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(54) **Enhancing boro-aluminosilicate zeolite structures**

Verbesserung von boroaluminosilikatverwandten Zeolitstrukturen

Amélioration des structures zéolithiques de type boro-aluminosilicate

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Description

[0001] The present invention relates to enhancing properties of boroaluminosilicate zeolite structures having EUO and NES topology; and further relates to use thereof in wax isomerization.

[0002] It is known from EP 0494535 to enhance or restore the activity of silica based catalysts used for producing ϵ -caprolactam from cyclohexanon oxime by contacting said catalysts with either an aqueous solution of ammonium salts and at least one basic material selected from ammonia, lower alkylamines, allylamines and alkylammonium hydroxydes or ammonia water.

[0003] It is further known that EU-1 is a high activity aluminosilicate zeolite catalyst (U.S. Patent 4,537,754) having 10-ring pores and high internal volume. It is useful as a catalyst and sorbent and shows interesting shape selectivity (U.S. Patent 4,537,545; Sovererijns et al, Microporous Materials, 4, page 123 (1995)). Its compositional variations include the replacement of Al by Ga, Fe or B. As the acidity of these different metal (M) forms decreases in the order Al, Ga, Fe, B, reactions requiring the lowest acidity, such as paraffin isomerization are probably best carried out with the borosilicate form or those materials having high Si/M ratios (i.e., lower number of acid sites). Unfortunately, when made at the higher silica ratios (those greater than about 40) some EU-1 materials have poor sorption capacity after removal of the templates normally used in its synthesis, resulting in poor accessibility of reactants and low catalytic reactivity. This may be caused by partial framework collapse (reflected in deteriorating X-ray diffraction evidence) or trapped detrital material blocking the pores (indicated by stable X-ray diffraction profiles but inferior n-hexane sorption capacities). Evidence seems to point to the latter cause in these subject materials and may be inherent to the high silica synthesis process, which requires excess silica in the mother liquor, resulting in entrainment, primarily, of siliceous species within the zeolite structure. In constrained pore systems such as EU-1, a small amount of detritus may readily block major parts of the accessible structure. Whilst it is well known that post acid treatments or chemical treatments with complexing agents may restore structural accessibility in some zeolites, including EU-1, in this case, such treatments would tend to remove the framework boron, or other M entities, responsible for the desired selective catalytic activity.

SUMMARY OF THE INVENTION

[0004] The instant invention is directed to a process for selectively removing detrital material from boro-aluminosilicate selected from EUO, NES and intergrown mixtures of EUO and NES boro-aluminosilicate topology zeolites having a Si/M ratio of greater than about 40, comprising treating said boro-aluminosilicate with a base selected from NaOH, KOH, $\text{Ca}(\text{OH})_2$, $\text{Si}(\text{OH})_2$, $\text{Li}(\text{OH})$, $\text{Rb}(\text{OH})$, CsOH , $\text{Ba}(\text{OH})_2$ and mixtures thereof for a time and at a temperature sufficient to remove said detrital material from said boro-aluminosilicate wherein the concentration of said base is less than about 0.5 normal. Base concentrations in excess of this level may cause the removal of framework components leading to subsequent structural degradation.

[0005] The invention is likewise especially directed to a boro-aluminosilicate EU-1 having improved wax isomerization properties, said boro-aluminosilicate prepared by treating a boro-aluminosilicate EU-1 containing detrital material with a base for a time and at a temperature sufficient to remove said detrital material from said boro-aluminosilicate EU-1.

BRIEF DESCRIPTION OF THE FIGURES**[0006]**

Figure 1 shows the conversion or selectivity of examples 1 and 3. Example 1 is labeled A and Example 3 is labeled B. In the Figure, C, D, and E represent conversion, constraint, and cracking, respectively.

Figure 2 depicts the n-hexane adsorption isotherm measured at room temperature. The % weight uptake is plotted against pressure (133 Pa (torr)) for boro-aluminosilicate EU-1 (triangles), .1 N NaOH treated boro-aluminosilicate EU-1 (circles), and 0.2 N NaOH treated boro-aluminosilicate EU-1 (squares).

DETAILED DESCRIPTION OF THE INVENTION

[0007] Applicants have discovered that mild base treatment of a boro-aluminosilicate EU-1, frees the pores of detrital material blockages, enhances the properties, and does not destroy the structure. The so treated boro-aluminosilicate EU-1 has enhanced wax isomerization activity. Such activity is improved by a factor of at least two, and preferably at least 4. Selectivity is concomitantly improved, producing a desirable wax isomerization catalyst when compared to other framework substituted EU-1 materials.

[0008] Although boro-aluminosilicate EU-1 has a desirable selective acidity for wax isomerization, the activity is such

that its use in wax isomerization processes is not practical in the as synthesized form, in the required Si/M range of greater than about 40, to yield desirable catalysts for the subject process. The instant treatment method affords boro-aluminosilicate EU-1 having a Si/M of greater than about 40 with an activity and selectivity suitable for wax isomerization processes.

[0009] Applicants believe that the mild base treatment of the instant invention removes detrital material, such as silica, from the boro-aluminosilicate EU-1 channels without destroying the structure of the boro-aluminosilicate EU-1.

[0010] The bases utilizable in the instant invention are selected from NaOH, KOH, Ca(OH)₂, Sr(OH)₂, LiOH, RbOH, CsOH, Ba(OH)₂ and mixtures thereof. The base utilized will have a concentration of less than about 0.5 normal, preferably from about 0.1 to about 0.5 normal, and most preferably from about 0.1 to about 0.4 N.

[0011] The time and temperature for the base treatment are those under which the detrital material is removed. Typically, temperatures of about room temperature for several hours (e.g., overnight) up to reflux (~ 100°C) for less than one hour are utilized. Whilst it is recognized that lower temperatures and longer times, or higher temperatures (and therefore pressures over one atmosphere) and shorter times, are also functional, the increased cost of such temperature reactions make them economically undesirable. Similarly, although solvents other than water for the bases (particularly polar organic solvents) are acceptable (e.g., alcohols, ketones, ethers, etc.), their cost, safety, pollution and process concerns render them less desirable. Higher temperature treatments also require more control to prevent structural destruction in the zeolite.

[0012] Though the instant invention is primarily directed to EU-1 boro-aluminosilicates, since NU-85, NU-86, and NU-87 are related structures topologically or by intergrowths (i.e., structure types EUO, NES and intergrowths and mixtures of the two, as described in 4th Edn. of the "Atlas of zeolite structure types", Ed. Meier, Olson and Baerlocher, Elsevier (1996)), the instant process should be equally applicable to them. Such structures are well documented in the literature. See for example, NU-85 (Euro. Patent Application 0462 745), NU-86 (U.S. Patent 5,108,579), NU-87 (U.S. Patent 5,102,641; Shanon et al, Nature, v. 353, p. 417 (1991)), and ZSM-50 (U.S. Patent 4,640,829; Moini et al Zeolites, v. 14, p. 504 (1994) herein incorporated by reference). Boro-gallosilicate analogs are similarly acceptable. Preferably, the NU-87 zeolite will be used.

[0013] Typical preferred treatment times range from about 5 minutes to about 4 hours.

[0014] The zeolites treated in accordance with the instant invention can be utilized in a catalytic isomerization process conducted under catalytic isomerization conditions. Typical conditions include those well known to the skilled artisan. For example, the process is carried out in the presence of hydrogen at temperatures of about 200 to 450°C and pressures ranging from 100 to about 21000 kPa (atmospheric to about 3000 pounds).

[0015] The following examples are illustrative and are not meant to be limiting in any way.

Example 1

[0016] A sample of B-EU-1 obtained from the IFP company was evaluated. The chemical analysis of this is shown in Table 1. 7B-MASNMR of this material showed a single peak at 4.7 ppm indicative of tetrahedra framework boron. This sample was measured for n-hexane sorption capacity and catalytic activity (Figure 1) using methylcyclohexane as a model compound. Samples were made into catalysts by impregnating with 0.5 wt% Pt from Pt(NH₃)₄Cl₂ solutions, calcined, pillled then crushed to 10/20 mesh granules before testing in a standard acidity test using methylcyclohexane (MCH) as a model feed (H₂/feed=5/ MCH=20 ml/h 1310⁵ Pa (200) psig H₂). This test has proved to be useful in selecting desirable zeolite wax isomerization catalysts. A desirable catalyst has a high isomerization selectivity to ethylcyclopentane (ECP) with low cracking activity. The data shown in Figure 1 (obtained at 320°C) shows good selectivity but very poor activity. Surprisingly, the sorption capacity was negligible compared to similar, but less desirable from a catalytic viewpoint, gallo- and ferri-aluminosilicate analogs of the original base aluminosilicate EU-1. The good crystallinity but poor sorption capacity indicated structural blockage.

Example 2

[0017] A 1 gram sample of the EU-1 described in Example 1 was reacted with 20 ml of a 0.1N NaOH solution at 60°C for one hour. After filtering, washing and drying the sample was evaluated by X-ray diffraction, activated under vacuum on a Cahn sorption balance, then cooled to room temperature and an n-hexane sorption isotherm measured. The X-ray structure is unchanged by the base treatment, but shows improved sorption capacity compared to the base material (Figure 2).

Example 3

[0018] The process of Example 2 was repeated except that the base concentration was increased to 0.2 N NaOH. The X-ray structure was unchanged by the treatment and a major improvement in sorption capacity (Figure 2) was

observed. A larger sample was given a repeated treatment then exchanged with 10% wt. ammonium chloride solution (4 gm/40 ml/50°C/1 hr) and was analyzed for constituent elements by ICPAES (Table 1), showing that silica was removed. This material was converted to a catalyst by impregnation with 0.5% wt. Pt (as $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$) and reacted under the conditions described in Example 1, the activity of B-EU-1 improves by a factor of four and selectivity is improved.

Example 4

[0019] The process of Example 2 was repeated except that the base concentration was increased to 0.5N NaOH. The X-ray diffraction indicated that the structure suffered major degradation by the treatment confirmed by a decrease in sorption capacity compared to Example 3.

Example 5

[0020] A sample of aluminosilicate EU-1, having an Si/Al ratio of 194, was evaluated on a Cahn sorption balance with n-hexane, giving a sorption capacity of 0.63 wt% (22°C/6,783 Pa (51 torr)). After the base treatment described in Example 3, the n-hexane sorption capacity increased to 4.2 wt%, again indicative of detrital material removal from the pore space.

[0021] The Examples show that a mild base treatment is sufficient to clean up the blocked EU-1 structure to improve catalytic activity by the removal of detrital material, primarily silica, from the channels of the zeolite without significant removal of B (or Al) from the framework, so retaining catalytic activity and selectivity.

Table 1 -

CHEMICAL ANALYSIS OF B-EU-1 SAMPLES					
Sample	%B	%Al	%Si	%Na	B:Al:Si Atomic Ratio
Example 1	0.12	0.12	44.0	0.06	1:0.40:141
Example 3	0.11	0.19	43.0	0.02	1:0.68:150

Claims

1. A process for selectively removing detrital material from a boro-aluminosilicate selected from EUO and NES topology boro-aluminosilicate zeolites and intergrown mixtures of the two, having a Si/M ratio greater than about 40; the process comprising treating the boro-aluminosilicate with a base for a time and at a temperature sufficient to remove detrital material from said boro-aluminosilicate, the base having a concentration up to 0.5 normal and being selected from LiOH, NaOH, KOH, RbOH, CsOH, $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, and mixtures thereof.
2. The process of claim 1, wherein the concentration of the base is below 0.5N.
3. The process of claim 2, wherein the concentration of the base is from 0.1 N to 0.4N.
4. A process according to any preceding claim, wherein the EUO topology boro-aluminosilicate is a boro-aluminosilicate EU-1 zeolite.
5. The process of any one of claims 1 to 3, wherein the boro-aluminosilicate is an intergrowth of EU-1 and NES topology zeolites.
6. The process of any one of claims 1 to 3 and 5, wherein said NES topology boro-aluminosilicate zeolite is selected from NU-85, NU-86, and NU-87 zeolites and mixtures thereof.
7. A boro-aluminosilicate EU-1 having improved wax isomerization properties, said boro-aluminosilicate prepared by treating a boro-aluminosilicate EU-1 containing detrital material with a base selected from LiOH, NaOH, KOH, RbOH, CsOH, $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, and mixtures thereof in a concentration up to 0.5 normal for a time and at a temperature sufficient to remove detrital material.
8. A catalytic isomerization process, comprising contacting a feedstock comprising a C_{16} to C_{46} carbon containing feedstock, under catalytic isomerization conditions, with an isomerization catalyst comprising a boro-aluminosili-

cate product of the process of any one of claims 1 to 6, or of claim 7.

Patentansprüche

1. Verfahren zur selektiven Entfernung von Schuttmaterial aus Boraluminiumsilikat ausgewählt aus Boraluminiumsilikatzeolithen mit EUO- und NES-Topologie und verwachsenen Mischungen der beiden mit einem Si/M-Verhältnis von mehr als etwa 40; bei dem das Boraluminiumsilikat mit einer Base für eine Zeitdauer und bei einer Temperatur behandelt wird, die ausreichen, um Schuttmaterial aus dem Boraluminiumsilikat zu entfernen, wobei die Base eine Konzentration bis zu 0,5 normal hat und ausgewählt ist aus LiOH, NaOH, KOH, RbOH, CsOH, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂ und Mischungen derselben.
2. Verfahren nach Anspruch 1, bei dem die Konzentration der Base unter 0,5 N liegt.
3. Verfahren nach Anspruch 2, bei dem die Konzentration der Base 0,1 N bis 0,4 N beträgt.
4. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Boraluminiumsilikat mit EUO-Topologie ein Boraluminiumsilikat-EU-1-Zeolith ist.
5. Verfahren nach einem der Ansprüche 1 bis 3, bei dem das Boraluminiumsilikat aus Zeolithen mit EU-1- und NES-Topologie verwachsenes Material ist.
6. Verfahren nach einem der Ansprüche 1 bis 3 und 5, bei dem der Boraluminiumsilikatzeolith mit NES-Topologie ausgewählt ist aus NU-85-, NU-86- und NU-87-Zeolithen und Mischungen derselben.
7. Boraluminiumsilikat-EU-1 mit verbesserten Wachsisomerisierungseigenschaften, wobei das Boraluminiumsilikat hergestellt ist, indem ein Boraluminiumsilikat-EU-1, das Schuttmaterial enthält, mit einer Base ausgewählt aus LiOH, NaOH, KOH, RbOH, CsOH, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂ und Mischungen derselben in einer Konzentration bis zu 0,5 normal für eine Zeitdauer und bei einer Temperatur behandelt wird, die ausreichen, um Schuttmaterial zu entfernen.
8. Katalytisches Isomerisierungsverfahren, bei dem ein Einsatzmaterial, das C₁₆- bis C₄₆-Kohlenstoff enthaltendes Einsatzmaterial umfasst, unter katalytischen Isomerisierungsbedingungen mit Isomerisierungskatalysator kontaktiert wird, der Boraluminiumsilikatprodukt des Verfahrens gemäß einem der Ansprüche 1 bis 6 oder gemäß Anspruch 7 umfasst.

Revendications

1. Procédé pour l'élimination sélective de matériaux détritiques d'un boro-aluminosilicate choisi parmi les zéolites boro-aluminosilicatées de topologies EUO et NES et de mélanges complexes des deux, ayant un rapport Si/M supérieur à environ 40; le procédé comprenant le traitement du boro-aluminosilicate avec une base pendant une période de temps et à une température suffisantes pour éliminer les matériaux détritiques dudit boro-aluminosilicate, la base ayant une concentration allant jusqu'à 0,5N et étant choisie parmi LiOH, NaOH, KOH, RbOH, CsOH, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂ et leurs mélanges.
2. Procédé selon la revendication 1, dans lequel la concentration de la base est inférieure à 0,5N.
3. Procédé selon la revendication 2, dans lequel la concentration de la base est de 0,1N à 0,4N.
4. Procédé selon l'une quelconque des revendications précédentes; dans lequel le boro-aluminosilicate de topologie EUO est une zéolite boro-aluminosilicatée EU-1.
5. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le boro-aluminosilicate est un mélange complexe de zéolites de topologies EU-1 et NES.
6. Procédé selon l'une quelconque des revendications 1 à 3 et 5, dans lequel ladite zéolite boro-aluminosilicatée de topologie NES est choisie parmi les zéolites NU-85, NU-86 et NU-87 et leurs mélanges.

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7. Boro-aluminosilicate EU-1 ayant des propriétés améliorées d'isomérisation de cires, ledit boro-aluminosilicate étant préparé par traitement d'un boro-aluminosilicate EU-1 contenant des matériaux détritiques avec une base choisie parmi LiOH, NaOH, KOH, RbOH, CsOH, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂ et leurs mélanges en concentration allant jusqu'à 0,5N pendant une période de temps et à une température suffisantes pour éliminer les matériaux détritiques.
8. Procédé d'isomérisation catalytique, comprenant la mise en contact d'une charge de base comprenant une charge de base contenant une chaîne d'atomes de carbone en C₁₆-C₄₆ dans des conditions d'isomérisation catalytique, avec un catalyseur d'isomérisation comprenant un produit boro-aluminosilicaté du procédé selon l'une quelconque des revendications 1 à 6 ou de la revendication 7.

Figure 1

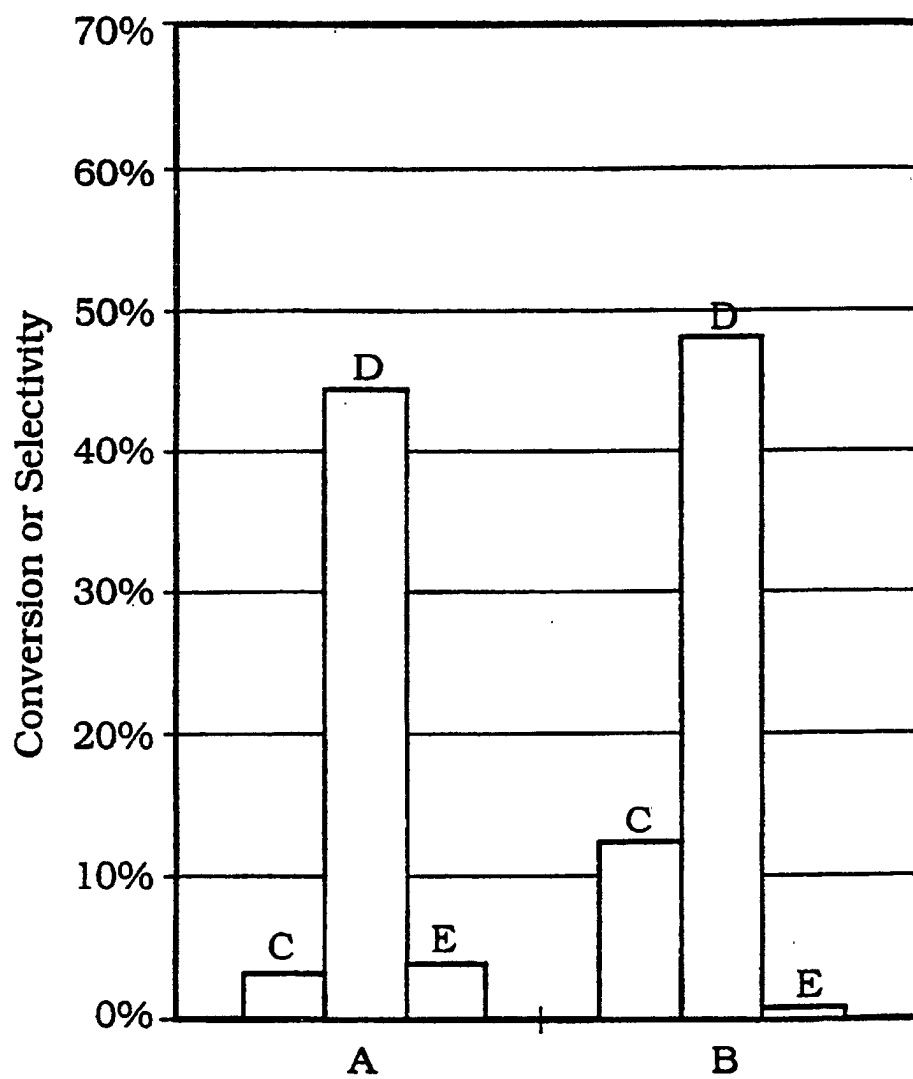


Figure 2

N-Hexane Adsorption

