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(54) **Synthesis of ZSM-type zeolites**

(57) A crystalline zeolite of the ZSM family is prepared by acid-leaching a calcined clay mineral at a temperature and for a time sufficient to extract at least part of the aluminium oxide content of said calcined clay mineral and increase the molar ratio of  $\text{SiO}_2:\text{Al}_2\text{O}_3$  in the calcined clay mineral, washing the acid-leached product with water; mixing the washed product with water and a quaternary compound or with water and a mixture of a quaternary compound and an alkali metal compound, at least a major proportion of the quaternary compound or of the quaternary compound and the alkali metal compound being a hydroxide, in the proportions required to form a zeolite of the ZSM family; heating the mixture thus formed at

an elevated pressure and at an elevated temperature for a time sufficient to form a crystalline zeolite, and separating the crystalline zeolite from the reaction mixture in which it is formed. The temperature at which the method is carried out is not greater than 200°C.

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## SPECIFICATION

**Manufacture of zeolites**

5 This invention relates to the manufacture of zeolites and, more particularly but not exclusively, is concerned with the manufacture of the family of zeolites which have come to be identified by the code ZSM. 5

Zeolites are crystalline aluminosilicates which have a uniform crystal structure characterised by a large number of regular small cavities interconnected by a large number of even smaller rectangular channels. It was discovered that, by virtue of this structure consisting of a network of interconnected uniformly sized cavities and channels, crystalline zeolites are able to accept for absorption molecules having sizes below a certain well defined value whilst rejecting molecules of larger size, and for this reason they have come to be known as "molecular sieves". This characteristic structure also gives them catalytic properties, especially for certain types of hydrocarbon conversions. 10 15

The ZSM family of zeolites are well known and their preparation and properties have been extensively described. Thus, for example, one type of the ZSM family of zeolites is that known as ZSM-5. This type of crystalline zeolite which has been found to be especially effective as a catalyst for hydrocarbon conversions, is described in United States Patent Specification No. 3,702,886. The ZSM-5 type of crystalline zeolite is characterised by a particular X-ray diffraction pattern and by a particular range of chemical compositions. The characteristic X-ray diffraction pattern is set forth in Table 1 below:- 20

Table 1

25	Interplanar Spacing d(A)	Relative Intensity	25
	11.1 ± 0.3	S	
30	10.0 ± 0.3	S	30
	7.4 ± 0.2	W	
	7.1 ± 0.2	W	
	6.3 ± 0.2	W	
	6.04 ± 0.2	W	
35	5.56 ± 0.1	W	35
	5.01 ± 0.1	W	
	4.60 ± 0.08	W	
	4.25 ± 0.08	W	
	3.85 ± 0.07	VS	
40	3.71 ± 0.05	S	40
	3.04 ± 0.03	W	
	2.99 ± 0.02	W	
	2.94 ± 0.02	W	

45 where d(A) is in Angstrom units and VS = very strong, S = strong, and W = weak. The chemical composition of a ZSM-5 type of zeolite can be represented, in terms of the molar ratios of oxides, as follows: 45

50  $(0.9 \pm 0.2)M_{2/n}O:Al_2O_3:10-200 SiO_2:zH_2O$  50

wherein M is a cation, n is the valency of the cation M, and z ranges from 0 to 40. A particularly useful group of the ZSM-5 type of zeolite are those which can be represented by the following formula: 55

55  $(0.9 \pm 0.2) M_2O:Al_2O_3:10-200 SiO_2:zH_2O$  55

wherein M is a monovalent cation and z ranges from 0 to 40. The monovalent cation M can be derived, for example, from a quaternary compound or from a mixture of a quaternary compound and an alkali metal. The quaternary compound can be, for example, a quaternary ammonium compound, e.g. a quaternary alkylammonium compound or a quaternary arylammonium compound, a quaternary phosphonium compound, a quaternary arsenium compound or a quaternary stilbonium compound. When M includes an alkali metal cation the latter is preferably a sodium cation and when M is or includes a quaternary alkylammonium cation or a quaternary arylammonium cation, the or each of the alkyl groups preferably contains from 2 to 5 carbon 60 65

atoms.

British Patent Specification No. 1,132,096 describes a method for producing a crystalline zeolitic molecular sieve, which comprises forming an aqueous reactant mixture having an initial overall composition defined in oxide mole ratios as follows:-

$$\begin{array}{rcl}
 5 & \text{M}_2\text{O}/\text{SiO}_2 & = \text{a} \\
 & \text{SiO}_2/\text{Al}_2\text{O}_3 & = \text{b} \\
 & \text{H}_2\text{O}/\text{M}_2\text{O} & = \text{c}
 \end{array}$$

10 wherein the values of a, b and c are the essential determinants for the type of crystalline zeolitic molecular sieve desired and M is an alkali metal, thermally treating the mixture at a temperature from 20 to 120°C, until crystals of the molecular sieve form, and separating and recovering the crystals, at least part of the thermal treatment being under at least autogenous pressure and at least a portion of the silicon oxide and aluminium oxide of the reactant mixture being provided  
 15 by a kaolin-type clay which has been rendered amorphous to X-ray diffraction by an attrition treatment or by calcining at a temperature of from 550° to 850°C, and then contacted with an aqueous mineral acid solution so as to increase the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of the clay to from 6 to 270, separated, dried and, when the silica/alumina ratio in the final zeolitic molecular sieve is to be greater than 3 subsequently fired at a temperature of from 500°C to 825°C for at least  
 20 one hour.

Zeolites of the ZSM family have a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio greater than 3. It has now been found unexpectedly that when manufacturing zeolites of the ZSM family by a process in which the molar ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is increased by acid extraction of alumina, it is not necessary (contrary to the teaching of British Patent Specification No. 1,132,096) subsequently to fire the  
 25 aluminosilicate at a temperature of from 550°C to 825°C for at least one hour.

More particularly, according to the present invention there is provided a method of manufacturing a crystalline zeolite of the ZSM family which method comprises the steps of:

(a) treating an aluminosilicate with a strong acid at a temperature and for a time sufficient to extract at least part of the aluminium oxide content of said aluminosilicate and increase the  
 30 molar ratio of SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> in the aluminosilicate to a value not less than 10:1, the aluminosilicate having been obtained by removing from a clay mineral at least part of its chemically bound water,

(b) washing the product of step (a) with water;

(c) mixing the product of step (c) with water and a quaternary compound or with water and a  
 35 mixture of a quaternary compound and an alkali metal compound, at least a major proportion of the quaternary compound or of the quaternary compound and the alkali metal compound being a hydroxide, in the proportions required to form a zeolite of the ZSM family, and heating the mixture thus formed at an elevated pressure and at an elevated temperature for a time sufficient to form a crystalline zeolite of the ZSM family, and

(d) separating the crystalline zeolite from the reaction mixture in which it is formed; and  
 40 wherein during and subsequent to the carrying out of step (a) the aluminosilicate is not subjected to temperatures in excess of 200°C.

Advantageously, after the crystalline zeolite prepared by the method of the invention has been separated from the reaction mixture in which it is formed, it is washed and dried.

45 The aluminosilicate starting material is derived from a clay mineral, preferably a clay mineral of the kandite group, such as a kaolinite, (in which case the molar ratio SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> is 2:1) or a clay mineral of the smectite group, such as bentonite, (in which case the molar ratio SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> is 5:1) by removing at least part of the chemically bound water with heat. Conveniently, the aluminosilicate starting material is obtained by heating a clay mineral to a temperature in the  
 50 range of from 500°C to 1000°C to remove at least part of the chemically bound water.

Advantageously the clay mineral is heated at a temperature ranging from 600°C to 950°C for at least 1 hour. In any event, the heat treatment of the clay mineral should preferably be such that, after heating a dry sample of the heat-treated product for 2 hours at 1000°C, the loss in weight on ignition does not exceed 10%.

55 In step (a), the acid used preferably has a pK<sub>a</sub> value not greater than 2 and most preferably has a pK<sub>a</sub> value of less than 0. Suitable acids include hydrochloric acid, sulphuric acid, nitric acid and orthophosphoric acid. The acid should be used at a concentration of at least 2M, preferably at least 5M, and most preferably at least 7M. The optimum acid concentration depends upon the weight ratio of acid solution to dry aluminosilicate and upon the type of acid  
 60 used and thus the nature of the aluminium salt formed and its solubility in the acid solution. The weight ratio of acid solution to dry aluminosilicate is preferably at least 5:1. The acid treatment is preferably performed at a temperature in the range of from 50°C to 120°C for at least 1 hour, and under conditions such that the molar ratio of SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> in the acid-treated aluminosilicate is in the range 10-200:1. Usually, after the acid treatment the molar ratio of SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> in the  
 65 aluminosilicate is in the range 10-50:1.

In step (b), the acid-treated aluminosilicate is advantageously dried after being washed.

In step (c) the acid-treated, washed and preferably dried aluminosilicate is mixed with the quaternary compound, for example a tetraalkylammonium compound, optionally in admixture with an alkali metal compound, and water in the appropriate proportions to form the desired ZSM zeolite, and the mixture is then heated in a pressure vessel to a temperature which is preferably in the range of from 100°C to 180°C for a period of from about 1 to about 2 days. In order to form a ZSM-5 zeolite at least 70% by weight of the quaternary compound or of the mixture of the quaternary compound and the alkali metal compound should be in the form of the hydroxide.

It has been found that the method of the invention enables a crystalline zeolite of the ZSM-5 type, for example, to be formed from a reaction mixture containing the constituents in appropriate molar proportions at a lower temperature and/or in a shorter time as compared with prior art processes, thus saving energy.

The preparation of a ZSM-5 type zeolite by the method of the invention is illustrated by the following Examples.

#### EXAMPLE 1

500g of an English kaolin, having a particle size distribution such that 0.1% by weight thereof consisted of particles having an equivalent spherical diameter larger than 10 microns and 95% by weight thereof consisted of particles having an equivalent spherical diameter smaller than 2 microns, was calcined at a temperature of 870°C for 3 hours to form metakaolin. After heating a dry sample of the metakaolin at 1000°C for 2 hours, it was found that on ignition the loss in weight was 0.2%. The calcination yielded 439g. of metakaolin which was allowed to cool, and was then mixed with approximately 2 litres of an 11M concentrated hydrochloric acid solution, giving a weight ratio of acid solution to dry metakaolin of 5.44:1. The mixture was heated to reflux temperature, 112°C, and stirred at this temperature for approximately 2½ hours. The reaction mixture was then cooled and washed with distilled water until free of acid. The mineral residue was dried and the yield of acid-treated metakaolin found to be approximately 220g. The mole ratio  $\text{SiO}_2:\text{Al}_2\text{O}_3$  was 29:1.

100g. of the acid-treated metakaolin was mixed with 1500 ml of water, 150g. of tetrapropylammonium hydroxide and 10g. of sodium hydroxide. The mixture was heated in a glass-lined autoclave at 150°C for 2 days and then allowed to cool to room temperature. The white product was recovered by filtration, washed and dried, and shown by X-ray analysis to be crystalline zeolite ZSM-5.

A sample of crystalline zeolite ZSM-5 was also prepared by the method described in Example 1 of United States Patent Specification No. 3,702,886. 45.8g. of amorphous silica were partially dissolved in 200 ml. of 2.18N tetrapropylammonium hydroxide by heating to a temperature of about 100°C. There was then added 6.8 g. of sodium aluminate dissolved in 108 ml. of water. The amounts of silica and sodium aluminate were such as to give a molar ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  approximately equal to that which obtained in the acid-leached metakaolin prepared as described above. The resultant mixture was placed in an autoclave lined with borosilicate glass and heated at 150°C for five days. The resultant solid product was cooled to room temperature, removed, filtered, washed with water and dried at 110°C.

A sample of the product obtained using the method described in United States Patent Specification No. 3,702,886 was subjected to X-ray analysis and the area of the peak obtained on the recorder chart for the interplanar spacing of 3.85 Å was measured. In comparison, the area of the peak for the interplanar spacing of 3.85 Å obtained on subjecting to X-ray analysis a sample of the crystalline ZSM-5 prepared in accordance with the method of the invention was found to be 3.6 times greater than the area of the corresponding peak obtained for the crystalline ZSM-5 prepared by the prior art method. This indicates that the yield of pure crystalline ZSM-5 is increased at least threefold by using the method of this invention.

#### EXAMPLE 2

A further quantity of the same English kaolin as was used in Example 1 was calcined under identical conditions to yield metakaolin which was found to show a loss of weight of 0.2% on ignition at 1000°C for 2 hours. 500g. samples of this metakaolin were treated with various acid solutions and under different conditions of temperature and reaction time. In each case the weight ratio of acid solution to dry metakaolin was 10:1. The reaction mixture was cooled and washed with distilled water until free of acid. The mineral residue was then dried and the molar ratio of  $\text{SiO}_2:\text{Al}_2\text{O}_3$  measured. The results obtained are set forth in the Table below:—

	Acid	Molarity	Temp (°C)	Reaction time (hr)	Molar ratio SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>	
5	Sulphuric	3	100	1	60:1	5
	Hydrochloric	3	100	1	18:1	
	"	3	100	2	22:1	
	"	9	100	1	34:1	
10	"	9	100	3	50:1	10
	"	9	112	1	66:1	
	"	9	112	3	200:1	
	Nitric	3	100	1	25:1	
	"	3	100	2	50:1	
15						15

In each case 100g of the acid-leached metakaolin was mixed with 1500 ml of water, 150g of tetrapropylammonium and 10g of sodium hydroxide. The mixture was heated in a glass-lined autoclave at 150°C for 2 days and then allowed to cool at room temperature. The white product was recovered by filtration and dried, and shown by X-ray analysis to be crystalline zeolite ZSM-5.

#### CLAIMS

1. A method of manufacturing a crystalline zeolite of the ZSM family which method comprises the steps of:
  - (a) treating an aluminosilicate with a strong acid at a temperature and for a time sufficient to extract at least part of the aluminium oxide content of said aluminosilicate and increase the mole ratio of SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> in the aluminosilicate to a value not less than 10:1, the aluminosilicate having been obtained by removing from a clay mineral at least part of its chemically bound water;
  - (b) washing the product of step (a) with water;
  - (c) mixing the product of step (b) with water and a quaternary compound or with water and a mixture of a quaternary compound and an alkali metal compound, at least major proportion of the quaternary compound or of the quaternary compound and the alkali metal compound being a hydroxide, in the proportions required to form a zeolite of the ZSM family, and heating the mixture thus formed at an elevated pressure and at an elevated temperature for a time sufficient to form a crystalline zeolite of the ZSM family, and
  - (d) separating the crystalline zeolite from the reaction mixture in which it is formed, and wherein during and subsequent to the carrying out of step (a) the aluminosilicate is not subjected to temperatures in excess of 200°C.
2. A method according to Claim 1, wherein the aluminosilicate has been obtained from a clay mineral of the kandite group or of the smectite group of clay minerals.
3. A method according to Claim 2, wherein the aluminosilicate has been obtained by heating the clay mineral at a temperature ranging from 600°C to 950°C for at least 1 hour.
4. A method according to Claim 1, 2 or 3, wherein the acid used in step (a) is hydrochloric acid, sulphuric acid, nitric acid or orthophosphoric acid.
5. A method according to Claim 4, wherein the acid is used at a concentration of at least 7M.
6. A method according to Claim 4 or 5, wherein the aluminosilicate is treated with the strong acid at a temperature in the range of from 50°C to 100°C for at least 1 hour.
7. A method according to any one of Claims 1 to 6, wherein the acid-treated aluminosilicate is dried after being washed with water.
8. A method according to any one of Claims 1 to 7, wherein the mixture formed in step (c) is heated in a pressure vessel to a temperature in the range of from 100°C to 180°C for a period of from about 1 to about 2 days.
9. A method according to any one of Claims 1 to 8, wherein, in step (c), at least 70% by weight of the quaternary compound or of the mixture of the quaternary compound and the alkali metal compound is in the form of the hydroxide.
10. A method according to Claim 1, substantially as described in the foregoing Example 1 or 2.