

SPECIFICATION

Method of producing zeolites

- 5 The invention relates to a method for synthesizing zeolite ZSM-5 or ZSM-11.

Zeolites ZSM-5 and ZSM-11, like zeolites Beta, TEA mordenite and ZSM-12, are usually crystallized from a solution containing organic cations, particularly

- 10 alkyl ammonium cations, as described in US specifications 3,702,886 and 3,709,979 respectively.

In accordance with the invention, there is provided a method for producing a catalyst containing ZSM-5 or ZSM-11 crystalline aluminosilicate containing no
15 more than about 0.2% by weight of nitrogen, which comprises carrying out the reaction to form said zeolite in the presence of from 0.01 to 10 weight per cent of ZSM-5 or ZSM-11 seeds, and mixtures thereof with NH_4OH and optionally alcohol. ZSM-5
20 seeds produce ZSM-5 and ZSM-11 seeds produce ZSM-11, whether used alone or in a mixture. The zeolite produced is combined with a porous matrix to yield a catalyst comprising 1% to 95% by weight zeolite.

- 25 The aliphatic alcohol preferably is an alcohol containing 2 to 5 carbon atoms. Illustrative are ethanol, propanol, butanol and pentanol. It is contemplated that the alcohols may be straight or branch chain.

- ZSM-5 and ZSM-11 seeds may be from previously
30 prepared batches of ZSM-5 and ZSM-11 made by prior art methods. Alternatively, seeds of ZSM-5 and ZSM-11 prepared by the method of this invention may be used. Furthermore, it has been discovered that when subsequent batches of ZSM-5 or ZSM-11
35 zeolites are made in the same equipment, the residual zeolite can be sufficient to supply the requisite amount of seeds.

- Only a small amount of seeds are needed for the practice of this invention. Generally, from about
40 0.01% by weight to about 10% by weight of final product is sufficient. We prefer, however, to use from about 1% by weight to 6% by weight.

- ZSM-5 has the characteristic X-ray diffraction pattern set forth in Table 1 of U.S. 3,702,886, whether
45 produced by prior art methods or by the method of this invention. ZSM-5 compositions (as well as ZSM-11 compositions) can also be identified in terms of mole ratios of oxides as follows:
 $0.9 \pm 0.2 \text{ M}_2\text{O} : \text{W}_2\text{O}_3 : \text{X YO}_2 : \text{ZH}_2\text{O}$

- 50 wherein M is a cation, n is the valence of said cation, W is selected from the group consisting of alumina and gallium, Y is selected from the group consisting of silicon and germanium, X is from about 5 to about
55 3000 and Z is from 0 to 40. In a preferred form as synthesized by prior art methods the zeolite has a formula, in terms of mole ratios of oxides as follows:
 $0.9 \pm 0.2 \text{ M}_2\text{O} : \text{Al}_2\text{O}_3 : \text{X SiO}_2 : \text{ZH}_2\text{O}$

- 60 wherein M is selected from the group consisting of a mixture of alkali metal cations, especially sodium, and tetraalkylammonium cations, the alkyl groups of which preferably contains 2-5 carbon atoms. In this preferred embodiment of ZSM-5, W is aluminum
65 and Y is silicon. Also the preferred silica/alumina

ratio is from about 15 to about 900. More preferably, the silica/alumina ratio is from about 30 to about 350.

- According to the prior art zeolite ZSM-5 is prepared by forming a solution containing water, tetra-
70 propyl ammonium hydroxide and the elements of sodium oxide, an oxide of aluminum or gallium and an oxide of silica, and having a composition, in terms of mole ratios of oxides, falling within the following ranges:

TABLE A

	Broad	Preferred	Particularly Preferred
OH-			
SiO ₂	0.07-1.0	0.1-0.8	0.2-0.75
RA ⁺			
(R _n N ⁺ + Na ⁺)	0.2-0.95	0.3-0.9	0.4-0.9
H ₂ O			
OH-	10-300	10-300	10-300
YO ₂			
W ₂ O ₃	5-100	10-60	10-40

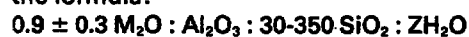
- 75 The solution is maintained at reaction conditions until the crystals of the zeolite are formed. Thereafter the crystals are separated from the liquid and recovered. Typical reaction conditions consist of a temperature of from about 75°C to 175°C for a period of
80 about six hours to 60 days. A more preferred temperature range is from about 90 to 150°C, with the amount of time at a temperature in such range being from about 12 hours to 20 days.

- According to the prior art zeolite ZSM-11 can be
85 prepared by forming a solution of (R_nX)₂O, sodium oxide, an oxide of aluminum or gallium, an oxide of silicon or germanium and water and having a composition, in terms of mole ratios of oxides, falling within the following ranges:

TABLE B

	Broad	Preferred
YO ₂		
W ₂ O ₃	10-150	20-90
Na ₂ O		
YO ₂	0.05-0.70	0.05-0.40
(R _n X) ₂ O		
YO ₂	0.02-0.20	0.02-0.15
H ₂ O		
Na ₂ O	50-800	100-600

- 90 wherein R_nX is a cation of a quaternary compound of an element of Group 5A of the Periodic Table, W is aluminum or gallium and Y is silicon or germanium maintaining the mixture until crystals of the zeolite are formed. Preferably, crystallization is performed
95 under pressure in a stirred autoclave or static bomb reactor. The temperature ranges from 100°C to 200°C generally, but at lower temperatures, e.g., about 100°C, crystallization time is longer. Thereafter the crystals are separated from the liquid and recovered.
100 The zeolite is preferably an aluminosilicate, having the formula:



- wherein M is an alkali metal or an alkaline earth
105 metal and Z is 0 to 40.

The ZSM-5 made by the method of this invention is, as is the same zeolite made according to the prior

art, preferably formed as the aluminosilicate, and it can be prepared utilizing materials which supply the elements of the appropriate oxide. Such materials include aluminum sulfate, a mineral acid such as sulfuric acid, sodium aluminate, alumina, sodium silicate, silica hydrosol, silica gel, silicic acid, sodium hydroxide, along with the reagents of the improved method of this invention. It will be understood that each oxide component utilized in the reaction mixture for preparing ZSM-5 can be supplied by one or more initial reactants, and they can be mixed together in any order. For example, sodium oxide can be supplied by an aqueous solution of sodium hydroxide or an aqueous solution of sodium silicate.

The reaction mixture can be prepared in either a batchwise or continuous manner. Crystal size and crystallization time of the ZSM-5 composition will vary with the nature of the reaction mixture employed.

ZSM-11 made by the method of this invention is also preferably made as the aluminosilicate utilizing reactants which supply the needed oxides. Thus, the reaction mixture may comprise reactants to yield an alkalimetal oxide, e.g., sodium oxide, alumina and silica.

ZSM-5 and ZSM-11 zeolites are useful as cracking and hydrocracking catalysts as well as catalysts for isomerization and dewaxing. However, in order to increase their range of activities and their stability, it is necessary to remove the original metal ion, usually sodium. The original metal of most zeolites can be removed by conventional exchange procedures, as by multiple exchanges. Some zeolites, ZSM-5 and ZSM-11 included, are not susceptible to this method of exchange, the sodium content reaching a plateau and remaining there regardless of the number of additional exchanges. It has been previously discovered that calcination of the zeolite by removing the organic N-containing cations "frees" the sodium so it can thereafter be removed easily. Typical replacing cations would include hydrogen, ammonium and metal cations, including mixtures of the same. Of the replacing cations, particular preference is given to cations of hydrogen, ammonium, rare earth, magnesium, zinc, calcium, nickel, and mixtures thereof, generally employed in the form of their salts, preferably the chlorides, nitrates or sulfates. Although not necessary, calcination may still be assist in removing the sodium cation from the products of this invention.

Following contact with the salt solution of the desired replacing cation, the zeolites prepared in accordance with this invention may be washed with water and dried at a temperature ranging from 150°F (65°C) to about 600°F (315°C) and thereafter may be heated in air or other inert gas at temperatures ranging from about 500°F (260°C) to 1500°F (815°C) for periods of time ranging from 1 to 48 hours or more.

It is also possible to treat the zeolite with steam at elevated temperatures ranging from 800°F (426°C) to 1800°F (982°C) and preferably 1000°F (537°C) and 1500°F (815°C), if such is desired. The treatment may be accomplished in atmospheres consisting partially or entirely of steam. A similar treatment can be accomplished at lower temperatures and elevated

pressures, e.g., 350-700°F (176-371°C) at 10 to about 200 atmospheres (68.94 to about 1378.95 kPa).

The zeolites produced in the method of this invention may be used in a porous matrix. The zeolites can be combined, dispersed or otherwise intimately admixed with a porous matrix in such proportions that the resulting product contains from 1% to 95% by weight, and preferably from 1 to 70% by weight of the zeolite in the final composite.

The term "porous matrix" includes organic compositions with which the aluminosilicates can be combined, dispersed or otherwise intimately admixed wherein the matrix may be active or inactive. It is to be understood that the porosity of the compositions employed as a matrix can either be inherent in the particular material or it can be introduced by mechanical or chemical means. Inorganic compositions especially those of a siliceous nature are preferred. Of these matrices inorganic oxides such as clay, chemically treated clay, alumina, silica, silica-alumina, etc. are particularly preferred because of their superior porosity, attrition resistance and stability. More preferably, alumina is the matrix, and it is preferably combined with the zeolite prior to calcination.

Techniques for incorporating the zeolites in a matrix are conventional in the art and are set forth in U.S. Specification 3,140,253.

The following Examples serve to illustrate the scope of the invention showing that ZSM-5 crystalline aluminosilicates containing very low levels of organic nitrogen can be made by various techniques. It will be understood that the examples are not intended in any way to place a limitation on the invention.

A typical preparation of ZSM-5 according to the invention is given hereinbelow. The details and results for the product are listed in the Tables. An acid alumina solution comprising $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 98% H_2SO_4 and of H_2O was added to a sodium silicate solution made by mixing Q-Brand sodium silicate (28.8% SiO_2 , 8.9% Na_2O , 62.4% H_2O) and water. To the resultant gel was added the further component by which the invention is characterized. The gel was mixed until homogeneous and crystallized at autogenous pressure in a stirred autoclave at 350°F (176°C) for 24 hours. The resultant solid material was water washed and dried at 230°F (110°C).

Several of these examples were ion exchanged with ammonium salts without any prior calcination to show that sodium was easily replaced in such a procedure. Results were excellent as indicated in the appropriate tables.

Table 1

Seeds in absence of
alcohol or hydroxide

Examples	1	2
Starting Components, gms.		
A. Q-Brand	45.0	450
H ₂ O	56.3	563
B. Al ₂ (SO ₄) ₃ · 18H ₂ O	1.54	15.4
H ₂ SO ₄ (98%)	3.75	37.5
H ₂ O	77.0	770
C. ZSM-5 seeds (19.3% Solids)	3.25	32.5
Mixed Ratio — Moles		
Na ₂ O	8.6	8.6
Na ₂ SO ₄	19.0	19.0
Al ₂ O ₃	1.0	1.0
SiO ₂	94.0	94.0
H ₂ O	3870	3870
ZSM-5, % Final Product	5.7	5.7
Crystallization	Static	Stirred
Temp. °F (°C)	350(176)	350(176)
Time, hrs.	96	24
Product		
X-Ray Analysis	ZSM-5	ZSM-5
% Crystallinity	90	105
Composition, wt %		
N	0.02	0.03
Na	1.50(1)	1.79(1)
Al ₂ O ₃	2.40	2.44
SiO ₂		97.2
Composition, Molar Ratio		
Na ₂ O	1.38	1.63
Al ₂ O ₃	1.0	1.0
SiO ₂		67.8
Catalytic Properties		
(M-Forming Screening Test) (600°F (315°C)), 400 psig (2859.23kPa) 15 WHSV, 3/1 H ₂ /HC, 1.5 gms. cat.)		
Type Catalyst		H ⁺ (2)
n-Heptane Conv., wt%		89.6
Benzene, Conv., wt%		30.8
C ₇ + Aromatics Prod., wt%		29.2
Selectivity		0.31
(1) This value is reduced to 0.087% on Example 1 and 0.04% on Example 2 when exchanged with NH ₄ Cl without any precalcination.		
(2) Pre-calcination, 1000°F (537°C) + NH ₄ exchange.		

Table 2

Ethanol
+NH₄OH

Example	3
Mix Components, gms	
A. Q-Brand	362
H ₂ O	478
B. Al ₂ (SO ₄) ₃ · 18H ₂ O	13.1
H ₂ SO ₄ (98%)	31.9
H ₂	658
C. Ethanol	131
NH ₄ OH, Conc., ml	148
Mole Ratio of Mix	
Ethanol	146
NH ₄ OH	114
Na ₂ O	8.6
Al ₂ O ₃	1.0
SiO ₂	94.0
H ₂ O	3870
Na ₂ SO ₄	19.0
Crystallization	Stirred
Temp., °F (°C)	350 (176)
Time, hrs	21
Product	
X-Ray Analysis	ZSM-5
% Cryst.	110
Composition, wt %	
N	0.044
Na	0.94
Al ₂ O ₃	2.41
SiO ₂	96.1
Composition, mole Ratio	
N ₂ O	0.07
Na ₂ O	0.87
Al ₂ O ₃	1.00
SiO ₂	67.8
Catalytic Properties	
M-Forming Screening Test (600°F (315°C), 400 psig (2859.23kPa) 15 WHSV, 3/1 H ₂ /HC) (1.5 g catalyst-charged 50/50 wt n-heptane/benzene)	
Type Catalyst	H ⁺ (1)
n-Heptane Conv., wt%	76.6
Benzene Conv., wt%	26.4
C ₇ + Aromatics Prod., wt%	24.9
Selectivity	0.31
(1) NH ₄ Exch., 210°F (98°C) without pre-calcination Na ⁺ = 0.01%	

Table 3
Ethanol + NH₄OH + Seeds

Example	4	5	6	7	8
Mix Components — gms.					
A. Q-Brand	360	45	45	255.2	45
H ₂ O	450	56.3	56.3	280	56.3
Ludox (TM) (29.5% SiO ₂)	450	56.3	56.3	280	56.3
B. Al ₂ (SO ₄) ₃ · 18H ₂ O	12.42	1.54	1.54	20.0	6.0
H ₂ SO ₄	30.0	3.75	3.75	20.0	2.25
H ₂ O	616	77.0	77.0	480	77.0
C. Ethanol	124	15.5	15.5	124	15.5
NH ₄ OH conc., ml.	140	17.5	17.5	140	17.5
D. ZSM-5 seeds (19.3% solids)	26.0	3.25	3.25	21.0	3.25
Mole Ratio of Mix					
Ethanol	73	73	146	90	336
NH ₄ OH	115	115	115	69	28.5
Na ₂ O	8.6	8.6	8.6	2.56	1.66
Al ₂ O ₃	1.0	1.0	1.0	1.0	1.0
SiO ₂	94.0	94.0	94.0	40.8	23.9
H ₂ O	3870	2870	3870	1700	990
Na ₂ SO ₄	19.0	19.0	19.0	9.7	5.4
ZSM-5 Seeds, % Final Product	5.7	5.7	5.7	5.5	4.5
Crystallization	stirred	static	static	stirred	static
Temp., °F (°C)	350 (176)	446 (230)	255 (123)	350 (176)	400 (204)
Time, hrs.	17	22	334	120	96
Product					
X-Ray Analysis	ZSM-5	ZSM-5	ZSM-5	ZSM-5	ZSM-5
% Cryst.	95	110	95	80	65
Composition, wt%					
N	0.053	0.13	0.19	0.011	0.016
C	0.42				
Na	1.3(1)	0.98		1.7(1)	3.2
Al ₂ O ₃	2.53	2.13		4.36	6.40
SiO ₂	97.2	95.6		92.8	88.2
Composition, mole ratio					
N ₂ O	0.08	0.24		0.01	
Na ₂ O	1.14	1.02	0.87	1.1	
Al ₂ O ₃	1.0	1.0		1.00	1.0
SiO ₂	65.3	76.2	36.1	23.4	
Catalytic Properties					
M-Forming Screening Test (600°F (315°C), 400 psig (2859kPa), 15 WHSV, 3/1 H ₂ /HC 1.5 g. catalyst — charge 50/50 wt. N - Heptane/Benzene)					
Type Catalyst	H ⁺ (2)	H ⁺ (2)			
n - Heptane Conv., wt%	80.2	95.0			
Benzene Conv., Wt%	32.0	27.8			
C ₇ ⁺ Aromatics Prod., wt	28.9	27.4			
Selectivity	0.32	0.28			

(1) These values are reduced to 0.03% for Example 4 and 0.05% for Example 7. When uncalcined samples are exchanged with NH₄Cl.

(2) Calcination 1000°F (537°C) + NH₄⁺ Exchange

CLAIMS

1. A method of producing a catalyst containing zeolite ZSM-5 or ZSM-11 which method comprises reacting a mixture comprising sources of silica and alumina, alkali metal and water until crystals of the zeolite form, said mixture further comprising from 0.01 to 10 weight percent, relative to zeolite obtained, of seeds of that zeolite, said obtained zeolite containing no more than 0.2 weight percent of organic nitrogen, and combining the zeolite with a porous matrix in such proportion that the resulting catalyst contains from 1% to 95% by weight of the zeolite.

2. A method according to claim 1 further characterized in that the reaction mixture contains

ammonium hydroxide.

3. A method according to claim 2 further characterized in that the reaction mixture contains a two- to five-carbon atom alcohol.

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Table 3
Ethanol + NH₄OH + Seeds

Example	4	5	6	7	8
Mix Components — gms.					
A. Q-Brand	360	45	45	255.2	45
H ₂ O	450	56.3	56.3	280	56.3
Ludox (TM) (29.5% SiO ₂)	450	56.3	56.3	280	56.3
B. Al ₂ (SO ₄) ₃ · 18H ₂ O	12.42	1.54	1.54	20.0	6.0
H ₂ SO ₄	30.0	3.75	3.75	20.0	2.25
H ₂ O	616	77.0	77.0	480	77.0
C. Ethanol	124	15.5	15.5	124	15.5
NH ₄ OH conc., ml.	140	17.5	17.5	140	17.5
D. ZSM-5 seeds (19.3% solids)	26.0	3.25	3.25	21.0	3.25
Mole Ratio of Mix					
Ethanol	73	73	146	90	336
NH ₄ OH	115	115	115	69	28.5
Na ₂ O	8.6	8.6	8.6	2.56	1.66
Al ₂ O ₃	1.0	1.0	1.0	1.0	1.0
SiO ₂	94.0	94.0	94.0	40.8	23.9
H ₂ O	3870	2870	3870	1700	990
Na ₂ SO ₄	19.0	19.0	19.0	9.7	5.4
ZSM-5 Seeds, % Final Product	5.7	5.7	5.7	5.5	4.5
Crystallization	stirred	static	static	stirred	static
Temp., °F (°C)	350 (176)	446 (230)	255 (123)	350 (176)	400 (204)
Time, hrs.	17	22	334	120	96
Product					
X-Ray Analysis	ZSM-5	ZSM-5	ZSM-5	ZSM-5	ZSM-5
% Cryst.	95	110	95	80	65
Composition, wt%					
N	0.053	0.13	0.19	0.011	0.016
C	0.42				
Na	1.3(1)	0.98		1.7(1)	3.2
Al ₂ O ₃	2.53	2.13		4.36	6.40
SiO ₂	97.2	95.6		92.8	88.2
Composition, mole ratio					
N ₂ O	0.08	0.24		0.01	
Na ₂ O	1.14	1.02	0.87	1.1	
Al ₂ O ₃	1.0	1.0		1.00	1.0
SiO ₂	65.3	76.2	36.1	23.4	
Catalytic Properties					
M-Forming Screening Test (600°F (315°C), 400 psig (2859kPa), 15 WHSV, 3/1 H ₂ /HC 1.5 g. catalyst — charge 50/50 wt. N - Heptane/Benzene)					
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