AUSTRA

PATENTS ACT

APPLICATION FOR A PATENT (CONVENTION OR NON CONVENTION)

42496/78

We, W.R. GRACE & CO., a corporation organised and existing under the laws of the State of Connecticut, United States of America, of Grace Plaza, 1114 Avenue of the Americas, New York, New York 10036, United States of America,

hereby apply for the grant of a Patent for an invention entitled

"PREPARATION OF ZEOLITE"

which is described in the accompanying specification.

The application is a Convention application and is based on the application(s) for patent or similar protection made in United States of America, on 19th December, 1977 under number 862.031.

Our address for service is care of DAVIES & COLLISON, Patent Attorneys, of A.M.P. Building, Hobart Place, Canberra, Australian Capital Territory, Commonwealth of Australia.

Dated this 13th day of December, 1978.

(A member of the firm of DAVIES & COLLISON) for and on behalf of W.R. GRACE & CO.

To: THE COMMISSIONER OF PATENTS
Davies & Collison, Melbourne and Canberra.
DECLARATION IN SUPPORT OF A CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

In support of the application No. (a) made by (b), W.R. GRACE & CO.,

for a patent for an invention entitled (c), "PREPARATION OF ZEOLITE"

1. (d) William Woods McDowell, Jr.
   Assistant Secretary
   of (e), W.R. GRACE & CO., a Corporation, organized and existing under the laws of the State of Connecticut, United States of America, of Grace Plaza, 1114, Avenue of the Americas, New York, New York 10036, United States of America, do solemnly and sincerely declare as follows:

   1. (g) I am authorized by the above-mentioned applicant for the patent, to make this declaration on its behalf.

   2. The basic application as defined by Section 141 of the Act was made in the following country or countries on the following dates by the following applicant(s) namely:

      (i) U.S.A. No. 862,031, on (j) 19th December, 1977.

      (k) CURTIS HOMER ELLIOTT, JR., a citizen of the United States of America,

      of (n), 637, Plymouth Road, Baltimore, Maryland 21229, United States of America,

      is the actual inventor of the invention and the facts upon which the applicant(s) is entitled to make the application are as follows:

      (o) by virtue of a Deed of Assignment dated 9th February, 1978, made between the said CURTIS HOMER ELLIOTT, JR., of the one part and W.R. GRACE & CO., of the other part.

   3. The basic application(s) referred to in paragraph 2 of this declaration was the first application made in a Convention country in respect of the invention the subject of the application.

Declared at Columbia, Md. this 15th day of August 1978,

William Woods McDowell, Jr.
Claim 1. A process for preparing a Type Y zeolite which comprises heating a Type Y reaction mixture containing a source of silica, alumina, sodium hydroxide and water in the following mole ratios: 3 to 6 Na_2O: Al_2O_3: 8 to 12 SiO_2: 120 to 200 H_2O, to produce the zeolite and a mother liquor containing excess silica and sodium hydroxide, which comprises combining said mother liquor with aluminium sulphate to obtain a precipitated silica-alumina hydrogel and using said hydrogel as part of a subsequent Type Y reaction mixture.
Name of Applicant: W.R.GRACE & CO.

Address of Applicant: Grace Plaza, 1114 Avenue of the Americas, New York, New York 10036, United States of America.

Actual Inventor: CURTIS HOMER ELLIOTT, JR.


Complete Specification for the invention entitled: "PREPARATION OF ZEOLITE"

The following statement is a full description of this invention, including the best method of performing it known to us:-

- 1 -
The present invention relates to the synthesis of crystalline aluminosilicate zeolites and is concerned to carry out a known process for preparing zeolite, especially a Y zeolite more economically hitherto.

Crystalline aluminosilicate zeolites, including Type Y zeolite, are normally prepared by reacting a source of silica and alumina, sodium hydroxide and water at temperatures of about 100°C. In general, the zeolite formation reaction requires a substantial excess of both silica and sodium hydroxide which remain in the crystallization mother liquor and which must be ultimately utilized or discarded.

Disposal of considerable quantities of silica and sodium hydroxide as dilute sodium silicate solution represents both a considerable economic waste and a substantial pollution control problem. Previous attempts to recycle the excess sodium silicate solution to a Type Y zeolite synthesis process have not been particularly successful. Methods for utilization of zeolite crystallization mother liquor are disclosed in the
following.

United States Patent 3,898,319 to Weber discloses a method for utilizing waste liquor obtained in a Type Y zeolite synthesis wherein the excess silicate is recovered as solid amorphous silica by precipitation with carbon dioxide. The precipitated silica is then utilized to prepare additional Type Y zeolite.

United States 2,882,244 to Milton discloses the preparation of Type X zeolite by a process wherein it is suggested that the mother liquor may be reused after enrichment with proper amounts of reactants to give a properly proportioned reaction mixture.

It is an object of the present invention to provide a method by which the excess silicate present in zeolite mother liquor may be economically and efficiently utilized to produce additional zeolite.

According to the present invention there is provided a process for preparing a Type Y zeolite which comprises heating a Type Y reaction mixture containing a source of silica, alumina, sodium hydroxide and water in the following mole ratios 3 to 6 Na₂O:Al₂O₃:8 to 12 SiO₂:120 to 200 H₂O, to produce the zeolite and a mother liquor containing excess silica and sodium hydroxide characterized in that the said mother liquor is combined with aluminium sulphate to obtain a precipitated silica-alumina hydrogel and using said hydrogel as part of a subsequent Type Y reaction mixture.
The silicate values in the mother liquor can be economically recovered in the form of a precipitated silica-alumina hydrogel which is recycled and efficiently utilized in a zeolite crystallization reaction.

By precipitating and recovering mother liquor silica as freshly precipitated reactive silica-alumina hydrogel and discarding the excess water from the filtration, a waste product is converted into a recyclable raw material of high reactivity for Type Y zeolite production, and the water balance necessary for this recycling to the process is maintained.

The invention will be further explained by reference to the drawing which is a flow-chart of a typical zeolite preparation process which incorporates the present invention. In the process set forth in the drawing a zeolite synthesis, i.e., crystallization, reaction mixture yields a finely divided zeolite suspended in mother liquor which is subjected to a filtration step. During the filtration the zeolite product is recovered and washed with water and subsequently sent to zeolite storage. The filtrate and washings from the zeolite filtration step are then...
conducted to mother liquor storage. The mother liquor at this point comprises primarily a relatively dilute solution of sodium silicate in water. In addition, the mother liquor contains minor quantities of alumina as well as finely divided particles of zeolite. From mother liquor storage the mother liquor is conducted to a tank to which an appropriate amount of aluminium salt solution (preferably aluminium sulphate solution) is added. Upon addition of the aluminium sulphate the silicate present in the mother liquor reacts to form a finely divided silica/alumina hydrogel. Gelation is most effective at pH 6 to 7. The silica/alumina hydrogel which precipitates from the solution is recovered by a filtration step as indicated in the drawing, and the silica/alumina hydrogel is washed with water to remove excess sodium sulphate solution. The sodium sulphate solution is then discarded or further utilized as desired. The silica/alumina hydrogel which at this point comprises a filter cake containing approximately 15-22 percent solids is then placed in a silica/alumina hydrogel slurry storage tank.

As indicated in the drawing the silica/alumina hydrogel slurry, which contains from about 10 to 13 percent by weight silica, 2 to 3 percent by weight alumina, and 78 to 85 percent by weight water,
the rest being Na₂O and Na₂SO₄, is utilized in the zeolite synthesis reaction. Typically the hydrogel is pumped from storage to a crystallization zeolite crystallization reactor in which additional reactants are added such as sodium silicate solution, sodium aluminate solution and preferably finely divided zeolite nucleation centres, i.e. seeds.

A typical Type Y zeolite synthesis reaction mixture is set forth in United States Patent 3,639,099. Typically the reaction mixture will contain the following molar ratios reactants: 3 to 6 Na₂O: Al₂O₃: 8 to 12 SiO₂: 120 to 200 H₂O. This mixture is obtained by mixing solutions of sodium silicate, sodium aluminate and the aforementioned silica/alumina hydrogel which is obtained by combining an acid aluminium sulphate salt with the alkaline metal silicate constituents present in zeolite crystallization mother liquor. In addition the reaction mixture may contain zeolitic nucleation centres having an average particle size below about 0.1 micron which are prepared from a reaction mixture comprising SiO₂, Al₂O₃, Na₂O, and H₂O in amounts which range from about 0.1 to 10 percent by weight of the reaction mixture. The Type Y zeolite synthesis is conducted by heating at temperatures of about 100°C to 105°C for a time long enough to obtain crystallization, typically from 10
to 18 hours.

The nucleation centres are utilized in a preferred practice of the present invention have the following molar ratios:

\[
\begin{align*}
\text{SiO}_2 \text{ to } \text{Al}_2\text{O}_3 & \quad 14 \text{ to } 16 \\
\text{Na}_2\text{O} \text{ to } \text{Al}_2\text{O}_3 & \quad 15 \text{ to } 17 \\
\text{H}_2\text{O} \text{ to } \text{Na}_2\text{O} & \quad 19 \text{ to } 21
\end{align*}
\]

The use of nucleation centres in synthesis of zeolites is in itself well known.

In a preferred embodiment, therefore, the process of the present invention comprises:

(a) preparing an aqueous reaction mixture containing the following reactants providing a source of alumina, silica and sodium hydroxide in the following molar ratio:

\[
3 \text{ to } 6 \text{ Na}_2\text{O} : 8 \text{ to } 12 \text{ SiO}_2 : \text{Al}_2\text{O}_3 : 120 \text{ to } 200 \text{ H}_2\text{O};
\]

(b) including in said reaction mixture zeolitic nucleation centres having the following mol composition:

\[
15 \text{ to } 17 \text{ Na}_2\text{O} : 14 \text{ to } 16 \text{ SiO}_2 : \text{Al}_2\text{O}_3 : 285 \text{ to } 357 \text{ H}_2\text{O};
\]

(c) heating said mixture to obtain Type Y zeolite and mother liquor which contains silicate;

(d) separating said mother liquor from said Type Y zeolite

(e) reacting said mother liquor with aluminium sulphate to precipitate silica-alumina hydrogel;
(f) recovering and washing said hydrogel to remove sodium sulphate; and

(g) including said hydrogel as part of the reaction mixture prepared in step (a).

Type Y zeolite produced by the process of this invention may be used to prepare fluid catalytic cracking catalysts which contain Type Y zeolite in a mixture with inorganic matrix components.

The following example illustrates a specific embodiment of the invention.

**EXAMPLE**

Using the process outlined in the drawing Type Y zeolite was prepared as follows:

A nucleation centre (seed) slurry was prepared as follows:

8.7 lbs (3.95 kg) commercial aluminium trihydrate was dissolved in 101.5 lbs (46 kg) of commercial 50 percent sodium hydroxide solution previously heated to 210°F (99°C). The temperature was maintained until solution was complete after which the sodium aluminate solution was
cooled to 80°F.

177.5 lbs. of 40 percent Be sodium silicate (SiO₂/Na₂O = 3.36) was diluted with 143.3 lbs. water and the mixture was cooled to 80°F.

The sodium aluminate solution was slowly added to the dilute silicate solution being careful to keep the mixture temperature below 90°F and the mixture well agitated. Agitation was continued for half an hour after the two solutions were mixed. The agitator was turned off and the mixture aged for 16 hours at 90°F.

The reactant mol ratio is as follows:

1 Al₂O₃: 16 Na₂O: 15 SiO₂: 3?J H₂O

A Type Y zeolite synthesis batch was prepared as follows:

A total of 341.4 lbs. of 41°Be sodium silicate solution (SiO₂/Na₂O ratio = 3.36) was diluted with 100 lbs. of water. The dilute silicate solution was mixed with 92.2 lbs. commercial aluminium sulphate solution (Al₂O₃ = 7.5%). A sodium aluminate solution was prepared by dissolving 19.2 lbs. of commercial aluminium trihydrate in 27.4 lbs. of commercial 50% sodium hydroxide previously heated to 220°F and maintained at this temperature until total solution occurred. The solution was diluted with 44 lbs. of water and cooled to 100°F. The sodium aluminate
solution was added to the previous silicate and alum mixture. Then 78.4 lbs. of nucleation centres were added to the other reactants. The reaction slurry had the following mol ratio:

\[ 1 \text{ Al}_2\text{O}_3 : 3.1 \text{ Na}_2\text{O} : 9.1 \text{ SiO}_2 : 143 \text{ H}_2\text{O} \]

The slurry of components was agitated and heated to 212°F and maintained at this temperature for 16 hours. X-ray diffraction pattern of the product showed it contained 99 percent Y zeolite and a mol SiO$_2$/Al$_2$O$_3$ ratio of 5.0.

Subsequent to reaction at 100°C for 16 hours a Type Y zeolite was recovered by filtration and a zeolite crystallization mother liquor was obtained which contained the following: 4.6 percent by weight Na$_2$O, 8.8 percent by weight SiO$_2$, <.1 percent by weight Al$_2$O$_3$, 86.6 percent by weight water. The Type Y zeolite was washed with 350 lbs. of water and this water was added to the mother liquor filtrate. 594 lbs. of the above mother liquor filtrate was combined with 142 lbs. of aluminium sulphate solution which contained 7.5 percent by weight Al$_2$O$_3$. On addition of the aluminium sulphate, a silica-alumina hydrogel formed which was recovered by filtration. The hydrogel was washed with 350 lbs. of water to remove soluble sodium sulphate. The precipitated silica
alumina hydrogel was found to contain 12.1 percent by weight $\text{SiO}_2$ and 2.66 percent by weight $\text{Al}_2\text{O}_3$.

A Type Y zeolite synthesis was prepared by combining 266.7 lbs. of the silica alumina hydrogel obtained above with 115.3 lbs. of sodium silicate solution which contained 9.9 percent by weight $\text{Na}_2\text{O}$, 29.1 percent by weight $\text{SiO}_2$; 51.85 lbs. of the seed preparation described above; and 23.3 lbs. of sodium aluminate solution which contained 5.6 lbs. by weight $\text{Na}_2\text{O}$ and 5.5 lbs. by weight $\text{Al}_2\text{O}_3$. The mixture was maintained at a temperature of 100°C for 11½ hours.

The reactant mol ratio was:

$$1 \text{Al}_2\text{O}_3 : 3.3 \text{Na}_2\text{O} : 9.1 \text{SiO}_2 : 142 \text{H}_2\text{O}$$

The Type Y zeolite which formed was recovered by filtration and was found to have a mol silica/alumina ratio of 5.3 and a crystallinity of 101 percent as measured by X-ray diffraction means, as compared to a "standard" sample, the crystallinity of which is set at 100%. Cell size was 24.62Å and $N_2$ surface area was 868 m$^2$/g. The crystallization mother-liquor recovered from the batch was found to contain the following: 5.1 percent by weight $\text{Na}_2\text{O}$, 8.2 percent by weight $\text{SiO}_2$, <1 percent by weight $\text{Al}_2\text{O}_3$ and 86.7 percent by weight water. This mother liquor combined with wash water from Y filtration was reacted with aluminium sulphate solution as indicated above and the recovered silica alumina hydrogen was combined with additional make-up.
ingredients to prepare a zeolite synthesis batch as indicated above. Recovery of the zeolite and mother liquor from several batches indicated that the zeolite was of consistent quality, i.e. essentially the same as that prepared without the use of silica alumina hydrogel and that prepared using the silica alumina hydrogel previously recovered. Hence it is concluded that the process represents a means by which Type Y zeolite of a high quality may be produced using the recovered silicate values from crystallization mother liquor.
The claims defining the invention are as follows.

1. A process for preparing a Type Y zeolite which comprises heating a Type Y reaction mixture containing a source of silica, alumina, sodium hydroxide and water in the following mole ratios:
   3 to 6 Na\(_2\)O: Al\(_2\)O\(_3\): 8 to 12 SiO\(_2\): 120 to 200 H\(_2\)O, to produce the zeolite and a mother liquor containing excess silica and sodium hydroxide, which comprises combining said mother liquor with aluminium sulphate to obtain a precipitated silica-alumina hydrogel and using said hydrogel as part of a subsequent Type Y reaction mixture.

2. A process according to claim 1 in which said reaction mixture includes zeolitic nucleation centres.

3. A process according to claim 1 or 2 which comprises:
   (a) preparing an aqueous reaction mixture containing the following reactants providing a source of alumina, silica and sodium hydroxide in the following molar ratio:
   3 to 6 Na\(_2\)O: 8 to 12 SiO\(_2\): Al\(_2\)O\(_3\): 120 to 200 H\(_2\)O;
   (b) including in said reaction mixture zeolitic nucleation centres having the following mol composition:
15 to 17 Na₂O: 14 to 16 SiO₂: Al₂O₃: 285 to 357 H₃O;
  
(c) heating said mixture to obtain Type Y zeolite and mother liquor which contains silicate;
  
(d) separating said mother liquor from said Type Y zeolite;
  
(e) reacting said mother liquor with aluminium sulphate to precipitate silica-alumina hydrogel;
  
(f) recovering and washing said hydrogel to remove sodium sulphate; and
  
(g) including said hydrogel as part of the reaction mixture prepared in step (a).

4. A process according to claim 3 in which the heating step (c) is conducted at a temperature of 100 to 105°C.

5. A process according to claim 1, substantially as described in the Example.

6. A Type Y zeolite whenever prepared by a process according to any preceding claim.

DATED this 30th day of September, 1981

W.R. GRACE & CO.

by its Patent Attorneys
DAVIES & COLLISON
SODIUM SILICATE SOLUTION

ZEOLITE SYNTHESIS (CRYSTALLIZATION)

ZEOLITE FILTRATION

ZEOLITE STORAGE

SODIUM ALUMINATE SOLUTION

WASH WATER

MOTHER LIQUOR STORAGE AND WASH WATER

ALUMINUM SULFATE SOLUTION

SILICA-ALUMINA HYDROGEL FORMATION

SILICA-ALUMINA HYDROGEL SLURRY STORAGE

SILICA-ALUMINA HYDROGEL FILTRATION AND WASHING

FILTRATE TO SEWER (SOLUBLES AND WASH WATER)