

616794

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

Shell Internationale Research Maatschappij B.V., a Netherlands Company, of Carel van Bylandtlaan 30, 2596 HR, The Hague, THE NETHERLANDS, hereby apply for the grant of a standard patent for an invention entitled:

Novel Crystalline (Metallo)silicates and Process for Preparing Such (Metallo)silicates

which is described in the accompanying complete specification.

Details of basic application(s):-

<u>Basic Applic. No:</u>	<u>Country:</u>	<u>Application Date:</u>
8821237	GB	9 September 1988

The address for service is:-

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DATED this TWENTY THIRD day of AUGUST 1989

Shell Internationale Research Maatschappij B.V.

By:

Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS  
OUR REF: 104798  
S&F CODE: 61750

5009990 07/09/89

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA  
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A  
CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made for a patent for an invention entitled:

Novel crystalline (metallo)silicates and process for preparing such (metallo)silicates

I, Onno Aalbers, of Carel van Bylandtlaan 30, 2596 HR The Hague, the Netherlands, do solemnly and sincerely declare as follows:-

1. I am authorised by SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., the applicant for the patent to make this declaration on its behalf.
2. The basic application(s) as defined by Section 141 of the Act was, were made in Great Britain  
on 9th September, 1988  
by Shell Internationale Research Maatschappij B.V.
3. Johannes Jacobus KEIJSPER, a Netherlands citizen; Munro MACKAY, a British citizen and Martin Franciscus Maria POST, a Netherlands citizen, all of Badhuisweg 3, 1031 CM Amsterdam, the Netherlands

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

The Applicant is the assignee of the actual inventor(s).

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

DECLARED at The Hague this 17<sup>th</sup> day of July 1989

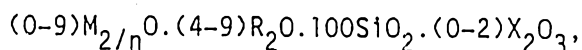
TO: THE COMMISSIONER OF PATENTS  
AUSTRALIA

Onno Aalbers

**(12) PATENT ABRIDGMENT (11) Document No. AU-B-41130/89**  
**(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 616794**

- (54) Title  
**NOVEL CRYSTALLINE (METALLO)SILICATES AND PROCESS FOR PREPARING SUCH (METALLO)SILICATES**
- (51)<sup>4</sup> International Patent Classification(s)  
**C01B 033/32 B01J 029/02 B01J 029/28 C01B 033/24**  
**C01B 033/28**
- (21) Application No. : **41130/89** (22) Application Date : **07.09.89**
- (30) Priority Data
- (31) Number (32) Date (33) Country  
**8821237 09.09.88 GB UNITED KINGDOM**
- (43) Publication Date : **15.03.90**
- (44) Publication Date of Accepted Application : **07.11.91**
- (71) Applicant(s)  
**SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.**
- (72) Inventor(s)  
**JOHANNES JACOBUS KEIJSPER; MARTIN FRANCISCUS MARIA POST; MUNRO MACKAY**
- (74) Attorney or Agent  
**SPRUSON & FERGUSON , GPO Box 3898, SYDNEY NSW 2001**
- (56) Prior Art Documents  
**AU 22814/83 C01B 33/26**
- (57) Claim

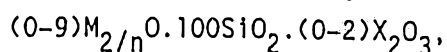
1. Crystalline (metallo)silicates having in the as-synthesized, anhydrous form a molar composition expressed by the formula:



wherein M represents an alkali or alkaline earth metal ion of valency n, R represents a tetramethylammonium cation or a precursor thereof, X represents at least one of Al, Fe, B or Ga, and having an X-ray diffraction pattern containing at least the following lines:

<u>d(A)</u>	<u>Intensity</u>
10.27 ± 0.2	s-vs
4.89 ± 0.1	w-m
4.18 ± 0.1	m
3.85 ± 0.1	m
3.82 ± 0.1	w-m
3.62 ± 0.1	w-m
3.48 ± 0.1	m-vs
3.32 ± 0.05	w-m
3.23 ± 0.05	w-m

5. Crystalline (metallo)silicates being the substantially R<sub>2</sub>O-free form of the crystalline (metallo)silicates according to any one of claims 1-4, and having the formula:



(11) AU-B-41130/89  
(10) 616794

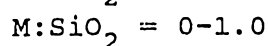
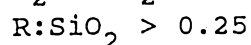
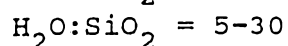
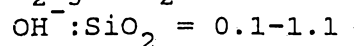
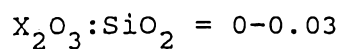
-2-

wherein M, n and X have the meanings as described hereinabove, and having an X-ray diffraction pattern containing at least the following lines:

d(A)	Intensity
8.99 ± 0.2	vs
6.72 ± 0.1	m
4.40 ± 0.1	w
4.29 ± 0.1	w-m
3.85 ± 0.1	w
3.77 ± 0.1	w
3.42 ± 0.1	w-m
3.29 ± 0.05	w
3.26 ± 0.05	w
3.22 ± 0.05	w

11. A process for preparing (metallo)silicates as defined in any one of claims 1-4, which comprises maintaining an aqueous mixture comprising a source of silicon, optionally a source of at least one of aluminium, iron, boron or gallium, a source of an alkali or alkaline earth metal (M) and a source of tetramethyl ammonium cations or precursors thereof at a temperature of between 140-240 °C whereby the following requirement is fulfilled:

$T \geq 244.5 - 18.2 \ln t$ , wherein T is the temperature (in °C) and t is the period of time (in hours) during which the mixture is kept at temperature T, until a crystalline material is produced which is subsequently separated from the mother liquor and dried, in which mixture the various components are initially present in the following molar ratios:



S & F Ref: 104798

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

616794

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class      Int Class

Complete Specification Lodged:

Accepted:

Published:

Priority:

Related Art:

Name and Address  
of Applicant:

Shell Internationale Research Maatschappij B.V.  
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The Hague  
THE NETHERLANDS

Address for Service:

Spruson & Ferguson, Patent Attorneys  
Level 33 St Martins Tower, 31 Market Street  
Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

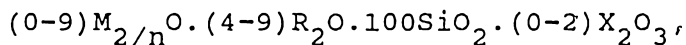
Novel Crystalline (Metallo)silicates and Process for  
Preparing Such (Metallo)silicates

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

A B S T R A C T

NOVEL CRYSTALLINE (METALLO)SILICATES AND  
PROCESS FOR PREPARING SUCH (METALLO)SILICATES

Crystalline (metallo)silicates having in the as-synthesized, anhydrous form a molar composition expressed by the formula:



wherein M is an alkali or alkaline earth metal ion having a valency n, R represents a tetramethylammonium cation or a precursor thereof, X represents at least one of Al, Fe, B or Ga, and having a specific X-ray diffraction pattern.

The silicates can be prepared from an aqueous mixture comprising a source of silicon, optionally a source of at least one of aluminium, iron, boron or gallium, and a source of tetramethylammonium cations or precursors thereof, which mixture is kept at a temperature of between 140-240 °C whereby the following requirement is fulfilled:  $T \geq 244.5 - 18.2 \ln t$ , wherein T is the temperature (in °C) and t is the period of time (in hours) during which the mixture is kept at temperature T, until a crystalline silicate is formed which is subsequently separated from the mother liquor and dried, and which may subsequently be calcined.

NOVEL CRYSTALLINE (METALLO)SILICATES AND  
PROCESS FOR PREPARING SUCH (METALLO)SILICATES

The present invention relates to novel crystalline (metallo)silicates, a process for preparing such (metallo)silicates and to the use of these novel crystalline (metallo)silicates as catalysts, catalyst carriers, molecular sieves and as membranes.

In general, crystalline aluminosilicates in both natural and synthetic forms, often referred to as zeolites, are of particular interest since they find wide and promising application in industry as, for instance, catalyst carriers or catalysts in various types of hydroconversion processes.

It has now been found that novel synthetic crystalline (metallo)silicates can be prepared from reaction mixtures wherein the various components are present in defined molar ratios and use is made of a specific organic nitrogen-containing cation.

The present invention thus relates to crystalline (metallo)silicates having in the as-synthesized, anhydrous form a molar composition expressed by the formula:

$$(0-9)M_{2/n}O \cdot (4-9)R_2O \cdot 100SiO_2 \cdot (0-2)X_2O_3,$$
 wherein M represents an alkali or alkaline earth metal ion of valency n, R represents a tetramethylammonium cation or a precursor thereof, X represents at least one of Al, Fe, B or Ga, and having an X-ray diffraction pattern containing at least the following lines:

<u>d(A)</u>	<u>Intensity</u>
10.27 ± 0.2	s-vs
4.89 ± 0.1	w-m
4.18 ± 0.1	m
3.85 ± 0.1	m
3.82 ± 0.1	w-m
3.62 ± 0.1	w-m
3.48 ± 0.1	m-vs
3.32 ± 0.05	w-m
3.23 ± 0.05	w-m

vs = very strong

s = strong

m = medium

w = weak

5  
The present invention in particular relates to crystalline (metallo)silicates as described hereinabove having in the as-synthesized, anhydrous form a molar composition expressed by the formula:

10  
 $(0-3)M_{2/n}O \cdot (4.5-6.5)R_2O \cdot 100SiO_2 \cdot (0-1)X_2O_3$ , wherein M, n, R and X are as defined hereinbefore.

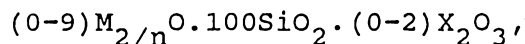
In particular, the present invention relates to crystalline (metallo)silicates as described hereinabove wherein X represents aluminium.

15  
As alkali metal ion preferably a sodium ion is present in the crystalline (metallo)silicates according to the present invention.

20  
The crystalline (metallo)silicates according to the present invention can be subjected to a treatment after which crystalline (metallo)silicates with a reduced amount of  $R_2O$  or even in the  $R_2O$ -free form are obtained. Suitably, the crystalline (metallo)silicates according to the present invention are subjected to calcination in order to obtain stable, crystalline, hydrophobic and microporous materials.



Therefore, the present invention also relates to crystalline (metallo)silicates having in the R<sub>2</sub>O-free form a molar composition expressed by the formula:



5 wherein M, n and X have the meanings as described hereinabove, and having an X-ray diffraction pattern containing at least the following lines:

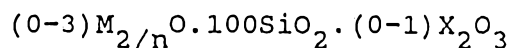
d(A)	Intensity
8.99 ± 0.2	vs
6.72 ± 0.1	m
4.40 ± 0.1	w
4.29 ± 0.1	w-m
3.85 ± 0.1	w
3.77 ± 0.1	w
3.42 ± 0.1	w-m
3.29 ± 0.05	w
3.26 ± 0.05	w
3.22 ± 0.05	w

vs = very strong

m = medium

w = weak

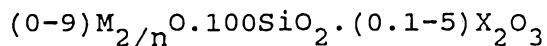
10 Preferably, the crystalline (metallo)silicates in the R<sub>2</sub>O-free form according to the present invention have a molar composition expressed by the formula:



15 The crystalline (metallo)silicates according to the present invention can also suitably be subjected to a (partial) substitution of at least one of Al, Fe, B or Ga, e.g. a so-called remetallization treatment, wherein an (additional) amount of at least one of Al, Fe, B or Ga can be added to crystalline (metallo)-  
20 silicates according to the present invention. In this context reference can be made to U.S. patent specification No. 4,524,140.

The present invention therefore further relates to crystalline (metallo)silicates in the R<sub>2</sub>O-free form as described hereinabove containing an additional amount of at least one of Al, Fe, B or Ga.

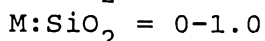
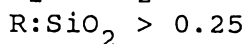
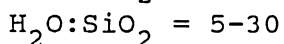
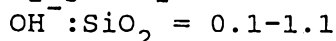
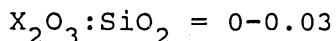
5 Preferably, the crystalline (metallo)silicates containing in the R<sub>2</sub>O-free form an additional amount of X have a molar composition expressed by the formula:



10 The present invention also relates to a process for preparing crystalline (metallo)silicates in the as-synthesized, anhydrous form as defined hereinabove, which comprises maintaining an aqueous mixture comprising a source of silicon, optionally a source of at least one of aluminium, iron, boron or gallium, a

15 source of an alkali or alkaline earth metal (M) and a source of tetramethyl ammonium cations or precursors thereof at a temperature between 140-240 °C whereby the following requirement is fulfilled;

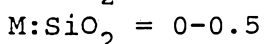
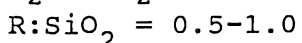
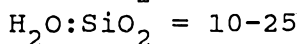
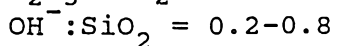
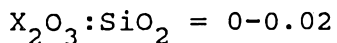
20  $T \geq 244.5 - 18.2 \ln t$ , wherein T is the temperature (in °C) and t is the period of time (in hours) during which the mixture is kept at temperature T, until a crystalline material is produced which is subsequently separated from the mother liquor and dried, in which mixture the various components are initially present in the following molar ratios:



The expression OH<sup>-</sup> as used herein comprises hydroxyl ions added to the forming solution originating from both the source of tetramethyl ammonium hydroxide or precursors thereof and the appropriate metal hydroxide(s).

35

The crystalline (metallo)silicates according to the present invention are preferably prepared from an aqueous mixture as described hereinabove wherein the various components are initially present in the following molar ratios:



Normally, the novel crystalline (metallo)silicates will be produced when the reaction mixture has been maintained under the appropriate conditions and for a sufficient period of time fulfilling the above defined requirement.

The preparation of the crystalline (metallo)silicates according to the present invention is preferably carried out by maintaining the aqueous mixture at a temperature of between 160-200 °C, for a period of at least 110 hours.

Suitably, the reaction mixture is agitated by stirring during the preparation. The process according to the present invention can be carried out either at autogeneous pressure or at a more elevated pressure. The crystalline product obtained can suitably be calcined at a temperature of between 500-800 °C. Preferably, tetramethylammonium hydroxide is used as source of tetramethylammonium cations.

Examples of suitable silicon, aluminium, iron, boron or gallium sources comprise amorphous solid silicas, silica sols, silica gels and siliceous acid; aluminium hydroxide, aluminium alkoxides, aluminium sulphate, gamma-alumina and preferably sodium aluminate; iron nitrates; boric acid and boron oxide; gallium nitrate and freshly prepared gallium hydroxide.

5 Examples of suitable alkali or alkaline earth metal ion sources which can be used in the preparation of the crystalline (metallo)silicates according to the present invention comprise the appropriate nitrates, carbonates, hydroxides and oxides. Preferably, a sodium compound in particular sodium hydroxide is used as source of alkali metal ions.

10 The novel (metallo)silicates according to the present invention can suitably be used as molecular sieves, membranes, or as catalysts or catalyst carriers in the operation of various catalytic processes.

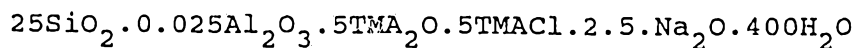
15 If desired, one or more compounds having catalytic activity, in particular one or more salts of metals of Group IVB, VIB, VIIB or VIII as well as ammonium ions and/or protons, can be incorporated into the crystalline (metallo)silicates according to the present invention. They can be incorporated by well-known techniques such as, for example, impregnation and ion-exchange.

20 If, the (metallo)silicates according to the present invention have been used as catalyst or catalyst carrier they may be exposed to any regeneration method known in the art.

25 The invention will now be illustrated by the following Examples.

EXAMPLE 1

30 A crystalline aluminosilicate according to the present invention was prepared by mixing in the appropriate amounts an aqueous mixture of silica sol, NaOH, NaAlO<sub>2</sub>, tetramethylammonium hydroxide (TMAOH) and tetramethylammonium chloride (TMACl) in water until a homogeneous gel was obtained. The molar composition of the aqueous mixture was as follows:



The gel obtained was subsequently kept at 190 °C for a period of 64 hours in a stirred autoclave.

5 After synthesis the solid product (SCS-5) was separated by filtration, water washed, and dried at 120 °C. In the as-synthesized form the material contained 38.7 %w Si, 0.1 %w Al, 7.6 %w C, 2.7 %w H, and 2.3 %w N.

Its X-ray diffraction pattern contained at least the lines as given in Table I.

Table I

<u>d(A)</u>	<u>Intensity</u>
10.37	vs
4.89	m
4.34	w
4.18	m
3.93	w
3.85	m
3.82	w
3.62	w
3.48	m
3.38	w
3.32	w
3.23	w

10 Subsequently the crystalline product obtained was calcined in air at 550 °C for a period of 16 hours, and has an X-ray diffraction pattern containing at least the lines as given in Table II.

Table II

<u>d(A)</u>	<u>Intensity</u>
8.88	vs
6.71	m
4.40	w
4.29	m
3.85	w
3.77	w
3.42	m
3.29	w
3.26	w
3.22	w

EXAMPLE 2

An experiment has been carried out in a substantially analogous manner as described in Example 1, except that the mixture was kept at 170 °C for a period of 120 hours and that the reaction mixture had the following molar composition:  $10\text{SiO}_2 \cdot 8\text{TMAOH} \cdot 200\text{H}_2\text{O}$ .

The product obtained was a crystalline product of the silicate type containing in the as-synthesized form 39.0 %w Si, less than 0.05 %w Al, 7.6 %w C, 2.6 %w H, and 2.1 %w N.

Its X-ray diffraction pattern contained at least the lines as given in Table III.

Table III

<u>d(A)</u>	<u>Intensity</u>
10.34	s
6.43	m
4.87	w
4.36	m
4.34	m
4.23	m
4.17	m
3.92	m
3.82	m
3.65	w
3.61	m
3.53	m
3.48	vs
3.30	m
3.21	m

COMPARATIVE EXAMPLE A

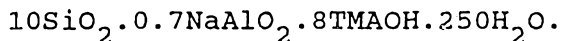
An experiment has been carried out by mixing an aqueous mixture having a molar composition:  $10\text{SiO}_2 \cdot 10\text{TMAOH} \cdot 150\text{H}_2\text{O}$ . This mixture was kept under stirring at 150 °C for a period of 72 hours. After cooling, a crystalline compound of different nature was obtained having an X-ray diffraction pattern containing at least the following lines as given in Table IV.

Table IV

<u>d(A)</u>	<u>Intensity</u>
13.8 ± 0.2	vs
4.8 ± 0.1	m
3.8 ± 0.1	m
3.40 ± 0.05	m
2.70 ± 0.05	m

COMPARATIVE EXAMPLE B

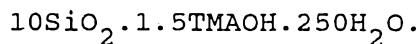
An experiment has been carried out in a substantially analogous manner as described in Example 2, except that the reaction mixture had the following molar composition:



The product obtained was a crystalline aluminium silicate of the sodalite type.

COMPARATIVE EXAMPLE C

An experiment has been carried out in a substantially analogous manner as described in Example 2, except that the reaction mixture had the following molar composition:



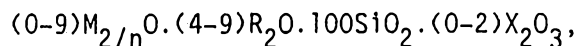
The product obtained was a crystalline silicate of the ZSM-39 type.

It is apparent from the result of the experiments described hereinabove that products according to the present invention are prepared when the specific requirements of the process according to the present invention are fulfilled. If, preparations are carried out under even slightly deviating conditions undesired products are obtained.



The claims defining the invention are as follows:

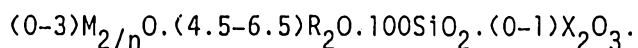
1. Crystalline (metallo)silicates having in the as-synthesized, anhydrous form a molar composition expressed by the formula:



5 wherein M represents an alkali or alkaline earth metal ion of valency n, R represents a tetramethylammonium cation or a precursor thereof, X represents at least one of Al, Fe, B or Ga, and having an X-ray diffraction pattern containing at least the following lines:

	<u>d(A)</u>	<u>Intensity</u>
10	10.27 ± 0.2	s-vs
	4.89 ± 0.1	w-m
	4.18 ± 0.1	m
	3.85 ± 0.1	m
	3.82 ± 0.1	w-m
15	3.62 ± 0.1	w-m
	3.48 ± 0.1	m-vs
	3.32 ± 0.05	w-m
	3.23 ± 0.05	w-m

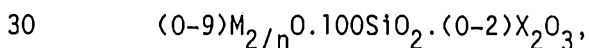
20 2. Crystalline (metallo)silicates according to claim 1 having in the as-synthesized, anhydrous form the formula:



3. Crystalline (metallo)silicates according to claim 1 or 2, wherein X represents Al.

25 4. Crystalline (metallo)silicates according to any one of claims 1-3, wherein M represents a sodium ion.

5. Crystalline (metallo)silicates being the substantially R<sub>2</sub>O-free form of the crystalline (metallo)silicates according to any one of claims 1-4, and having the formula:



wherein M, n and X have the meanings as described hereinabove, and having an X-ray diffraction pattern containing at least the following lines:

d(A)	Intensity
8.99 ± 0.2	vs
6.72 ± 0.1	m
4.40 ± 0.1	w
4.29 ± 0.1	w-m
3.85 ± 0.1	w
3.77 ± 0.1	w
3.42 ± 0.1	w-m
3.29 ± 0.05	w
3.26 ± 0.05	w
3.22 ± 0.05	w

5 6. Crystalline (metallo)silicates according to claim 5 having in the substantially R<sub>2</sub>O-free form the formula:  $(0-3)M_{2/n}O \cdot 100SiO_2 \cdot (0-1)X_2O_3$ .

7. Crystalline (metallo)silicates according to claim 5 or 6 containing an additional amount of at least one of Al, Fe, B or Ga.

10 8. Crystalline (metallo)silicates according to claim 7 having in the substantially R<sub>2</sub>O-free form the formula:  $(0-9)M_{2/n}O \cdot 100SiO_2 \cdot (0.1-5)X_2O_3$ .

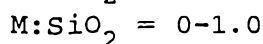
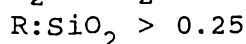
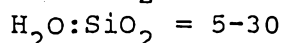
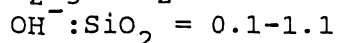
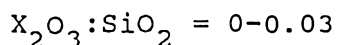
15 9. Crystalline (metallo)silicates according to any one of claims 1-8, wherein one or more catalytically active compounds have been incorporated.

10. Crystalline (metallo)silicates according to claim 9, wherein the catalytically active compounds comprise one or more salts of metals of Group IVB, VIB, VIIB or VIII.

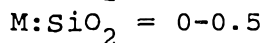
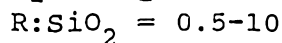
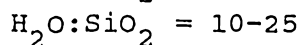
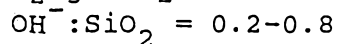
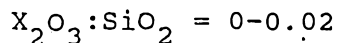
20 11. A process for preparing (metallo)silicates as defined in any one of claims 1-4, which comprises maintaining an aqueous mixture comprising a source of silicon, optionally a source of at least one of

aluminium, iron, boron or gallium, a source of an alkali or alkaline earth metal (M) and a source of tetramethyl ammonium cations or precursors thereof at a temperature of between 140-240 °C whereby the following requirement is fulfilled:

5  $T \geq 244.5 - 18.2 \ln t$ , wherein T is the temperature (in °C) and t is the period of time (in hours) during which the mixture is kept at temperature T, until a crystalline material is produced which is subsequently separated from the mother liquor and dried, in which mixture the various components are initially present in the following molar ratios:



12. A process according to claim 11, wherein the various components in the mixture are initially present in the following molar ratios:



13. A process according to claim 11 or 12, wherein the mixture is maintained at a temperature of between 160-200 °C, for a period of at least 110 hours.

14. A process according to any one of claims 11-13, wherein the mixture is stirred.

15. A process according to any one of claims 11-14, wherein the product obtained is calcined at a temperature of between 500-800 °C.



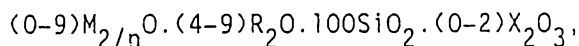
16. A process for carrying out catalytic reactions in which use <sup>as catalyst or catalyst carrier</sup> is made of a crystalline (metallo)silicate as claimed in anyone of claims 1-10.

5 17. ~~Use of~~ (metallo)silicates according to any one of claims 1-10, <sup>when used</sup> as molecular sieves.

18. ~~Use of~~ (metallo)silicates according to any one of claims 1-8, <sup>when used</sup> as catalyst carriers.

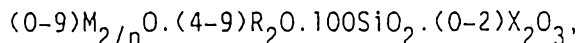
19. ~~Use of~~ (metallo)silicates according to anyone of claims 1-8, <sup>when used</sup> as membranes.

20. Crystalline (metallo)silicates having in the as-synthesized, anhydrous form a molar composition expressed by the formula:



wherein M represents an alkali or alkaline earth metal ion of valency n, R represents a tetramethylammonium cation or a precursor thereof, X represents at least one of Al, Fe, B or Ga substantially as hereinbefore described with reference to any one of the Examples excluding the comparative Examples.

21. A process for preparing crystalline (metallo)silicates having in the as-synthesized, anhydrous form a molar composition expressed by the formula:



wherein M represents an alkali or alkaline earth metal ion of valency n, R represents a tetramethylammonium cation or a precursor thereof, X represents at least one of Al, Fe, B or Ga substantially as hereinbefore described with reference to any one of the Examples excluding the comparative Examples.

22. The product of the process of any one of claims 11 to 16.

DATED this SIXTEENTH day of AUGUST 1989

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SPRUSON & FERGUSON

