

1 PREPARATION OF ZEOLITE L

2 Field of the Invention

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

5 Background

6 Prior art methods of preparing crystalline zeolite L typically produce finely divided
7 crystals which must be separated from an excess of liquid in which the zeolite is
8 crystallized. The liquid, in turn, must be treated for reuse or else be discarded, with
9 potentially deleterious environmental consequences. Preparing commercially useful
10 catalytic materials that contain the powdered zeolite also normally requires additional
11 binding and forming steps. Typically, the zeolite powder as crystallized must be mixed with
12 a binder material and then formed into shaped particles or agglomerates, using methods such
13 as extruding, agglomeration, spray drying, and the like. These binding and forming steps
14 greatly increase the complexity of catalyst manufacture involving zeolitic materials. The
15 additional steps may also have an adverse effect on the catalytic performance of the Y
16 zeolite so bound and 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
20 and water, wherein the H_2O/Na_2O mole ratio is 5 to 25. The mass is aged while maintaining
21 it 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.,
23 18 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 zeolite L can be made in
30 this manner.

1 U.S. Patent No. 3,216,789, issued November 9, 1965 to Breck et al., discloses zeolite
2 L. The zeolite L is prepared from reaction mixtures whose composition, expressed in terms
3 of mole ratios of oxides, falls within the ranges:

$K_2O/(K_2O + Na_2O)$	From about 0.33 to about 1
$(K_2O + Na_2O)/SiO_2$	From about 0.35 to about 0.5
SiO_2/Al_2O_3	From about 10 to about 28
$H_2O/(K_2O + Na_2O)$	From about 15 to about 41

4 or

$K_2O/(K_2O + Na_2O)$	From about 0.33 to about 1
$(K_2O + Na_2O)/SiO_2$	From about 0.4 to about 0.5
SiO_2/Al_2O_3	From about 10 to about 28
$H_2O/(K_2O + Na_2O)$	From about 15 to about 41

5 or

$K_2O/(K_2O + Na_2O)$	From about 0.26 to about 1
$(K_2O + Na_2O)/SiO_2$	From about 0.34 to about 0.5
SiO_2/Al_2O_3	From about 10 to about 28
$H_2O/(K_2O + Na_2O)$	From about 15 to about 51

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

13 U.S. Patent No. 5,064,630, issued November 12, 1991 to Verduijn, discloses the
14 preparation of zeolite L in very small crystalline form in which an alkaline reaction mixture
15 comprising water, a source of silicon, a source of alkali metal and a source of aluminum or
16 gallium is heated to a temperature of at least 80°C. for a period of time long enough to form
17 zeolite L, the composition of the reaction mixture having the following molar ratios
18 (expressed as oxides):

M ₂ O/SiO ₂	0.4 to 0.5
H ₂ O/M ₂ O	15 to 30
SiO ₂ /Al ₂ O ₃ or Ga ₂ O ₃	5 to 11

1 where M is potassium or a mixture of potassium and one or more alkali metals.

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

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

13 SUMMARY OF THE INVENTION

14 It is an object of the invention to provide a method for preparing crystalline zeolite L
15 using a minimum of liquid for crystallization.

16 It is a further object of the invention to provide a method for preparing crystalline
17 zeolite L while minimizing aqueous waste.

18 It is a further object of the invention to provide a method for preparing zeolite L in
19 the absence of added binder.

20 It is also an object of this invention to prepare crystalline zeolite L in the form of a
21 shape. It is a further object of the invention to provide a method for preparing zeolite L in
22 commercially useful forms without any post crystallization forming steps.

23 It is a further object of the invention to provide a method for preparing zeolite L
24 having a small crystallite size.

25 It is a further object of the invention to provide a method for preparing zeolite L at
26 reduced raw material costs.

27 Thus, in accordance with the present invention, there is provided a method for
28 preparing crystalline zeolite L, said method comprising preparing a self-supporting reaction
29 mixture comprising at least one active source of silica, at least one active source of alumina

1 and a source of hydroxide in amounts sufficient to produce zeolite L, and sufficient water to
2 produce zeolite L, wherein the reaction mixture has an OH/SiO₂ molar ratio of from 0.20 to
3 0.40 and heating said reaction mixture at a temperature from about 100°C. to about 200°C.
4 under crystallization conditions and in the absence of an added external liquid phase for
5 sufficient time to form crystals of zeolite L. The reaction mixture is extrudable and capable
6 of maintaining a shape.

7 The present invention also provides a method for preparing crystalline zeolite L, said
8 method comprising preparing a reaction mixture comprising at least one active source of
9 silica, at least one active source of alumina and a source of hydroxide in amounts sufficient
10 to produce zeolite L, and sufficient water to shape said mixture, wherein the reaction
11 mixture has an OH/SiO₂ molar ratio of from 0.20 to 0.40, forming said reaction mixture
12 into a shape; and heating said reaction mixture at a temperature from about 100°C. to about
13 200°C. under crystallization conditions and in the absence of an added external liquid phase
14 for sufficient time to form crystals of zeolite L. The reaction mixture is extrudable and
15 capable of maintaining a shape.

16 It is important, in preparing the reaction mixture of the present process, that the
17 amount of water present in the reaction mixture as prepared for the crystallization step be
18 sufficient to produce the zeolite L. Thus, the reaction mixture itself furnishes all the water
19 needed to crystallize the zeolite. This amount of water is less than the amount of water
20 required in conventional processes for preparing zeolites. It is an amount that is not
21 substantially greater than that required to produce the zeolite L. For example, the amount of
22 water used in the present invention is less than that required to dissolve the reaction mixture
23 components, or, if they are not dissolved, less than that required to immerse the reaction
24 mixture components in the water. Thus, during the crystallization step according to the
25 present process, there is no separate, added external liquid phase present which must be
26 removed from the crystallized material at the end of the crystallization step by, for example
27 filtering or decanting, prior to drying the crystals. This absence of an added external liquid
28 phase distinguishes the present invention from methods for making zeolite L wherein the
29 zeolite L crystals are formed from solution or where solid reactants are heated in an aqueous
30 solution until crystals of zeolite L form.

31 While it is not a requirement to form the mixture into a shape before the mixture is
32 subjected to crystallization conditions, it may be desired in many cases to do so. In that

1 case, the amount of water present in the reaction mixture is sufficient to form the reaction
2 mixture into a shape, but insufficient to cause the shaped reaction mixture to collapse or
3 "melt", i.e., once the reaction mixture is formed into the desired shape containing the
4 desired amount of water, the resulting shape is self-supporting.

5 Among other factors, the present invention is based on the discovery of a method for
6 crystallizing zeolite L from a reaction mixture which contains only enough water to form the
7 zeolite L. Further, the zeolite L prepared by the above-described method is made as very
8 small crystallites. As discussed during the aforementioned interview, the OH/SiO₂ molar
9 ratio is critical in Applicant's claimed method for making zeolite L. Applicant has
10 discovered that this molar ratio affects both the physical properties of the reaction mixture
11 and the degree of crystallization achieved. A critical balance must be achieved so that the
12 reaction mixture will have the desired physical properties, e.g., will be self-supporting and
13 capable of being shaped, while at the same time providing an acceptable degree of
14 crystallization. It has also been found that if the OH/SiO₂ molar ratio becomes too high, the
15 reaction mixture takes on undesirable physical properties. On the other hand, if the OH
16 /SiO₂ molar ratio is too low, crystallization is inadequate.

17 18 DETAILED DESCRIPTION OF THE INVENTION

19 PREPARING THE REACTION MIXTURE

20 The reaction mixture from which and in which the zeolite L is crystallized comprises
21 at least one active source of silica, at least one active source of alumina, and sufficient water
22 to form the zeolite L. This amount of water is considerably less than that required in
23 conventional processes for preparing zeolite L.

24 The amount of water required in the reaction mixture of the present invention is that
25 amount which is needed to adequately blend the mixture. Thus, a reaction mixture is
26 prepared by mixing water with active sources of the zeolite to form a uniform mass having
27 preferably a heavy paste-like consistency. The active sources will be in a form that can be
28 easily blended into a uniform mass, and may be, for example, powders, hydrated particles,
29 or concentrated aqueous solutions. Sufficient water is added to wet all the powders during
30 the mixing and kneading steps. Alternatively, sufficient water is added that the powders
31 may be kneaded into a uniform and generally homogeneous mixture that may be shaped. It
32 is not necessary that all of the active sources be readily soluble in water during kneading,

1 since the water added to the active sources will be insufficient to make a fluid-like mixture.
2 The amount of water added depends on the mixing apparatus and on the active sources
3 employed. Those familiar with the art can readily determine without undue experimentation
4 the amount of liquid required to properly mix active sources of the zeolite. For example,
5 hydrated sources of the zeolite may require relatively less water, and dried sources may
6 require relatively more. Though it is preferred that the mixture be blended and kneaded
7 until the mixture has a uniform, homogeneous appearance, the length of time devoted to
8 kneading the mixture is not critical in the present invention.

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

14 Typical sources of silicon oxide (SiO_2) include silicates, silica hydrogel, silicic acid,
15 colloidal silica, fumed silica, tetraalkyl orthosilicates silica hydroxides, precipitated silica
16 and clays. Typical sources of aluminum oxide (Al_2O_3) include aluminates, alumina, and
17 aluminum compounds such as AlCl_3 , $\text{Al}_2(\text{SO}_4)_3$, aluminum hydroxide ($\text{Al}(\text{OH}_3)$), and kaolin
18 clays. One advantage of the present invention is that the sources of silicon oxide and
19 aluminum oxide can all be non-zeolitic.

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

23 The reaction mixture also contains one or more active sources of potassium oxide.
24 Any potassium compound which is not detrimental to the crystallization process is suitable
25 here. Non-limiting examples include oxides, hydroxides, nitrates, sulfates, halogenides,
26 oxalates, citrates and acetates. The potassium is generally employed in an amount so that
27 the alkali metal/aluminum ratio is at least 1/1, preferably greater than 1/1. Mixtures of
28 potassium with one or more other alkali metals may also be used.

29 The reaction mixture should contain the following components in the amounts
30 indicated (expressed as mole ratios of oxides even though the actual starting materials may
31 not be oxides):

		<u>General</u>	<u>Preferred</u>
1			
2	$\text{SiO}_2/\text{Al}_2\text{O}_3$	= 5 - 20	5 - 15
3	$(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{SiO}_2$	= 0.15 - 0.45	0.20 - 0.40
4	$\text{K}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O})$	= 0.3 - 1.0	0.4 - 1.0
5	OH^-/SiO_2	= 0.2 - 0.40	0.25 - 0.40
6	$\text{H}_2\text{O}/\text{SiO}_2$	= 2 - 6	3 - 5

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

15 FORMING THE SHAPES

16 One advantage of the present invention is that the reaction mixture may be formed
 17 into a desired shape before the crystallization step, thereby reducing the number of process
 18 steps required to prepare catalytic materials containing the resulting zeolite. Prior to
 19 forming the reaction mixture, it may be necessary to change the liquid content of the
 20 reaction mixture, either by drying or by adding more liquid, in order to provide a formable
 21 mass which retains its shape. In general, for most shaping methods, water will generally
 22 comprise from about 20 percent to about 60 percent by weight, and preferably from about 30
 23 percent to about 50 percent by weight of the reaction mixture.

24 The reaction mixture is formed into a shape, e.g., particles. Methods for preparing
 25 such shapes are well known in the art, and include, for example, extrusion, spray drying,
 26 granulation, agglomeration and the like. When the shape is in the form of particles, they
 27 are preferably of a size and shape desired for the ultimate catalyst, and may be in the form
 28 of, for example, extrudates, cylinders, spheres, granules, agglomerates and prills. The
 29 particles will generally have a cross sectional diameter between about 1/64 inch and about
 30 1/2 inch, and preferably between about 1/32 inch and about 1/4 inch, i.e., the particles will
 31 be of a size to be retained on a 1/64 inch, and preferably on a 1/32 inch screen and will pass
 32 through a 1/2 inch, and preferably through a 1/4 inch screen.

1 The shape prepared from the reaction mixture will contain sufficient water to retain a
2 desired shape. Additional water is not required in the mixture in order to initiate or maintain
3 crystallization within the shaped reaction mixture. Indeed, it may be preferable to remove
4 some of the excess water from the shaped reaction mixture prior to crystallization.
5 Conventional methods for drying wet solids can be used to dry the reaction mixture, and
6 may include, for example drying in air or an inert gas such as nitrogen or helium at
7 temperatures below about 200°C and at pressures from subatmospheric to about 5
8 atmospheres pressure.

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

15 ZEOLITE CRYSTALLIZATION

16 According to the present process, the zeolite is crystallized either within the reaction
17 mixture or within the shape made from the reaction mixture. In either case, the composition
18 of the mixture from which the zeolite is crystallized has the molar composition ranges stated
19 above.

20 It is preferred that the total volatiles content of the reaction mixture during
21 crystallization be in the range of between about 20 wt.% and about 60 wt.% , and preferably
22 between about 30 wt.% and about 60 wt.%, based on the weight of the reaction mixture,
23 where the total volatiles content is the measure of total volatile liquid, including water, in
24 the reaction mixture. It is a feature of the present process that no additional liquid beyond
25 that required to produce the zeolite L is required for zeolite crystallization.

26 Crystallization of the zeolite takes place in the absence of an added external liquid
27 phase, i.e., in the absence of a liquid phase separate from the reaction mixture. In general, it
28 is not detrimental to the present process if some liquid water is present in contact with the
29 reaction mixture during crystallization, and it can be expected that some water may be on
30 the surface of the reaction mixture during crystallization, or that some water may be
31 expelled from the reaction mixture and may collect on or near the reaction mixture as the
32 reaction progresses. However, it is an objective of the present invention to provide a

1 method of crystallizing the zeolite in such a way as to minimize the amount of water that
2 must be treated and/or discarded following crystallization. To that end, the present method
3 provides a zeolite synthesis method that requires no additional water for crystallization
4 beyond a sufficient amount of liquid required to form the zeolite L.

5 Crystallization is conducted at an elevated temperature and usually in an autoclave
6 so that the reaction mixture is subject to autogenous pressure until the crystals of zeolite are
7 formed. The temperatures during the hydrothermal crystallization step are typically
8 maintained from about 90°C. to about 200°C., preferably from about 100°C. to about
9 170°C.

10 The crystallization is conducted under conditions that will prevent dehydration of the
11 reaction mixture. This may be accomplished by exposing the reaction mixture to a small
12 amount of water vapor or steam during crystallization.

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

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

24 SEED CRYSTALS

25 The zeolite made by the present process is crystallized within the reaction mixture
26 that comprises amorphous reagents. Crystalline material (i.e., "seed" crystals of zeolite L)
27 may be added to the mixture prior to the crystallization step, and methods for enhancing the
28 crystallization of zeolites by adding "seed" crystals are well known. However, the addition
29 of seed crystals is not a requirement of the present process. Indeed, it is an important feature
30 of the present process that the zeolite can be crystallized within the reaction mixture in the
31 absence of crystals added prior to the crystallization step.

1 DESCRIPTION OF ZEOLITE L

2 Zeolite L and its X-ray diffraction pattern are disclosed in U.S. Patent No.
3 3,216,789, which is incorporated herein by reference in its entirety. It is to be understood
4 that by referencing U.S. Patent No. 3,216,789, it is intended that identification of zeolite L
5 be resolved on the basis of its X-ray diffraction pattern. The present invention includes the
6 preparation of zeolite L regardless of its silica/alumina mole ratio. Thus, reference to U.S.
7 Patent No. 3,216,789 is not to be construed as limiting the present invention to the
8 preparation of zeolite L having the silica/alumina mole ratios disclosed in that patent. It is
9 the crystal structure, as identified by the X-ray diffraction pattern, which establishes the
10 identity of the zeolite L.

11 Zeolite L is characterized by unidimensional 12-member rings having 7.1 Å pores. It
12 is generally, but not necessarily, obtained in the potassium form. Its X-ray diffraction (for
13 the all-potassium form) is given in Table I below. In Table I, d is the distance between two
14 lattice planes, and I/I_0 is the ratio, expressed in percent, of the intensity of any given line (I)
15 to the intensity of the most intense line (I_0). The only lines considered are those with I/I_0
16 greater than 10. Of course, distances as well as relative intensities may be subject to small
17 variations according to the product analyzed. Such variations do not indicate a change of
18 structure but are due to the replacement of certain cations or to a deviation in the
19 silica/alumina ratio.

20 TABLE I

<u>d (Å)</u>	<u>I/I_0</u>
15.8	100
7.89	14
7.49	15
5.98	25
5.75	11
4.57	32
4.39	13
4.33	13
3.91	30
3.78	13
3.66	19

3.48	23
3.26	14
3.17	34
3.07	22
3.02	15
2.91	23
2.65	19
2.42	11
2.19	11

1 The zeolite L produced by the present invention typically has a silica/alumina mole
2 ratio of about 5 to about 7, preferably from about 5.5 to about 7.0.

3 ZEOLITE CRYSTALLITE SIZE

4 Typically, the zeolite crystals are less than 10 microns in diameter as determined by
5 Scanning Electron Microscopy. Since small crystals are desirable for certain catalytic
6 applications, crystallization conditions can be tailored to produce zeolite crystals with
7 diameters of less than 1.0 micron. The crystal size of the zeolite may be determined by, for
8 example, grinding the shaped particles to separate the individual crystals. High resolution
9 electron micrographs of the separated crystals can then be prepared, after which the average
10 size of individual zeolite crystals can be determined by reference to calibrated length
11 standards. An average crystal size may then be computed in various well-known ways,
12 including:

$$13 \quad \text{Number Average} = \frac{\sum_{i=1}^n (n_i \times L_i)}{\sum_{i=1}^n n_i}$$

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

20 Typically, the zeolite crystals are less than 10 microns in diameter as determined by
21 Scanning Electron Microscopy. Since small crystals are desirable for certain catalytic
22 applications, crystallization conditions can be tailored by, for example, reducing

1 crystallization temperature, by increasing aluminum content in the reaction mixture, and/or
2 by reducing the water content of the reaction mixture or the shaped particles prior to
3 crystallization, to produce zeolite crystals with diameters of less than 1.0 micron.

4 ZEOLITE POST-TREATMENT

5 A crystallized material containing crystals of zeolite is prepared in the process as
6 described above. The zeolite can be used as synthesized or can be thermally treated
7 (calcined). It may be desirable to partially remove the potassium cation by ion exchange and
8 replace it with hydrogen, ammonium, or any desired metal ion including other alkali metal
9 cations. It is important, however, that not all of the alkali metal be removed or replaced, as
10 this can cause the zeolite L to fall apart. Likewise, the zeolite L should not be steamed.

11 The zeolite can be used in intimate combination with hydrogenating components,
12 such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese,
13 or a noble metal, such as palladium or platinum, for those applications in which a
14 hydrogenation/ dehydrogenation function is desired. Typical replacing cations can include
15 metal cations, e.g., rare earth, Group IA, Group IIA and Group VIII metals, as well as their
16 mixtures. Of the replacing metallic cations, cations of metals such as rare earth, Mn, Ba, Sr,
17 Ca, Mg, Cs, Rb, Zn, Ga, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, Fe and Co are particularly preferred.

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

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

29 Following contact with the salt solution of the desired replacing cation, the zeolite is
30 typically washed with water and dried at temperatures ranging from 65°C. to about 315°C.
31 After washing, the zeolite can be calcined in air or inert gas at temperatures ranging from

1 about 200°C. to 820°C. for periods of time ranging from 1 to 48 hours, or more, to produce
2 a catalytically active product especially useful in hydrocarbon conversion processes.

3 Regardless of the cations present in the synthesized form of the zeolite, the spatial
4 arrangement of the atoms that form the basic crystal lattice of the zeolite remains essentially
5 unchanged. The exchange of cations has little, if any, effect on the zeolite lattice structures.

6 The zeolite may be used as a catalyst, without additional forming, if the reaction
7 mixture has been formed into a shape that is of a size and shape desired for the ultimate
8 catalyst. Alternatively, the zeolite can be composited with other materials resistant to the
9 temperatures and other conditions employed in organic conversion processes, using
10 techniques such as spray drying, extrusion, and the like. Such matrix materials include
11 active and inactive materials and synthetic or naturally occurring zeolites as well as
12 inorganic materials such as clays, silica and metal oxides. The latter may occur naturally or
13 may be in the form of gelatinous precipitates, sols, or gels, including mixtures of silica and
14 metal oxides. Use of an active material in conjunction with the synthetic zeolite, i.e.,
15 combined with it, tends to improve the conversion and selectivity of the catalyst in certain
16 organic conversion processes. Inactive materials can suitably serve as diluents to control the
17 amount of conversion in a given process so that products can be obtained economically
18 without using other means for controlling the rate of reaction. Frequently, zeolite materials
19 have been incorporated into naturally occurring clays, e.g., bentonite and kaolin. These
20 materials, i.e., clays, oxides, etc., function, in part, as binders for the catalyst. It is desirable
21 to provide a catalyst having good crush strength, because in petroleum refining the catalyst
22 is often subjected to rough handling. This tends to break the catalyst down into powders
23 that cause problems in processing.

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

31 In addition to the foregoing materials, the zeolite prepared by the present method can
32 be composited with porous matrix materials and mixtures of matrix materials such as silica,

1 alumina, titania, magnesia, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria,
2 silica-beryllia, silica titania, titania-zirconia as well as ternary compositions such as
3 silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and
4 silica-magnesia-zirconia. The matrix can be in the form of a cogel.

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

9 The zeolite prepared in the present process is useful in hydrocarbon conversion
10 reactions. Hydrocarbon conversion reactions are chemical and catalytic processes in which
11 carbon containing compounds are changed to different carbon containing compounds.
12 Examples of hydrocarbon conversion reactions include aromatization of C₆ paraffins to
13 produce benzene and reforming of C₆ to C₉ hydrocarbons to increase their octane. The
14 zeolite can be used to prepare a reforming catalyst as disclosed in U.S. Patent No.
15 4,104,320, issued August 1, 1978 to Bernard et al., and U.S. Patent No. 4,634,518, issued
16 January 6, 1987 to Buss et al., both of which are incorporated by reference herein in their
17 entirety.

18 EXAMPLE 1

19 150 Grams of silica (Hi-Sil 233, a hydrated silica manufacture by PPG) was placed
20 in a Baker-Perkins mixer. 40 Grams of NaAlO₂ was added to the mixer and the two were
21 mixed for about ten minutes. Then 75 grams of a 50% KOH aqueous solution was slowly
22 added to the mixer and mixing continued for about 3 hours. Deionized water (180 grams)
23 was then added slowly to the mixer to form a paste-like mixture. Heat (about 60-66°C.) was
24 applied to the mixture to dry it slightly and make it extrudable.

25 The mixture was extruded through a 1/12-inch die and the extrudates divided into
26 four parts (A, B, C and D). Parts A and B contained 50% volatiles, and parts C and D were
27 air dried to 43% volatiles. Molar composition of the extrudates was as follows:

28 $\text{SiO}_2/\text{Al}_2\text{O}_3 = 10$

29 $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{SiO}_2 = 0.25$

30 $\text{K}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O}) = 0.59$

31 $\text{OH}/\text{SiO}_2 = 0.29$

32 The H₂O/SiO₂ ratio was 5.0 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 containing parts A and C were then heated at 110°C. for four days, and the bottles containing parts B and D were heated at 150°C. for four days.

The resulting extrudates were washed with deionized water, filtered, dried in a vacuum oven at 120°C. overnight. The extrudates were analyzed by X-ray diffraction and determined to contain zeolite L with no other crystalline phases. The percent crystallinities, when compared to a 100% zeolite L reference, are shown in Table II.

Table II

<u>Part</u>	<u>Percent Crystallinity, XRD</u>
A	45
B	55
C	30
D	70

EXAMPLE 2

150 Grams of Hi-Sil 233 was placed in a Baker-Perkins mixer. To this was added 30 grams of NaAlO₂ and 7 grams of NaNO₃ and the resulting mixture was mixed for about 10 minutes. To this was slowly added 75 grams of a 50% aqueous solution of KOH and this mixture was mixed for three hours. Then, 100 grams of de-ionized water was slowly added to bring the mixture to a paste. The mixture was then heated at about 66°C to dry the mixture back to an extrudable form. The mix was extruded through a 1/12-inch die. A portion of the extrudate was air-dried to 46% volatiles. The molar composition of the extrudate was as follows:

$$\text{SiO}_2/\text{Al}_2\text{O}_3 = 13$$

$$(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{SiO}_2 = 0.24$$

$$\text{K}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O}) = 0.61$$

$$\text{OH}/\text{SiO}_2 = 0.29$$

$$\text{H}_2\text{O}/\text{SiO}_2 = 4.2$$

1 The extrudate was placed in a 1-quart Teflon bottle in a stainless steel autoclave and
2 heated at 150°C for four days and autogenous pressure. The extrudate was washed with
3 water adjusted to pH 12 using aqueous KOH solution, filtered, and dried overnight in a
4 vacuum oven at 120°C. The extrudate was finally calcined in air at 593°C for six hours.
5 The extrudate was analyzed by X-ray diffraction analysis and found to contain zeolite L as
6 the only zeolite phase.

7

1 WHAT IS CLAIMED IS:

- 2 1. A method for preparing crystalline zeolite L, said method comprising:
- 3 (A) preparing a self-supporting reaction mixture comprising at least one active
- 4 source of silica, at least one active source of alumina and a source of hydroxide in
- 5 amounts sufficient to produce zeolite L, and sufficient water to produce zeolite L,
- 6 wherein the reaction mixture has an OH^-/SiO_2 molar ratio of from 0.2 to 0.4; and
- 7 (B) heating said reaction mixture at a temperature from about 90°C. to about
- 8 200°C. under crystallization conditions and in the absence of an added external
- 9 liquid phase for sufficient time to form crystals of zeolite L.
- 10
- 11 2. The method according to Claim 1 wherein said reaction mixture has a water/silica
- 12 molar ratio during crystallization of no greater than about 6.
- 13
- 14 3. The method of Claim 2 wherein said reaction mixture during crystallization has a
- 15 water/silica molar ratio between about 2 and about 5.
- 16
- 17 4. The method according to Claim 1 wherein said reaction mixture has the following
- 18 molar composition ranges:
- | | | | |
|----|---|---|-------------|
| 19 | $\text{SiO}_2/\text{Al}_2\text{O}_3$ | = | 5 - 20 |
| 20 | $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{SiO}_2$ | = | 0.15 - 0.45 |
| 21 | $\text{K}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O})$ | = | 0.3 - 1.0 |
| 22 | OH^-/SiO_2 | = | 0.2 - 0.4 |
| 23 | $\text{H}_2\text{O}/\text{SiO}_2$ | = | 2 - 6 |
| 24 | | | |
- 25 5. The method according to Claim 4 wherein said reaction mixture has the following
- 26 molar composition ranges:



1	$\text{SiO}_2/\text{Al}_2\text{O}_3$	=	5 - 15
2	$(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{SiO}_2$	=	0.20 - 0.40
3	$\text{K}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O})$	=	0.4 - 1.0
4	OH^-/SiO_2	=	0.25 - 0.4
5	$\text{H}_2\text{O}/\text{SiO}_2$	=	3 - 5



- 6
- 7 6. The method according to Claim 1 wherein the silica/alumina mole ratio is from
- 8 about 5 to about 10.
- 9
- 10 7. The method according to Claim 6 wherein the silica/alumina mole ratio is from
- 11 about 5.5 to about 7.
- 12
- 13 8. The method according to Claim 1 wherein said reaction mixture further comprises at
- 14 least one active source of a Group VIII metal.
- 15
- 16 9. The method according to Claim 8 wherein said Group VIII metal is selected from
- 17 platinum, palladium and a combination thereof.
- 18
- 19 10. The method according to Claim 1 wherein the silica/alumina mole ratio in the zeolite
- 20 L product is from about 5 to about 7.
- 21
- 22 11. The method according to Claim 1 wherein the silica/alumina mole ratio in the zeolite
- 23 L product is from about 5.5 to about 7.0.
- 24 12. The method according to Claim 1 wherein the reaction mixture is extrudable and
- 25 capable of retaining a shape.
- 26
- 27 13. A method for preparing crystalline zeolite L, said method comprising:
- 28 (A) preparing a self-supporting reaction mixture comprising at least one active
- 29 source of silica, at least one active source of alumina and a source of hydroxide in
- 30 amounts sufficient to produce zeolite L, and sufficient water to shape said mixture,
- 31 wherein the reaction mixture has an OH^-/SiO_2 molar ratio of from 0.20 to 0.40;
- 32 (B) forming said reaction mixture into a shape; and

- 1 (C) heating said reaction mixture at a temperature of about 90°C. to about
2 200°C. under crystallization conditions and in the absence of an added external
3 liquid phase for sufficient time to form crystals of zeolite L.
4
- 5 14. The method according to Claim 13 wherein said reaction mixture has a water/silica
6 molar ratio during crystallization of no greater than about 6.
7
- 8 15. The method of Claim 14 wherein said reaction mixture during crystallization has a
9 water/silica molar ratio between about 2 and about 5.
10
- 11 16. The method according to Claim 13 wherein said reaction mixture has the following
12 molar composition ranges:
- | | | | |
|----|---|---|-------------|
| 13 | $\text{SiO}_2/\text{Al}_2\text{O}_3$ | = | 5 - 20 |
| 14 | $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{SiO}_2$ | = | 0.15 - 0.45 |
| 15 | $\text{K}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O})$ | = | 0.3 - 1.0 |
| 16 | OH^-/SiO_2 | = | 0.2 - 0.4 |
| 17 | $\text{H}_2\text{O}/\text{SiO}_2$ | = | 2 - 6 |
| 18 | | | |
- 19 17. The method according to Claim 16 wherein said reaction mixture has the following
20 molar composition ranges:
- | | | | |
|----|---|---|-------------|
| 21 | $\text{SiO}_2/\text{Al}_2\text{O}_3$ | = | 5 - 15 |
| 22 | $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{SiO}_2$ | = | 0.20 - 0.40 |
| 23 | $\text{K}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O})$ | = | 0.4 - 1.0 |
| 24 | OH^-/SiO_2 | = | 0.25 - 0.4 |
| 25 | $\text{H}_2\text{O}/\text{SiO}_2$ | = | 3 - 5 |
| 26 | | | |
- 27 18. The method according to Claim 13 wherein the silica/alumina mole ratio is from
28 about 5 to about 10.
29
- 30 19. The method according to Claim 18 wherein the silica/alumina mole ratio is from
31 about 5.5 to about 7.
32



- 1 20. The method according to Claim 13 wherein said reaction mixture further comprises
2 at least one active source of a Group VIII metal.
3
- 4 21. The method according to Claim 20 wherein said Group VIII metal is selected from
5 platinum, palladium and a combination thereof.
6
- 7 22. 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 23. The method according to Claim 22 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 24. The method according to Claim 13 wherein the silica/alumina mole ratio in the
16 zeolite L product is from about 5 to about 7.
17
- 18 25. The method according to Claim 13 wherein the silica/alumina mole ratio in the
19 zeolite L product is from about 5.5 to about 7.0.
- 20 26. The method according to Claim 13 wherein the reaction mixture is extrudable and
21 capable of retaining a shape.
22
23

