4/

(NON-CONVENTION. By one or more persons and/or a Company.)

606743

Form 1.

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

APPLICATION FOR A PATENT

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address (es).

~~I~~/We (1) UNION CARBIDE CORPORATION of Old Ridgebury Road, Danbury, State of Connecticut 06817, United States of America

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2)

PREPARATION OF ULTRAHYDROPHOBIC Zeolite

which is described in the accompanying ~~PROVISIONAL~~ COMPLETE specification.

~~My~~/Our address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys, 50 Queen Street, Melbourne, Victoria, Australia.

DATED this 2nd day of September 19 88

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 20-11-90

(3) Signature (s) of Applicant (s) or Seal of Company and Signatures of its Officers as prescribed by its Articles of Association.

(3) UNION CARBIDE CORPORATION

by

Ian A. Scott

02/09/88

COMMONWEALTH OF AUSTRALIA

SC-15727-AS

Patents Act 1952-1969

DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT OR PATENT OF ADDITION

(1) Here insert (in full) Name of Company.

In support of the Application made by(1) UNION CARBIDE CORPORATION

(2) Here insert title of Invention.

for a Patent ..... for an invention entitled:(2) PREPARATION OF ULTRAHYDROPHOBIC ZEOLITE

(3) Here insert full Name and Address, of Company Official authorized to make declaration.

I,(3) Timothy N. Bishop

of 39 Old Ridgebury Road, Danbury, State of Connecticut (06817) United States of America

do solemnly and sincerely declare as follows:

1. I am authorized by(1) UNION CARBIDE CORPORATION

the applicant for the patent ..... to make this declaration on its behalf.

(4) Here insert (in full) Name and Address of Actual Inventor or Inventors.

2. (4) Mark Thomas Staniulis, residing at: Rancho Drive, Peekskill (10566) State of New York, United States of America

is / are

the actual inventor of the invention and the facts upon which(1) UNION CARBIDE CORPORATION

is entitled to make the application, are as follow:

The said(1) UNION CARBIDE CORPORATION

(5) Full Name of Actual Inventor or Inventors

is the assignee of the said(5) invention from said actual inventor

Paragraph 2 should be completed by showing devolution of title, e.g., "The said (Name of applicant) is the assignee of the said (Name of inventor(s))".

DECLARED at Danbury, Ct., U.S.A.

this 18th day of August 1988

UNION CARBIDE CORPORATION

(6) By: Timothy N. Bishop

(6) Signature

Timothy N. Bishop

(12) PATENT ABRIDGMENT (11) Document No. AU-B-21814/88
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PREPARATION OF ULTRAHYDROPHOBIC ZEOLITE

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(56) Prior Art Documents
EP 220616
EP 124120
EP 139291

(57) Claim

1. A process for the preparation of ultrahydrophobic zeolites wherein a Y zeolite is subjected to a secondary synthesis procedure followed by a single steaming step.

7. An ultrahydrophobic zeolite comprising a Y zeolite which has been subjected to a secondary synthesis procedure followed by a single steaming step.

COMMONWEALTH OF AUSTRALIA 606743 Form 10

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

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Complete Specification Lodged:
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This document contains the amendments made under Section 49 and is correct for printing.

Name of Applicant : UNION CARBIDE CORPORATION

Address of Applicant : Old Ridgebury Road, Danbury, State of Connecticut 06817, United States of America

Actual Inventor: MARK THOMAS STANIULIS

Address for Service : EDWD. WATERS & SONS,
50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

PREPARATION OF ULTRAHYDROPHOBIC ZEOLITE

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

PREPARATION OF ULTRAHYDROPHOBIC ZEOLITE

Field of the Invention

The present application relates to the field of ultrahydrophobic zeolites and particularly to the field of Y zeolites which have been subjected to a secondary synthesis procedure, followed by a single steaming step. The preparation procedure of the present invention allows one to prepare a LZ-210 ultrahydrophobic molecular sieves without the necessity of utilizing a stabilizing step and an ammonium exchange step.

Background of the Invention

Hydrophobic molecular sieves have been employed to a great advantage as catalyst supports for use in various catalyst systems including Fischer-Tropsch type catalysts and hydrocracking catalysts.

Work done by Earls disclosed in detail in commonly assigned U.S. application Serial No. 880,561, filed February 23, 1978 (corresponding to Canadian Patent No. 1,131,195, Issued June 9, 1982), indicates that in order to produce UHP-Y (ultrahydrophobic-Y) it is necessary to ammonium exchange zeolite Y after the first steaming step, otherwise the material loses a substantial fraction of its X-ray crystalliosity, and the framework IR bands become broader and ill defined regardless of the steaming procedure.

It would be an important contribution to the art if an alternate procedure were developed to produce ultrahydrophobic zeolite without the need for subjecting the material to a stabilizing ammonium exchange step. Amongst the known prior art references of which the applicant is aware are the following:

US Patent No. 3,293,172 - Issued December 20, 1966 - Zeolite Z-14US and Method of Preparation Thereof - C.V. McDaniel and P.K. Maher.

U.S. Patent No. 3,447,070 - Issued June 10, 1969 - Stabilized Zeolites - C.V. McDaniel and P.K. Maher.

U.S. Patent Application Serial No. 880561 - Filed February 23, 1978 - Ultrahydrophobic Zeolite - D. Earls.

U.S. Patent No. 4,401,556 Issued August 30, 1983 - Midbarrel Hydrocracking - R.D. Bezman and J.A. Rabo.

U.S. Patent No. 3,506,400 Issued in 1970 - re. Acid Extraction of Steamed y - P.E. Eberly, Jr.

Although none of the foregoing references teach the present invention, various aspects of these references, which are understood to be within the knowledge of one skilled in the are, form the basis for what follows:

Summary of the Invention

The present invention is directed to a procedure for producing a ultrahydrophobic zeolite and particularly to the field of Y zeolites which have been subjected to a secondary synthesis procedure, followed by a single steaming step. The preparation procedure of the present invention allows one to prepare a LZ-210 ultrahydrophobic molecular

sieves without the necessity of utilizing a stabilizing step and an ammonium exchange step.

Description of the Invention

We have found that by using a Y zeolite that has been subjected to the LZ-210 (disclosed in U.S. Patent Nos. 4,503,023, Issued March 5, 1985, and 4,610,856, Issued September 9, 1986) secondary synthesis procedure a quality ultrahydrophobic zeolite can be made without a ammonium exchange and second steaming as required by the ultrahydrophobic zeolite Y (UHP-Y) process.

A set of experiments were done, aimed at making HP-Y (hydrophobic Y) then acid extracting it to make Hyper Y from Y-72, Y-82 and LZ-210 starting materials. Using the procedures outlined by Earls in his UHP-Y work (U.S. Application Serial No. 880,561, Filed February 23, 1978). The work with Y-72 and Y-82 was done to supply baseline information so a comparison could be made with LZ-210. The Y-72 and Y-82 work supported the Earls UHP-Y work by showing that in order to make UHP-Y it is necessary to NH_4^+ exchange zeolite Y after the first steaming.

EXAMPLES

While the invention has been generally described above, the details of the present invention will be better understood by recourse by the following examples which serve to illustrate the present invention.

EXAMPLE I

Starting with commercial Y-72, Y-82 was made by ammonium exchanging the Y-72. This was done to eliminate variations in the Y-62 or the steaming conditions in making the Y-72. These represent the controls of the following Examples.

EXAMPLE II

LZ-210 having a SiO_2/Al_2O_3 ratio 9.1 was synthesized (using the preparation disclosed in U.S. Patent No. 4,503,023, Issued March 5, 1985) in a semi-works facility using a aluminum sulfate crystal wash treatment to help wash out the fluoride used in the secondary synthesis step, as disclosed by R.S. Hinchey, U.S. Patent No. 4,597,956, Issued July 1, 198 .

EXAMPLE III

Samples of the Y-72, Y-82 and LZ-210, prepared in Examples I-II were then stirred in 6 N HCl for 3 hours at room temperature and then characterized. While the acid extraction destroyed the crystallinity of all three zeolites, almost all the alumina was extracted from the LZ-210. The Y-72 and Y-82 retained a 4.5 wt % alumina. (See Table 1).

TABLE 1

Properties of 6N HCL Extracted Zeolites

Zeolite	Wt % Na_2O	Wt % $(NH_4)_2O$	Wt % SiO_2	Wt % Al_2O_3
Y-72	0.17	<0.05	95.9	4.3
Y-82	0.11	0.17	95.2	4.5
LZ-210	0.03	0.05	100.0	0.18

EXAMPLE IV

Two different steaming conditions were investigated; 1) a three hour dry air calcination of the zeolites at 400° C then cooling to room temperature in a desicator, followed by steaming at 750° C in a preheated tube furnace with 100% steam for one hour. 2) Steaming the zeolite at 750° C for 16 hours in 100% steam. The tube furnace was preheated to 750° C prior to inserting the sample into the furnace.

Following the steaming by either procedure the products were acid extracted with either concentrated HCL twice at room temperature for one hour then 16 hours or twice with 6 N HCL solutions at reflux for four hours and three hours respectively.

As a class of products, the steamed Y-72 samples lost at least a substantial fraction of their X-ray crystallinity. The framework infrared spectra are broad and ill defined regardless of the steaming and acid extraction procedures.

The steamed Y-82 samples maintained their X-ray crystallinity and the framework infrared spectra were sharpened as would be expected for a typical UHP-Y. In all cases the acid extracted product shows a higher SiO_2/Al_2O_3 ratio for the steamed Y-82 product than the steamed Y-72 (Table 2).

The LZ-210 samples maintained their x-ray crystallinity and the framework infrared spectra were sharpened as might be expected for a typical UHP-Y made from a Y-82 by known procedures. The difference lies in the fact that the LZ-210, which was only steamed once, displayed properties similar to the Y-82, which was steamed and ammonium exchanged and steamed again. Another significant difference between the LZ-210 and Y-82 was the Na_2O level. The LZ-210 used contained 1.2 wt % Na_2O which is significantly higher than the 0.25 wt % of Y-82. Contrary to the teachings of the art which has taught that the Na_2O level must be below 1.0 wt %. All prior work of which the applicant is aware has taught that an upper limit of 6 on SiO_2/Al_2O_3 ratio was necessary to produce a UHP-Y material. Thus the use of an LZ-210 with a SiO_2/Al_2O_3 ratio of 8.0 and above and high Na_2O level is completely contraindicated by known prior art.

TABLE 2

Characteristics of Steamed Samples

		a_0	% Crystal Retention Area	Ht.	Chem. SiO/Al_2O_3	H_2O Cap 4.6 tore	Stm. Hrs.	Acid Concen.
Y-72								
Sample	1	24.21	65.2	57.2	27	9.0	1	conc. HCl
	2	24.13	33.2	19.8	45	6.6	1	6N HCl
	3	24.26	9.1	5.5	9	3.8	16	conc. HCl
	4	24.27	7.7	5.5	12	5.6	16	6N HCl
Y-82								
Sample	1	24.26	94.9	86.6	33	5.8	1	conc. HCl
	2	24.26	93.7	85.1	79	7.6	1	6N HCl
	3	24.27	91.7	80.9	21	4.1	16	conc. HCl
	4	24.27	84.7	72.6	113	2.5	16	6N HCl
LZ-210 (9.1)								
Sample	1	24.28	92.7	79.7	50	4.1	1	conc. HCl
	2	24.24	105.2	99.4	68	1.7	1	6N HCl
	3	24.26	76.3	66.1	18	<0.1	16	conc. HCl
	4	24.26	69.9	59.9	23	1.4	16	6N HCl

EXAMPLE V

LZ-210 samples with SiO_2/Al_2O_3 ratio of 6.2 and 9.0 were steamed using the Y-72 procedure (600° C, 100% steam for 1 hr.), then ammonium exchanged making them like a Y-82. The samples were steamed at 750° C 100% steam for 1 hr. to make a UHP/Y type product. The x-ray diffraction pattern showed very highly crystalline zeolites with a IR framework typical of a ultrahydrophobic Y zeolite. The surface areas are about 100 and 150 m^2/g greater than a typical UHP/Y for LZ-210 6.2 and 9.0 respectively. So even when LZ-210 is steamed to make a UHP/Y it yields a more stable crystalline zeolite.

It has been found that, preferably the ultrahydrophobic LZ-210 zeolites of the present invention will have a SiO_2/Al_2O_3 ratio above 8, more preferably they will have a ratio of from about 9-15 and still more preferably they will have a ratio of from about 9-11.

Steamed ultrahydrophobic LZ-210 of the present invention is a new zeolitic material with a more variable range of mild acid strength and hydrophobicity than conventional UHP-Y.

While the invention has been described with respect to the various embodiments, it is to be understood that the invention is not limited thereto and can be practiced within the scope of the various claims.

~~XXXX~~CLAIMS~~XXX~~

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

~~XXClaim~~

1. A process for the preparation of ultrahydrophobic zeolites wherein a Y zeolite is subjected to a secondary synthesis procedure followed by a single steaming step.

2. A process according to claim 1 wherein the secondary synthesis procedure is an LZ-210 secondary synthesis.

3. The process of claim 2 wherein the LZ-210 produced has a SiO_2/Al_2O_3 ratio equal to 8 or above.

4. The process of claim 2 wherein the LZ-210 produced has a SiO_2/Al_2O_3 ratio of from ~~about~~ 9.0 to 15.0.

5. The process of claim 2 wherein the LZ-210 produced has a SiO_2/Al_2O_3 ratio of from ~~about~~ 9.0 to 11.0.

6. A process for the preparation of an ultrahydrophobic zeolite according to claim 1 wherein the UHP zeolite produced has a SiO_2/Al_2O_3 ratio above ~~about~~ 8 and has an x-ray diffraction pattern similar to that of a Y zeolite.

7. An ultrahydrophobic zeolite comprising a Y zeolite which has been subjected to a secondary synthesis procedure followed by a single steaming step.

8. An ultrahydrophobic zeolite according to claim 7 wherein the secondary synthesis procedure is an LZ-210 synthesis procedure.

9. An ultrahydrophobic zeolite according to claim 7, which has SiO_2/Al_2O_3 ratio above 8.

10. An ultrahydrophobic zeolite according to claim 7 which has a SiO_2/Al_2O_3 ratio of from ~~about~~ 9 to 15.

11. An ultrahydrophobic zeolite according to claim 7 which has a SiO_2/Al_2O_3 ratio of from ~~about~~ 9 to 11.

12. An ultrahydrophobic zeolite according to claim 7 which has a SiO_2/Al_2O_3 ratio above ~~about~~ 8 and has an X-ray diffraction pattern similar to that of a Y zeolite.

13. A catalyst comprising as a support an ultrahydrophobic zeolite produced in accordance with the process of claim 1.

14. A catalyst comprising as a support an ultrahydrophobic zeolite produced in accordance with claim 1, said ultrahydrophobic zeolite having a SiO_2/Al_2O_3 ratio above 8.

15. A catalyst comprising as a support an ultrahydrophobic zeolite produced in accordance with claim 1, said ultrahydrophobic zeolite having a SiO_2/Al_2O_3 ratio of from ~~about~~ 9 to 15.

16. A catalyst comprising as a support an ultrahydrophobic zeolite produced in accordance with claim 1, said ultrahydrophobic zeolite having a SiO_2/Al_2O_3 ratio of from ~~about~~ 9 to 11.

17. A process according to claim 3 wherein the product is subsequently cation exchanged.

18. A process according to claim 17 wherein the cation used is ammonium.

19. A process according to claim 3 wherein the product is subsequently acid extracted.

20. A process according to claim 19 wherein the product is acid extracted with HCL.

21. A catalyst comprising as a support an ultrahydrophobic zeolite produced in accordance with claim 17.

22. A catalyst comprising as a support an ultrahydrophobic zeolite produced in accordance with claim 19.

DATED this 2nd day of September 1988.
UNION CARBIDE CORPORATION

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