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(54) **PREPARATION DE ZEOLITE L**
(54) **PREPARATION OF ZEOLITE L**

(57) L'invention concerne un procédé de préparation de zéolite L d'aluminosilicate cristallin, à partir d'un mélange réactionnel contenant seulement la quantité d'eau suffisante pour la production de zéolite L. Dans un mode de réalisation, le mélange réactionnel est auto-suffisant et peut être façonné si on le désire. Dans le procédé de l'invention, le mélange réactionnel est chauffé dans des conditions de cristallisation et en l'absence d'une phase liquide externe ajoutée, de manière qu'il ne soit pas nécessaire de supprimer le liquide excédentaire du produit cristallisé avant le séchage des cristaux.

(57) A method is disclosed for preparing crystalline aluminosilicate zeolite L from a reaction mixture containing only sufficient water to produce zeolite L. In one embodiment, the reaction mixture is self-supporting and may be shaped if desired. In the method, the reaction mixture is heated at crystallization conditions and in the absence of an added external liquid phase, so that excess liquid need not be removed from the crystallized product prior to drying the crystals.

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(54) Title: PREPARATION OF ZEOLITE L

(57) **Abstract**

A method is disclosed for preparing crystalline aluminosilicate zeolite L from a reaction mixture containing only sufficient water to produce zeolite L. In one embodiment, the reaction mixture is self–supporting and may be shaped if desired. In the method, the reaction mixture is heated at crystallization conditions and in the absence of an added external liquid phase, so that excess liquid need not be removed from the crystallized product prior to drying the crystals.

PREPARATION OF ZEOLITE L

Field of the Invention

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

Background

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

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

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

U.S. Patent No. 3,216,789, issued November 9, 1965 to Breck et al., discloses zeolite L. The zeolite L is prepared from reaction mixtures whose composition, expressed in terms 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

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

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

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

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

M_2O/SiO_2	0.4 to 0.5
H_2O/M_2O	15 to 30
SiO_2/Al_2O_3 or Ga_2O_3	5 to 11

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

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

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

SUMMARY OF THE INVENTION

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

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

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

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

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

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

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

and a source of hydroxide in amounts sufficient to produce zeolite L, and sufficient water to produce zeolite L, wherein the reaction mixture has an OH^-/SiO_2 molar ratio of from 0.20 to 0.40 and heating said reaction mixture at a temperature from about 100°C. to about 200°C. under crystallization conditions and in the absence of an added external liquid phase for sufficient time to form crystals of zeolite L. The reaction mixture is extrudable and capable of maintaining a shape.

The present invention also provides a method for preparing crystalline zeolite L, said method comprising preparing a reaction mixture comprising at least one active source of silica, at least one active source of alumina and a source of hydroxide in amounts sufficient to produce zeolite L, and sufficient water to shape said mixture, wherein the reaction mixture has an OH^-/SiO_2 molar ratio of from 0.20 to 0.40, forming said reaction mixture into a shape; and heating said reaction mixture at a temperature from about 100°C. to about 200°C. under crystallization conditions and in the absence of an added external liquid phase for sufficient time to form crystals of zeolite L. The reaction mixture is extrudable and capable of maintaining a shape.

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

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

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

Among other factors, the present invention is based on the discovery of a method for crystallizing zeolite L from a reaction mixture which contains only enough water to form the zeolite L. Further, the zeolite L prepared by the above-described method is made as very small crystallites. As discussed during the aforementioned interview, the OH^-/SiO_2 molar ratio is critical in Applicant's claimed method for making zeolite L. Applicant has discovered that this molar ratio affects both the physical properties of the reaction mixture and the degree of crystallization achieved. A critical balance must be achieved so that the reaction mixture will have the desired physical properties, e.g., will be self-supporting and capable of being shaped, while at the same time providing an acceptable degree of crystallization. It has also been found that if the OH^-/SiO_2 molar ratio becomes too high, the reaction mixture takes on undesirable physical properties. On the other hand, if the OH^-/SiO_2 molar ratio is too low, crystallization is inadequate.

DETAILED DESCRIPTION OF THE INVENTION

PREPARING THE REACTION MIXTURE

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

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

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

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

Typical sources of silicon oxide (SiO_2) include silicates, silica hydrogel, silicic acid, colloidal silica, fumed silica, tetraalkyl orthosilicates silica hydroxides, precipitated silica and clays. Typical sources of aluminum oxide (Al_2O_3) include aluminates, alumina, and aluminum compounds such as $AlCl_3$, $Al_2(SO_4)_3$, aluminum hydroxide ($Al(OH_3)$), and kaolin clays. One advantage of the present invention is that the sources of silicon oxide and aluminum oxide can all be non-zeolitic.

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

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

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

	General	Preferred
SiO_2/Al_2O_3 =	5 - 20	5 - 15
$(K_2O + Na_2O)/SiO_2$ =	0.15 - 0.45	0.20 - 0.40
$K_2O/ (Na_2O + K_2O)$ =	0.3 - 1.0	0.4 - 1.0
OH^-/SiO_2 =	0.2 - 0.40	0.25 - 0.40
H_2O/SiO_2 =	2 - 6	3 - 5

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

FORMING THE SHAPES

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

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

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

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

ZEOLITE CRYSTALLIZATION

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

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

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

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

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

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

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

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

SEED CRYSTALS

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

DESCRIPTION OF ZEOLITE L

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

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

TABLE I

d (Å)	I/I_0
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

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

ZEOLITE CRYSTALLITE SIZE

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

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

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

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

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

ZEOLITE POST-TREATMENT

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

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

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

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

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

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

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

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

Naturally occurring clays which can be composited with the synthetic zeolite of this invention include the montmorillonite and kaolin families, which families include the sub-bentonites and 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. Fibrous clays such as sepiolite and attapulgite can also be used as supports. Such clays can be used in the raw state as originally mined or can be initially subjected to calcination, acid treatment or chemical modification.

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

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

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

The zeolite prepared in the present process is useful in hydrocarbon conversion reactions. Hydrocarbon conversion reactions are chemical and catalytic processes in which carbon containing compounds are changed to different carbon containing compounds. Examples of hydrocarbon conversion reactions include aromatization of C_6 paraffins to produce benzene and reforming of C_6 to C_9 hydrocarbons to increase their octane. The zeolite can be used to prepare a reforming catalyst as disclosed in U.S. Patent No. 4,104,320, issued August 1, 1978 to Bernard et al., and U.S. Patent No. 4,634,518, issued January 6, 1987 to Buss et al., both of which are incorporated by reference herein in their entirety.

EXAMPLE 1

150 Grams of silica (Hi-Sil 233, a hydrated silica manufacture by PPG) was placed in a Baker-Perkins mixer. 40 Grams of $NaAlO_2$ was added to the mixer and the two were mixed for about ten minutes. Then 75 grams of a 50% KOH aqueous solution was slowly added to the mixer and mixing continued for about 3 hours. Deionized water (180 grams) was then added slowly to the mixer to form a paste-like mixture. Heat (about 60-66°C.) was applied to the mixture to dry it slightly and make it extrudable.

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

$SiO_2/Al_2O_3 = 10$

$(Na_2O + K_2O)/SiO_2 = 0.25$

$K_2O/(Na_2O + K_2O) = 0.59$

$OH^-/SiO_2 = 0.29$

The H_2O/SiO_2 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

Part	Percent Crystallinity, XRD
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 $NaAlO_2$ and 7 grams of $NaNO_3$ 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:

$SiO_2/Al_2O_3 = 13$

$(Na_2O + K_2O)/SiO_2 = 0.24$

$K_2O/ (Na_2O + K_2O) = 0.61$

$OH^-/SiO_2 = 0.29$

$H_2O/SiO_2 = 4.2$

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

WHAT IS CLAIMED IS:

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

(A) preparing a self-supporting reaction mixture comprising at least one active source of silica, at least one active source of alumina and a source of hydroxide in amounts sufficient to produce zeolite L, and sufficient water to produce zeolite L, wherein the reaction mixture has an OH^-/SiO_2 molar ratio of from 0.2 to 0.4; and

(B) heating said reaction mixture at a temperature from about 90°C. to about 200°C. under crystallization conditions and in the absence of an added external liquid phase for sufficient time to form crystals of zeolite L.

2. The method according to Claim 1 wherein said reaction mixture has a water/silica molar ratio during crystallization of no greater than about 6.

3. The method of Claim 2 wherein said reaction mixture during crystallization has a water/silica molar ratio between about 2 and about 5.

4. The method according to Claim 1 wherein said reaction mixture has the following molar composition ranges:

SiO_2/Al_2O_3	=	5 - 20
$(Na_2O + K_2O)/SiO_2$	=	0.15 - 0.45
$K_2O/(Na_2O + K_2O)$	=	0.3 - 1.0
OH^-/SiO_2	=	0.2 - 0.4
H_2O/SiO_2	=	2 - 6

5. The method according to Claim 4 wherein said reaction mixture has the following molar composition ranges:

SiO_2/Al_2O_3	=	5 - 15
$(Na_2O + K_2O)/SiO_2$	=	0.20 - 0.40
$K_2O/(Na_2O + K_2O)$	=	0.4 - 1.0
OH^-/SiO_2	=	0.25 - 0.4
H_2O/SiO_2	=	3 - 5

6. The method according to Claim 1 wherein the silica/alumina mole ratio is from about 5 to about 10.

7. The method according to Claim 6 wherein the silica/alumina mole ratio is from about 5.5 to about 7.

8. The method according to Claim 1 wherein said reaction mixture further comprises at least one active source of a Group VIII metal.

9. The method according to Claim 8 wherein said Group VIII metal is selected from platinum, palladium and a combination thereof.

10. The method according to Claim 1 wherein the silica/alumina mole ratio in the zeolite L product is from about 5 to about 7.

11. The method according to Claim 1 wherein the silica/alumina mole ratio in the zeolite L product is from about 5.5 to about 7.0.

12. The method according to Claim 1 wherein the reaction mixture is extrudable and capable of retaining a shape.

13. A method for preparing crystalline zeolite L, said method comprising:

(A) preparing a self-supporting reaction mixture comprising at least one active source of silica, at least one active source of alumina and a source of hydroxide in amounts sufficient to produce zeolite L, and sufficient water to shape said mixture, wherein the reaction mixture has an OH^-/SiO_2 molar ratio of from 0.20 to 0.40;

(B) forming said reaction mixture into a shape; and

(C) heating said reaction mixture at a temperature of about 90°C. to about 200°C. under crystallization conditions and in the absence of an added external liquid phase for sufficient time to form crystals of zeolite L.

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

15. The method of Claim 14 wherein said reaction mixture during crystallization has a water/silica molar ratio between about 2 and about 5.

16. The method according to Claim 13 wherein said reaction mixture has the following molar composition ranges:

SiO_2/Al_2O_3	=	5 - 20
$(Na_2O + K_2O)/SiO_2$	=	0.15 - 0.45
$K_2O/(Na_2O + K_2O)$	=	0.3 - 1.0
OH^-/SiO_2	=	0.2 - 0.4
H_2O/SiO_2	=	2 - 6

17. The method according to Claim 16 wherein said reaction mixture has the following molar composition ranges:

SiO_2/Al_2O_3	=	5 - 15
$(Na_2O + K_2O)/SiO_2$	=	0.20 - 0.40
$K_2O/(Na_2O + K_2O)$	=	0.4 - 1.0
OH^-/SiO_2	=	0.25 - 0.4
H_2O/SiO_2	=	3 - 5

18. The method according to Claim 13 wherein the silica/alumina mole ratio is from about 5 to about 10.

19. The method according to Claim 18 wherein the silica/alumina mole ratio is from about 5.5 to about 7.

20. The method according to Claim 13 wherein said reaction mixture further comprises at least one active source of a Group VIII metal.

21. The method according to Claim 20 wherein said Group VIII metal is selected from platinum, palladium and a combination thereof.

22. The method according to Claim 13 wherein the shaped crystalline zeolite is a spherical or cylindrical particle having a cross sectional diameter between about 1/64 inch and about 1/2 inch.

23. The method according to Claim 22 wherein the shaped crystalline zeolite is a spherical or cylindrical particle having a cross sectional diameter between about 1/32 inch and about 1/4 inch in diameter.

24. The method according to Claim 13 wherein the silica/alumina mole ratio in the zeolite L product is from about 5 to about 7.

25. The method according to Claim 13 wherein the silica/alumina mole ratio in the zeolite L product is from about 5.5 to about 7.0.

26. The method according to Claim 13 wherein the reaction mixture is extrudable and capable of retaining a shape.