid, in turn, must be treated for reuse or else be discarded, with potentially deleterious
9 environmental consequences. Preparing commercially useful catalytic materials which
10 contain the powdered zeolite also normally requires additional binding and forming steps.
11 Typically, the zeolite powder as crystallized must be mixed with a binder material and then
12 formed into shaped particles or agglomerates, using methods such as extruding,
13 agglomeration, spray drying, and the like. These binding and forming steps greatly increase
14 the complexity of catalyst manufacture involving zeolitic materials. The additional steps may
15 also have an adverse effect on the catalytic performance of the Y zeolite so bound and
16 formed.

17 U.S. Patent No. 3,094,383, issued June 18, 1963 to Dzierzanowski et al., discloses a
18 method for making type A zeolites in the form of coherent polycrystalline aggregates by
19 forming reaction masses consisting of a mixture of sodium aluminate, a siliceous material and
20 water, wherein the H_2O/Na_2O mole ratio is 5 to 25. The mass is aged while maintaining it
21 out of contact with an external aqueous liquid phase while preventing the mass from
22 dehydrating. The aging step can include maintaining the mass at 100°F. (38°C.) for, e.g., 18
23 hours, followed by heating at 200°F (93°C.) for, e.g., 24 hours.

24 U.S. Patent No. 3,119,659, issued January 28, 1964 to Taggart et al., discloses a
25 method for producing an aluminosilicate zeolite in a preformed body by providing an
26 unreacted preformed body containing a reactive kaolin-type clay and alkali metal hydroxide,
27 and reacting the preformed body in an aqueous reaction mixture until crystals of the zeolite
28 are formed in the body. The aggregate of the preformed body and the aqueous reactant
29 mixture has a H_2O/Na_2O mole ratio of at least 20. It is stated that Y zeolite can be made in
30 this manner.

31 U.S. Patent No. 3,777,006, issued December 4, 1973 to Rundell et al., discloses a
32 process for preparing zeolitic bodies having a size in excess of 200 microns, by preparing clay

1 bodies in the desired size range, treating the clay bodies in a sodium silicate solution, and
2 heating the formed bodies in the solution until crystallization is complete. It is indicated that
3 Y zeolite can be made in this manner.

4 U.S. Patent No. 4,058,586, issued November 15, 1977 to Chi et al., discloses a
5 method for preparing zeolitic aluminosilicates, particularly those that are characterized by
6 pores in the 4 to 10 Angstrom sizes that are designated Zeolites A and X, in which compacts
7 of Zeolites A and X, metakaolin clay mixture undergo crystallization at a temperature of 200°
8 to 700°F (93° to 371°C.) . The crystallization is carried out in a calciner or other drying
9 equipment. Normally, the formed particles furnish all of the liquid needed for crystallization,
10 though steam may be added during the crystallization process.

11 WO 92/12928, published August 6, 1992, discloses that silica-bound extruded
12 zeolites may be converted into binder-free zeolite aggregates by aging the zeolite in an
13 aqueous ionic solution which contains hydroxy ions such that the initial molar ratio of OH⁻
14 :SiO₂ is up to 1.2 and which causes the silica binder to be converted substantially to zeolite of
15 the type initially bound. It is stated that this process can be used to make Y zeolite.

16 WO 94/13584, published June 23, 1994, discloses a method for preparing a
17 crystalline aluminosilicate zeolite from a reaction mixture containing only sufficient water so
18 that the reaction mixture may be shaped if desired. In the method, the reaction mixture is
19 heated at crystallization conditions and in the absence of an external liquid phase, so that
20 excess liquid need not be removed from the crystallized material prior to drying the crystals.

21 GB 2,160,517 A, published December 24, 1985, relates to a preformed synthetic
22 zeolite selected from the group consisting of Y, omega zeolite, offretite, erionite, L zeolite
23 and ferrierite whose Si/Al atomic ratio ranges from 1.5 to 100, the preformed zeolite being
24 obtained from a preformed aluminosilicic material whose Si/Al atomic ratio is lower than
25 that of the product and ranges from 0.5 to 90 by treating the material with a silica-containing
26 product in the presence of at least one organic or inorganic base.

SUMMARY OF THE INVENTION

1 It is an object of the invention to provide a method for preparing crystalline Y zeolite
2 using a minimum of liquid for crystallization.

3 It is a further object of the invention to provide a method for preparing crystalline
4 Y zeolite while minimizing aqueous waste.

5 It is a further object of the invention to provide a method for preparing Y zeolite in
6 the absence of added binder.

7 It is also an object of this invention to prepare crystalline Y zeolite in the form of a
8 shape.

9 It is a further object of the invention to provide a method for preparing Y zeolite in
10 commercially useful forms without any post crystallization forming steps.

11 It is a further object of the invention to provide a method for preparing Y zeolite
12 having a small crystallite size.

13 It is a further object of the invention to provide a method for preparing Y zeolite at
14 reduced raw material costs.

15 Thus, in accordance with the present invention, there is provided a method for
16 preparing crystalline Y zeolite, said method comprising preparing a reaction mixture
17 comprising at least one active, non-zeolitic source of silica and at least one active, non-
18 zeolitic source of alumina in amounts sufficient to produce Y zeolite, and sufficient water to
19 produce Y zeolite, and maintaining said reaction mixture at a temperature of up to about
20 130°C. under crystallization conditions and in the absence of an added external liquid phase
21 for sufficient time to form crystals of Y zeolite.

22 The present invention also provides a method for preparing crystalline Y zeolite, said
23 method comprising preparing a reaction mixture comprising at least one active, non-zeolitic
24 source of silica and at least one active, non-zeolitic source of alumina in amounts sufficient to
25 produce Y zeolite, and sufficient water to shape said mixture, forming said reaction mixture
26 into a shape; and maintaining said reaction mixture at a temperature of up to about 130°C.
27 under crystallization conditions and in the absence of an added external liquid phase for
28 sufficient time to form crystals of Y zeolite.

29 In a preferred embodiment, the present invention also provides a method for
30 preparing Y zeolite which includes an aging step prior to the crystallization step. The aging
31

1 is conducted at a temperature of from about 25°C. to about 75°C. in the absence of an added
2 external liquid phase.

3 It is important, in preparing the reaction mixture of the present process, that the
4 amount of water present in the reaction mixture as prepared for the crystallization step be
5 sufficient to produce the Y zeolite. Thus, the reaction mixture itself furnishes all the water
6 needed to crystallize the zeolite. This amount of water is less than the amount of water
7 required in conventional processes for preparing zeolites. It is an amount which is not
8 substantially greater than that required to produce the Y zeolite. For example, the amount of
9 water used in the present invention is less than that required to dissolve the reaction mixture
10 components, or, if they are not dissolved, less than that required to immerse the reaction
11 mixture components in the water. Thus, during the crystallization step according to the
12 present process, there is no separate, added external liquid phase present which must be
13 removed from the crystallized material at the end of the crystallization step by, for example
14 filtering or decanting, prior to drying the crystals. This absence of an added external liquid
15 phase distinguishes the present invention from methods for making Y zeolite wherein the
16 Y zeolite crystals are formed from solution or where solid reactants are heated in an aqueous
17 solution until crystals of Y zeolite form.

18 While it is not a requirement to form the mixture into a shape before the mixture is
19 subjected to crystallization conditions, it may be desired in many cases to do so. In that case,
20 the amount of water present in the reaction mixture is sufficient to form the reaction mixture
21 into a shape, but insufficient to cause the shaped reaction mixture to collapse or "melt", i.e.,
22 once the reaction mixture is formed into the desired shape containing the desired amount of
23 water, the resulting shape is self-supporting.

24 Among other factors, the present invention is based on the discovery of a method for
25 crystallizing Y zeolite from a reaction mixture which does not contain an organic template
26 capable of producing Y zeolite and which contains only enough water to form the Y zeolite.
27 Further, the Y zeolite prepared by the above described method is made as very small
28 crystallites.

29 DETAILED DESCRIPTION OF THE INVENTION

30 PREPARING THE REACTION MIXTURE

31 The reaction mixture from which and in which the Y zeolite is crystallized comprises
32 at least one active, non-zeolitic source of silica, at least one active, non-zeolitic source of

1 alumina, and sufficient water to form the Y zeolite. This amount of water is considerably less
2 than that required in conventional processes for preparing Y zeolite.

3 The amount of water required in the reaction mixture of the present invention is that
4 amount which is needed to adequately blend the mixture. Thus, a reaction mixture is
5 prepared by mixing water with active sources of the zeolite to form a uniform mass having
6 preferably a heavy paste-like consistency. The active sources will be in a form which can be
7 easily blended into a uniform mass, and may be, for example, powders, hydrated particles, or
8 concentrated aqueous solutions. Sufficient water is added to wet all the powders during the
9 mixing and kneading steps. Alternatively, sufficient water is added that the powders may be
10 kneaded into a uniform and generally homogeneous mixture which may be shaped. It is not
11 necessary that all of the active sources be readily soluble in water during kneading, since the
12 water added to the active sources will be insufficient to make a fluid-like mixture. The
13 amount of water added depends on the mixing apparatus and on the active sources employed.
14 Those familiar with the art can readily determine without undue experimentation the amount
15 of liquid required to properly mix active sources of the zeolite. For example, hydrated
16 sources of the zeolite may require relatively less water, and dried sources may require
17 relatively more. Though it is preferred that the mixture be blended and kneaded until the
18 mixture has a uniform, homogeneous appearance, the length of time devoted to kneading the
19 mixture is not critical in the present invention.

20 The water content of the reaction mixture after blending and kneading may be further
21 adjusted, for example, by drying or by the addition of water. When it desired that the
22 reaction mixture be formed into a shape, adjusting the amount of water can facilitate shaping
23 the reaction mixture and ensure that it will be self-supporting, i.e., the shape will not collapse
24 or "melt" due to an excess of water in the reaction mixture..

25 Typical non-zeolitic sources of silicon oxide (SiO_2) include silicates, silica hydrogel,
26 silicic acid, colloidal silica, fumed silica, tetraalkyl orthosilicates silica hydroxides,
27 precipitated silica and clays. Typical non-zeolitic sources of aluminum oxide (Al_2O_3) include
28 aluminates, alumina, and aluminum compounds such as AlCl_3 , $\text{Al}_2(\text{SO}_4)_3$, aluminum
29 hydroxide ($\text{Al}(\text{OH})_3$), and kaolin clays. One advantage of the present invention is that the
30 sources of silicon oxide and aluminum oxide are all non-zeolitic.

1 Salts, particularly alkali metal halides such as sodium chloride, can be added to or
2 formed in the reaction mixture. They are disclosed in the literature as aiding the
3 crystallization of zeolites while preventing silica occlusion in the lattice.

4 The reaction mixture also contains one or more active sources of alkali metal oxide.
5 Sources of lithium, sodium and potassium, are preferred. Any alkali metal compound which
6 is not detrimental to the crystallization process is suitable here. Non-limiting examples
7 include oxides, hydroxides, nitrates, sulfates, halogenides, oxalates, citrates and acetates.
8 The alkali metal is generally employed in an amount so that the alkali metal/aluminum ratio is
9 at least 1/1, preferably greater than 1/1.

10 The reaction mixture should contain the following components in the amounts
11 indicated (expressed as mole ratios of oxides even though the starting material may not be an
12 oxide):

		<u>General</u>	<u>Preferred</u>
13			
14	$\text{SiO}_2/\text{Al}_2\text{O}_3$	= 4 - 7	4.5 - 6.0
15	M^+/SiO_2	= 0.3 - 1.2	0.4 - 1.0
16	OH^-/SiO_2	= 0.2 - 0.6	0.25 - 0.5
17	$\text{H}_2\text{O}/\text{SiO}_2$	= 2 - 6	3 - 6

18 wherein M^+ is an alkali metal cation.

19 It should be noted that the reaction mixture described above does not include an
20 organic compound which serves as a template to form the zeolite (typically called an "organic
21 template"). In fact, the reaction mixtures used in this invention are organic template-free. As
22 used herein, the term "organic template-free" means that the reaction mixture contains either
23 no, or very small amounts of an organic template which is capable of forming the zeolite. If a
24 small amount of a compound which can serve as an organic template for the zeolite is present
25 in the reaction mixture, it should be in an amount substantially less than that required to form
26 the zeolite.

27 FORMING THE SHAPES

28 One advantage of the present invention is that the reaction mixture may be formed
29 into a desired shape before the crystallization step, thereby reducing the number of process
30 steps required to prepare catalytic materials containing the resulting zeolite. Prior to forming
31 the reaction mixture, it may be necessary to change the liquid content of the reaction mixture,
32 either by drying or by adding more liquid, in order to provide a formable mass which retains

1 its shape. In general, for most shaping methods, water will generally comprise from about 20
2 percent to about 60 percent by weight, and preferably from about 30 percent to about 50
3 percent by weight of the reaction mixture.

4 The reaction mixture is formed into a shape, e.g., particles. Methods for preparing
5 such shapes are well known in the art, and include, for example, extrusion, spray drying,
6 granulation, agglomeration and the like. When the shape is in the form of particles, they
7 are preferably of a size and shape desired for the ultimate catalyst, and may be in the form of,
8 for example, extrudates, cylinders, spheres, granules, agglomerates and prills. The particles
9 will generally have a cross sectional diameter between about 1/64 inch and about 1/2 inch,
10 and preferably between about 1/32 inch and about 1/4 inch, i.e., the particles will be of a size
11 to be retained on a 1/64 inch, and preferably on a 1/32 inch screen and will pass through a
12 1/2 inch, and preferably through a 1/4 inch screen.

13 The shape prepared from the reaction mixture will contain sufficient water to retain a
14 desired shape. Additional water is not required in the mixture in order to initiate or maintain
15 crystallization within the shaped reaction mixture. Indeed, it may be preferable to remove
16 some of the excess water from the shaped reaction mixture prior to crystallization.

17 Conventional methods for drying wet solids can be used to dry the reaction mixture, and may
18 include, for example drying in air or an inert gas such as nitrogen or helium at temperatures
19 below about 200°C and at pressures from subatmospheric to about 5 atmospheres pressure.

20 Naturally occurring clays, e.g., bentonite, kaolin, montmorillonite, sepiolite and
21 attapulgite, are not required, but may be included in the reaction mixture prior to
22 crystallization to provide a product having good crush strength. Such clays can be used in
23 the raw state as originally mined or can be initially subjected to calcination, acid treatment or
24 chemical modification. Microcrystalline cellulose has also been found to improve the
25 physical properties of the particles.

26 ZEOLITE CRYSTALLIZATION

27 According to the present process, the zeolite is crystallized either within the reaction
28 mixture or within the shape made from the reaction mixture. In either case, the composition
29 of the mixture from which the zeolite is crystallized has the molar composition ranges stated
30 above.

31 It is preferred that the total volatiles content of the reaction mixture during
32 crystallization be in the range of between about 20 wt.% and about 60 wt.% , and preferably

1 between about 30 wt.% and about 60 wt.%, based on the weight of the reaction mixture,
2 where the total volatiles content is the measure of total volatile liquid, including water, in the
3 reaction mixture. It is a feature of the present process that no additional liquid beyond that
4 required to produce the Y zeolite is required for zeolite crystallization.

5 Crystallization of the zeolite takes place in the absence of an added external liquid
6 phase, i.e., in the absence of a liquid phase separate from the reaction mixture. In general, it
7 is not detrimental to the present process if some liquid water is present in contact with the
8 reaction mixture during crystallization, and it can be expected that some water may be on the
9 surface of the reaction mixture during crystallization, or that some water may be expelled
10 from the reaction mixture and may collect on or near the reaction mixture as the reaction
11 progresses. However, it is an objective of the present invention to provide a method of
12 crystallizing the zeolite in such a way as to minimize the amount of water which must be
13 treated and/or discarded following crystallization. To that end, the present method provides
14 a zeolite synthesis method which requires no additional water for crystallization beyond a
15 sufficient amount of liquid required to form the Y zeolite.

16 Once the reaction mixture has been formed, it is preferably "aged" before the
17 Y zeolite is crystallized. This aging is accomplished by maintaining the reaction mixture at a
18 relatively low temperature (compared to the crystallization temperature) under conditions
19 which will prevent dehydration of the reaction mixture (such as placing the mixture in a
20 sealed container and/or exposing it to a small amount of water vapor). Thus, the reaction
21 mixture is maintained at room temperature or a slightly higher temperature. Typically, the
22 temperature at which the mixture is aged will be from about 25°C. to about 70°C., preferably
23 from about 25°C. to about 50°C. This temperature should be maintained for a time sufficient
24 to provide crystalline Y zeolite following the crystallization step. It is believed it is within the
25 skill of one skilled in this art to readily determine the length of this aging step without undue
26 experimentation. In general, the aging should be continued long enough to allow Y zeolite
27 nuclei to begin to form in the reaction mixture. Typically, though, the aging step will be at
28 least 24 hours, preferably 2 days or longer, with longer aging times leading to a more
29 crystalline product.

30 Crystallization is conducted after the aging step at an elevated temperature and
31 usually in an autoclave so that the reaction mixture is subject to autogenous pressure until the
32 crystals of zeolite are formed. The temperatures during the hydrothermal crystallization step

1 are typically maintained from about 70°C. to about 130°C., preferably from about 80°C. to
2 about 120°C. If the crystallization temperature is too high, the resulting product will be
3 analcime, not Y zeolite.

4 The crystallization is conducted under conditions which will prevent dehydration of
5 the reaction mixture. This may be accomplished by exposing the reaction mixture to a small
6 amount of water vapor or steam during crystallization.

7 The crystallization time required to form crystals will typically range from about 1
8 hour to about 10 days, and more frequently from about 3 hours to about 4 days. Under
9 certain circumstances, crystallization times of less than 24 hours are required to prepare
10 crystallized material of high crystallinity. In the present method, the crystallized material
11 collected following the crystallization step will typically comprise at least about 50 weight
12 percent crystals. Crystallized material containing at least about 80 weight percent crystals,
13 and even at least about 90 weight percent crystals, may also be prepared using the present
14 method.

15 Once the zeolite crystals have formed, the crystals may be water-washed and then
16 dried, e.g., at 90°C. to 150°C. for from 8 to 24 hours. The drying step can be performed at
17 atmospheric or subatmospheric pressures.

18 SEED CRYSTALS

19 The zeolite made by the present process is crystallized within the reaction mixture,
20 which comprises amorphous reagents. Crystalline material (i.e., "seed" crystals of Y zeolite)
21 may be added to the mixture prior to the crystallization step, and methods for enhancing the
22 crystallization of zeolites by adding "seed" crystals are well known. However, the addition
23 of seed crystals is not a requirement of the present process. Indeed, it is an important feature
24 of the present process that the zeolite can be crystallized within the reaction mixture in the
25 absence of crystals added prior to the crystallization step.

26 DESCRIPTION OF Y ZEOLITE

27 Y zeolite is disclosed in U.S. Patent No. 3,130,007, which is incorporated herein by
28 reference in its entirety. Y zeolite is characterized by a lattice of 3-dimensional channels
29 whose opening is about 8 Å ($8 \cdot 10^{-10}$ m). It is generally, but not necessarily, obtained in the
30 sodium form. Its X-ray diffraction is given in Table I below. In Table I, d is the distance
31 between two lattice planes, and I/I_0 is the ratio, expressed in percent, of the intensity of any
32 given line (I) to the intensity of the most intense line (I_0). The only lines considered are those

1 with I/I_0 greater than 10. Of course, distances as well as relative intensities may be subject to
2 small variations according to the product analyzed. Such variations do not indicate a change
3 of structure but are due to the replacement of certain cations or to a deviation in the
4 silica/alumina ratio.

5 TABLE I

<u>d (Å)</u>	<u>I/I₀</u>
14.29	100
7.46	24
5.68	44
4.76	23
4.38	35
3.91	12
3.77	47
3.31	37
3.02	16
2.92	21
2.86	48
2.77	20
2.64	19
2.59	11

6 The Y zeolite produced by the present invention typically has a silica/alumina mole
7 ratio of less than 6, preferably from about 4.5 to about 5.0. The silica/alumina mole ratio of
8 the product zeolite can be determined from a correlation with the unit cell constant as
9 calculated from X-ray diffraction analysis (see Sohn et al., Zeolites, 6, 225 (1986)).

10 ZEOLITE CRYSTALLITE SIZE

11 Typically, the zeolite crystals are less than 10 microns in diameter as determined by
12 Scanning Electron Microscopy. Since small crystals are desirable for certain catalytic
13 applications, crystallization conditions can be tailored to produce zeolite crystals with
14 diameters of less than 1.0 micron. The crystal size of the zeolite may be determined by, for
15 example, grinding the shaped particles to separate the individual crystals. High resolution
16 electron micrographs of the separated crystals can then be prepared, after which the average
17 size of individual zeolite crystals can be determined by reference to calibrated length

1 standards. An average crystal size may then be computed in various well-known ways,
2 including:

3
$$\text{Number Average} = \frac{\sum_{i=1}^n (n_i \times L_i)}{\sum_{i=1}^n n_i}$$

4 where n_i is the number of zeolite crystals where minimum length falls within an interval L_i .
5 For purposes of this invention, average crystal size will be defined as a number average. It is
6 important to note that for purposes of this invention, zeolite crystal size is distinguished from
7 what some manufacturers term "zeolite particle size," the latter being the average size of all
8 particles, including both individual crystals and polycrystalline agglomerates, in the
9 as-produced zeolite powder.

10 Typically, the zeolite crystals are less than 10 microns in diameter as determined by
11 Scanning Electron Microscopy. Since small crystals are desirable for certain catalytic
12 applications, crystallization conditions can be tailored by, for example, reducing
13 crystallization temperature, by increasing aluminum content in the reaction mixture, and/or by
14 reducing the water content of the reaction mixture or the shaped particles prior to
15 crystallization, to produce zeolite crystals with diameters of less than 1.0 micron.

16 ZEOLITE POST-TREATMENT

17 A crystallized material containing crystals of zeolite is prepared in the process as
18 described above. The zeolite can be used as synthesized or can be thermally treated
19 (calcined). In some cases, the synthesis product can contain silica which is not incorporated
20 in the zeolite structure. This excess silica can be removed by washing with dilute acid (e.g.,
21 0.2M HNO₃) or dilute base (e.g., 0.01M NH₄OH). This washing should be done prior to
22 thermal treatment of the zeolite. Usually it is desirable to remove the alkali metal cation by
23 ion exchange and replace it with hydrogen, ammonium, or any desired metal ion. The zeolite
24 can be leached with chelating agents, e.g., EDTA or dilute acid solutions, to increase the
25 silica/alumina mole ratio. These methods may also include the use of (NH₄)₂SiF₆ or acidic
26 ion-exchange resin treatment. The zeolite can also be steamed; steaming helps stabilize the
27 crystalline lattice to attack from acids. The zeolite can be used in intimate combination with
28 hydrogenating components, such as tungsten, vanadium, molybdenum, rhenium, nickel,
29 cobalt, chromium, manganese, or a noble metal, such as palladium or platinum, for those
30 applications in which a hydrogenation/ dehydrogenation function is desired. Typical

1 replacing cations can include metal cations, e.g., rare earth, Group IA, Group IIA and Group
2 VIII metals, as well as their mixtures. Of the replacing metallic cations, cations of metals
3 such as rare earth, Mn, Ca, Mg, Zn, Ga, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, Fe and Co are
4 particularly preferred.

5 The hydrogen, ammonium, and metal components can be exchanged into the zeolite.
6 The zeolite can also be impregnated with the metals, or, the metals can be physically
7 intimately admixed with the zeolite using standard methods known to the art. The metals can
8 also be occluded in the crystal lattice by having the desired metals present as ions in the
9 reaction mixture from which the zeolite is prepared.

10 Typical ion exchange techniques involve contacting the synthetic zeolite with a
11 solution containing a salt of the desired replacing cation or cations. Although a wide variety
12 of salts can be employed, chlorides and other halides, nitrates, and sulfates are particularly
13 preferred. Representative ion exchange techniques are disclosed in a wide variety of patents
14 including U.S. Patent Nos. 3,140,249; 3,140,251; and 3,140,253. Ion exchange can take
15 place either before or after the zeolite is calcined.

16 Following contact with the salt solution of the desired replacing cation, the zeolite is
17 typically washed with water and dried at temperatures ranging from 65°C. to about 315°C.
18 After washing, the zeolite can be calcined in air or inert gas at temperatures ranging from
19 about 200°C. to 820°C. for periods of time ranging from 1 to 48 hours, or more, to produce
20 a catalytically active product especially useful in hydrocarbon conversion processes.

21 Regardless of the cations present in the synthesized form of the zeolite, the spatial
22 arrangement of the atoms which form the basic crystal lattice of the zeolite remains
23 essentially unchanged. The exchange of cations has little, if any, effect on the zeolite lattice
24 structures.

25 The zeolite may be used as a catalyst, without additional forming, if the reaction
26 mixture has been formed into a shape which is of a size and shape desired for the ultimate
27 catalyst. Alternatively, the zeolite can be composited with other materials resistant to the
28 temperatures and other conditions employed in organic conversion processes, using
29 techniques such as spray drying, extrusion, and the like. Such matrix materials include active
30 and inactive materials and synthetic or naturally occurring zeolites as well as inorganic
31 materials such as clays, silica and metal oxides. The latter may occur naturally or may be in
32 the form of gelatinous precipitates, sols, or gels, including mixtures of silica and metal

1 oxides. Use of an active material in conjunction with the synthetic zeolite, i.e., combined
2 with it, tends to improve the conversion and selectivity of the catalyst in certain organic
3 conversion processes. Inactive materials can suitably serve as diluents to control the amount
4 of conversion in a given process so that products can be obtained economically without using
5 other means for controlling the rate of reaction. Frequently, zeolite materials have been
6 incorporated into naturally occurring clays, e.g., bentonite and kaolin. These materials, i.e.,
7 clays, oxides, etc., function, in part, as binders for the catalyst. It is desirable to provide a
8 catalyst having good crush strength, because in petroleum refining the catalyst is often
9 subjected to rough handling. This tends to break the catalyst down into powders which
10 cause problems in processing.

11 Naturally occurring clays which can be composited with the synthetic zeolite of this
12 invention include the montmorillonite and kaolin families, which families include the
13 sub-bentonites and kaolins commonly known as Dixie, McNamee, Georgia and Florida clays
14 or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or
15 anauxite. Fibrous clays such as sepiolite and attapulgite can also be used as supports. Such
16 clays can be used in the raw state as originally mined or can be initially subjected to
17 calcination, acid treatment or chemical modification.

18 In addition to the foregoing materials, the zeolite prepared by the present method can
19 be composited with porous matrix materials and mixtures of matrix materials such as silica,
20 alumina, titania, magnesia, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria,
21 silica-beryllia, silica titania, titania-zirconia as well as ternary compositions such as
22 silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and
23 silica-magnesia-zirconia. The matrix can be in the form of a cogel.

24 The zeolite can also be composited with other zeolites such as synthetic and natural
25 faujasites (e.g., X), and erionites. They can also be composited with purely synthetic zeolites
26 such as those of the ZSM, SSZ, KU, FU, and NU series. The combination of zeolites can
27 also be composited in a porous inorganic matrix.

28 The zeolite prepared in the present process is useful in hydrocarbon conversion
29 reactions. Hydrocarbon conversion reactions are chemical and catalytic processes in which
30 carbon containing compounds are changed to different carbon containing compounds.
31 Examples of hydrocarbon conversion reactions include hydrocracking and fluid catalytic
32 cracking of gas oils to produce transportation fuels such as gasoline and jet fuel.

EXAMPLE

150 Grams of silica (Hi-Sil 233, a hydrated silica manufacture by PPG) was placed in a Baker-Perkins mixer. 73.5 Grams of NaAlO_2 was added to the mixer and the two were mixed for about ten minutes. Then 55 grams of a 50% NaOH aqueous solution was slowly added to the mixer and mixing continued for about 3 hours. Deionized water (190 grams) was then added slowly to the mixer to form a paste-like mixture. Heat was applied to the mixture to dry it slightly (48.3% volatiles) and make it extrudable, and the mixture was stored overnight at room temperature in a sealed container.

The mixture was extruded at 1,200 psig and the extrudates divided into four parts (A, B, C and D). Parts A and B were air dried to 45% volatiles, and parts C and D were air dried to 40% volatiles. The molar composition of the extrudates was as follows:

$$\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.3$$

$$\text{Na}^+/\text{SiO}_2 = 0.68$$

$$\text{OH}/\text{SiO}_2 = 0.30$$

The $\text{H}_2\text{O}/\text{SiO}_2$ molar ratio was 4.7 for parts A and B and 3.8 for parts C and D.

Each of parts A, B, C and D was placed in its own one quart Teflon bottle with a hole in the cover, and each bottle was sealed in an autoclave which contained 12 cc water outside the bottles to prevent drying of the samples when heated (especially small samples in large autoclaves). At the end of crystallization, there was still about 12 cc water outside the bottles, so consumption of this water was negligible. The bottles were then left at room temperature for 24 hours. The bottles containing parts A and C were then heated at 110°C. for two days, and the bottles containing parts B and D were heated at 110°C. for four days.

The resulting crystalline extrudates were washed with deionized water, filtered, dried in a vacuum oven at 120°C. overnight and calcined for 4 hours at 593°C. The products were analyzed by X-ray. All four products were found to contain Y zeolite, with the extrudates crystallized at two days (parts A and C) having the highest degree of crystallinity. Scanning electron microscopy showed that part A had a crystal size of 0.5 micron or less. X-ray diffraction analysis showed a unit cell constant of 24.77 Å, corresponding to a framework silica/alumina mole ratio of 4.8.

1 WHAT IS CLAIMED IS:

2 1. A method for preparing crystalline Y zeolite, said method comprising:

3 (A) preparing a reaction mixture comprising at least one active, non-zeolitic
4 source of silica and at least one active, non-zeolitic source of alumina in amounts
5 sufficient to produce Y zeolite, and sufficient water to produce Y zeolite; and6 (B) maintaining said reaction mixture at a temperature of up to about 130°C.
7 under crystallization conditions and in the absence of an added external liquid phase
8 for sufficient time to form crystals of Y zeolite.
910 2. The method according to Claim 1 wherein said reaction mixture has a water/silica
11 molar ratio during crystallization of no greater than about 6.
1213 3. The method of Claim 2 wherein said reaction mixture during crystallization has a
14 water/silica molar ratio between about 2 and about 6.
1516 4. The method according to Claim 1 wherein said reaction mixture has the following
17 molar composition ranges:18 $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4 - 7$
19 $\text{M}^+/\text{SiO}_2 = 0.3 - 1.2$
20 $\text{OH}^-/\text{SiO}_2 = 0.2 - 0.6$
21 $\text{H}_2\text{O}/\text{SiO}_2 = 2 - 6$ 22 wherein M^+ is an alkali metal cation.
2324 5. The method according to Claim 4 wherein said reaction mixture has the following
25 molar composition ranges:26 $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.5 - 6.0$
27 $\text{M}^+/\text{SiO}_2 = 0.4 - 1.0$
28 $\text{OH}^-/\text{SiO}_2 = 0.25 - 0.5$
29 $\text{H}_2\text{O}/\text{SiO}_2 = 3 - 6$ 30 wherein M^+ is an alkali metal cation.
31

REPLACED SHEETS SG

- ☐ Description : paged to paged
☒ Claim(s) : paged 15 to paged 18
☐ Drawing(s) : paged to paged
☐ Abstract : paged to paged

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- 1 6. The method according to Claim 1 wherein the silica/alumina mole ratio is about 4 to
2 about 7.
3
- 4 7. The according to Claim 6 wherein the silica/alumina mole ratio is from about 4.5 to
5 about 6.
6
- 7 8. The method according to Claim 1 wherein said reaction mixture further comprises at
8 least one active source of a Group VIII metal.
9
- 10 9. The method according to Claim 8 wherein said Group VIII metal is selected from
11 platinum, palladium and a combination thereof.
12
- 13 10. The method according to Claim 1 wherein the silica/alumina mole ratio in the
14 Y zeolite product is less than 6.
15
- 16 11. The method according to Claim 1 wherein the silica/alumina mole ratio in the
17 Y zeolite product is about 4.5 to about 5.0.
18
- 19 12. The method of Claim 1 wherein, after the reaction mixture has been prepared and
20 prior to step B, the reaction mixture is maintained at a temperature from about 25°C.
21 to about 75°C. in the absence of an added external liquid phase.
22
- 23 13. A method for preparing crystalline Y zeolite, said method comprising:
24 (A) preparing a reaction mixture comprising at least one active, non-zeolitic
25 source of silica and at least one active, non-zeolitic source of alumina in amounts
26 sufficient to produce Y zeolite, and sufficient water to shape said mixture;
27 (B) forming said reaction mixture into a shape; and
28 (C) maintaining said reaction mixture at a temperature of up to about 130°C.
29 under crystallization conditions and in the absence of an added external liquid phase
30 for sufficient time to form crystals of Y zeolite.
31



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1 14. The method according to Claim 13 wherein the amount of water is sufficient to make
2 the reaction mixture self-supporting.

3
4 15. The method according to Claim 13 wherein said reaction mixture has a water/silica
5 molar ratio during crystallization of no greater than about 6.

6
7 16. The method of Claim 15 wherein said reaction mixture during crystallization has a
8 water/silica molar ratio between about 2 and about 6.

9
10 17. The method according to Claim 13 wherein said reaction mixture has the following
11 molar composition ranges:

12	$\text{SiO}_2/\text{Al}_2\text{O}_3$	=	4 - 7
13	M^+/SiO_2	=	0.3 - 1.2
14	OH^-/SiO_2	=	0.2 - 0.6
15	$\text{H}_2\text{O}/\text{SiO}_2$	=	2 - 6

16 wherein M^+ is an alkali metal cation.

17
18 18. The method according to Claim 17 wherein said reaction mixture has the following
19 molar composition ranges:

20	$\text{SiO}_2/\text{Al}_2\text{O}_3$	=	4.5 - 6.0
21	M^+/SiO_2	=	0.4 - 1.0
22	OH^-/SiO_2	=	0.25 - 0.5
23	$\text{H}_2\text{O}/\text{SiO}_2$	=	3 - 6

24 wherein M^+ is an alkali metal cation.

25
26 19. The method according to Claim 13 wherein the silica/alumina mole ratio is from
27 about 4 to about 7.

28
29 20. The according to Claim 19 wherein the silica/alumina mole ratio is from about 4.5 to
30 about 6.0.

31

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- 1 21. The method according to Claim 13 wherein said reaction mixture further comprises at
2 least one active source of a Group VIII metal.
3
- 4 22. The method according to Claim 21 wherein said Group VIII metal is selected from
5 platinum, palladium and a combination thereof.
6
- 7 23. The method according to Claim 13 wherein the shaped crystalline zeolite is a
8 spherical or cylindrical particle having a cross sectional diameter between about 1/64
9 inch and about 1/2 inch.
10
- 11 24. The method according to Claim 23 wherein the shaped crystalline zeolite is a
12 spherical or cylindrical particle having a cross sectional diameter between about 1/32
13 inch and about 1/4 inch in diameter.
14
- 15 25. The method according to Claim 13 wherein the silica/alumina mole ratio in the
16 Y zeolite product is less than 6.
17
- 18 26. The method according to Claim 13 wherein the silica/alumina mole ratio in the
19 Y zeolite product is about 4.5 to about 5.0.
20
- 21 27. The method of Claim 13 wherein, after the reaction mixture has been formed into a
22 shape and prior to step C, the reaction mixture is maintained at a temperature from
23 about 25°C. to about 75°C. in the absence of an added external liquid phase.



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