

Description

The present invention relates to steam-modified crystalline galloaluminosilicates, their preparation and their use as catalysts and catalyst supports.

US Patent No. 3702886 (Mobil Oil Corporation) describes a novel family of ultra-stable synthetic siliceous crystalline materials designated as "Zeolite ZSM-5" or simply "ZSM-5" having a characteristic X-ray diffraction pattern and a composition in terms of mole ratios of oxides as follows:



wherein M is a cation, n is the valence of said cation, W is selected from the group consisting of aluminium and gallium, Y is selected from the group consisting of silicon and germanium, and z is from 0 to 40. Crystalline aluminosilicates having the aforesaid composition and characteristic X-ray diffraction pattern are classified in the Atlas of Zeolite Structure Types by W. M. Meier and D. H. Olson, published by the Structure Commission of the International Zeolite Association, 1978, as MFI-type zeolites. This patent was the forerunner to a vast number of patents relating to novel synthetic crystalline aluminosilicate zeolites all of which are characterised by a high, that is 10:1 or greater, silica to alumina molar ratio, high stability, extremely high acidity and the ability to catalyse many kinds of conversion reactions, such as cracking, isomerisation of n-paraffins and naphthenes, polymerisation of olefinic and acetylenic compounds, reforming, alkylation, isomerisation of polyalkyl substituted aromatics and disproportionation.

The patent was also the forerunner of a number of patent publications relating to crystalline silicates. Examples of such patents include US Re. 29,948; GB-A-2023562; GB-A-2024790; GB-A-2033358 and GB-A-2071071.

US Re. 29,948 describes crystalline organosilicates having an MFI-type XRD pattern and a composition in the anhydrous state in terms of mole ratios of oxides as follows:



where M is a metal other than a metal of Group IIIA, i.e. not B, Al, Ga, In or Tl, n is the valence of said metal, R is an alkyl ammonium radical, and x is greater than 0 but not exceeding 1.

GB-A-2023562 describes a zeolite having an X-ray diffraction spectrum akin to that of zeolite ZSM-5 and having the general formula:



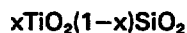
wherein M is a cation selected from H^+ and/or NH_4^+ and/or metallic cations and/or cations deriving from amino alcohols (especially ethanolamines), n is the valency of the cation, W is aluminium or gallium, Y is silicon or germanium and z is from 0 to 40.

GB-A-2024790 describes a modified silica characterised by the presence of a single crystalline phase and having the formula:



wherein M_nO_m is an oxide of the modifying element, which is preferably an element having, at least partially, an amphoteric character, e.g. Cr, Be, Ti, V, Mn, Fe, Co, Zn, Zr, Rh, Ag, Sn, Sb or B.

In GB-A-2071071 there is described a porous crystalline synthetic material having the formula:



wherein x is from 0.0005 to 0.04, and having a silicalite-type structure wherein the titanium substitutes for silicon.

GB-A-2033358 describes an anhydrous composition having an XRD pattern characteristic of ZSM-5 zeolites and a composition, in terms of mole ratios of oxides as follows:



wherein in W/X is from greater than 0.5 to less than 3, Y/X is greater than 20 and Z/X is from zero to less than about 100, R is a nitrogen containing cation.

None of the foregoing patent publications specifically describe a crystalline galloaluminosilicate. FR-A-2 374 283 discloses in its own acknowledgement of prior art the use of zeolites containing both gallium and aluminium as part of the crystal structure of the zeolite (galloaluminosilicates). However these are not disclosed to be of the ZSM-5 type.

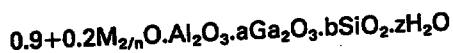
FR-A-2 374 283 goes on to describe ZSM-5 type zeolites which are not galloaluminosilicates but which are modified by impregnation with a gallium compound.

The deleterious effect of steam on zeolites has been recognised in the art. See, for example, USP 4,231,899 which contains the statement at column 1, lines 18 to 22:—

"The deleterious effect of steam on zeolites has been the subject of numerous papers and patents. This irreversible damage and loss of catalytic activity is thought to occur from hydrolysis of tetrahedral aluminium from the framework of the zeolite."

We have now prepared crystalline galloaluminosilicates having an XRD pattern substantially the same as an MFI-type zeolite. Although such materials have utility as catalysts and catalyst supports, particularly in hydrocarbon conversion processes, contrary to the teaching of the prior art with regard to aluminosilicates, steam treatment of crystalline galloaluminosilicates can improve their catalytic performance.

Accordingly, the present invention provides the hydrogen-form or ammonium-form of a crystalline galloaluminosilicate having an X-ray diffraction pattern substantially the same as that of an MFI-type zeolite and a composition in terms of mole ratios of oxides as follows:



wherein M is a cation, n is the valence of the cation, a has a value between 0.0001 and 2, b has a value of at least 12 and z has a value of from 0 to 40, modified by heating with steam at a temperature of from 400 to 700°C for a period of at least 0.5 hours.

The cation M may suitably be H^+ , NH_4^+ , a metallic cation or an organic nitrogen cation or a mixture of at least two such cations.

The aforesaid crystalline galloaluminosilicate may suitably be prepared by crystallisation at elevated temperature from a gel comprising (i) a source of silica (SiO_2), (ii) a source of alumina (Al_2O_3), (iii) a source of gallia (Ga_2O_3), (iv) a mineralising agent selected from oxides, hydroxides and salts of alkali and alkaline earth metals, (v) an organic base (B) and (vi) ROH wherein R is H and/or lower alkyl, in the following molar proportions:

$SiO_2:M_2O_3$ (wherein M_2O_3 is defined as total molar $Al_2O_3+Ga_2O_3$) greater than 12:1, preferably in the range 15:1 to 100:1,

$SiO_2:X_{2/n}O=1000:1$ to 50:1 (wherein X is the alkaline earth metal of the mineralising agent and n is the valency of X)

$SiO_2:B=50:1$ to 1:20

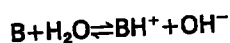
$SiO_2:ROH$ less than 1:10

$Al_2O_3:Ga_2O_3=500:1$ to 1:100, preferably 200:1 to 1:50 to form a crystalline galloaluminosilicate having an X-ray pattern substantially the same as that of an MFI-zeolite and a composition in terms of mole ratios of oxides as follows:



wherein M is a cation, n is the valence of the cation, a has a value between 0.0001 and 2, b has a value of at least 12 and z has a value of from 0 to 40, converting said galloaluminosilicate to substantially the hydrogen or ammonium form, and steam modifying said galloaluminosilicate by heating the galloaluminosilicate substantially in the hydrogen-form or the ammonium form with steam at a temperature in the range from 400 to 700°C for a period of at least 0.5 hour.

The term organic base as used hereinbefore means any organic material (B) for which $-\log_{10}[K_D]$ for the reaction:



is less than 7, where $K_D=[BH^+][OH^-]/[B]$.

Suitable organic bases include:

(i) tetraalkylammonium salts of the formula:



wherein R^1 , R^2 , R^3 and R^4 are independently either aryl, substituted aryl, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl or hydrogen and X^- is either an inorganic or an organic anion. Preferably R^1 , R^2 , R^3 and R^4 are alkyl groups containing from 1 to 5 carbon atoms. Preferably X^- is a halide or hydroxide ion. Suitable tetraalkylammonium salts include tetraethylammonium hydroxide and tetrapropylammonium hydroxide. Alternatively, the precursors of tetraalkylammonium compounds may be used.

(ii) amines having the formula:

either $R^1R^2R^3N$, or $R^1R^2N(CH_2)_xNR^3R^4$ wherein x is an integer in the range 1 to 10, or $R^1R^2N(CH_2)_yN(CH_2)_zNR^3R^4$ wherein y and z are integers in the range 1 to 10.

Suitable amines include C_1 to C_9 primary monoalkylamines, such as ethylamine, n-propylamine and n-butylamine.

(iii) Mono-, di- and tri-alkanolamines such as monoethanolamine, diethanolamine or triethanolamine,

or their precursors in the form of an alkylene oxide and ammonia, e.g. ethylene oxide and ammonia, or mixtures thereof.

Suitable sources of gallia include gallium salts, alkali metal gallates and gallium oxide.

Suitable sources of silica include, for example, sodium silicate, silica hydrosol, silica gel, silica sol and silicic acid. The preferred source of silica is an aqueous colloidal dispersion of silica particles. A suitable commercially available source of silica is LUDOX (Registered Trade Mark) Colloidal Silica manufactured by DuPont.

Suitable sources of alumina include, for example, sodium aluminate, aluminium sulphate and alumina. The preferred source of alumina is sodium aluminate prepared by dissolving particulate alumina in excess sodium hydroxide solution.

The preferred mineralising agents are alkali and alkaline earth metal hydroxides and halides, such as for example, lithium hydroxide, sodium hydroxide, potassium hydroxide, potassium bromide and calcium bromide. The preferred mineralising agent is sodium hydroxide.

It will be appreciated that each source of silica, alumina, alkali or alkaline earth metal can be supplied by one or more initial reactants and then mixed together in any order. For example, sodium silicate is a source of both alumina and silica and an aluminosilicate is a source of both alumina and silica. Thus, the source of alumina and the source of silica may be supplied in whole or in part by an aluminosilicate, which may be either crystalline or amorphous, for example a clay such as bentonite or montmorillonite or an acid-leached clay.

The crystallisation temperature may suitably be in the range from 80 to 220°C, preferably from 120 to 175°C. The crystallisation pressure may suitably be autogenous pressure, that is the pressure generated within a closed vessel at the crystallisation temperature employed.

The gel may suitably be held under crystallisation conditions for a time greater than 0.5 hours and up to 150 hours.

As crystallised from such a gel, the crystalline galloaluminosilicate will almost certainly contain alkali or alkaline earth metal ions and possibly also organic nitrogen cations.

These original cations can be replaced in accordance with techniques well known in the art, at last in part by ion-exchange with other cations. In accordance with the invention they are replaced by ammonium ions or hydrogen ions. It is preferred, before exchange, and optionally between exchanges or after exchange, to calcine the crystalline galloaluminosilicate, i.e. to reduce the value of z in the aforesaid compositional formula to zero. Calcination may be effected by heating, suitably in a stream of dry air, at a temperature in the range from 400 to 600°C for at least 0.5 hour. Replacement of exchangeable cations may be effected by conventional ion-exchange techniques.

In a preferred embodiment, the organic base in the aforescribed galloaluminosilicate preparation may be replaced by a source of ammonium ions, such as for example an aqueous ammonia solution. An advantage of using a source of ammonium ions is that a calcination step prior to ion-exchange can be avoided if so desired.

Alternatively, crystalline galloaluminosilicates may be produced by substituting a proportion of the alumina source by a gallia source in the processes described in for example US Patents Nos. 3775501; 3702886 and 3709979 and GB Patent Nos. 1334243, 1365317, 1365318, 1553209 and 1567948 and UK application publication No. 2018232A.

Surprisingly, in view of the teaching of USP 4321899 with regard to aluminosilicates, steam-modified hydrogen- or ammonium-exchanged galloaluminosilicates are better catalysts than their unsteamed counterparts for certain reactions, for example the aromatisation of hydrocarbons.

The steam-modified galloaluminosilicate may, if desired, be further modified by ion-exchange with catalytically desirable metal cations, for example cations of metals of Group VIII of the Periodic Table.

The treatment with steam is effected for at least 0.5 hour and suitably for as long as 12 hours, though longer periods may be used if so desired. The steam may be neat steam or admixed with inert gases such as air, nitrogen or helium.

Whilst we do not wish to be bound in any way as to the mechanistic effects of steam treatment, it is believed that the treatment causes gallium to be preferentially removed from the framework of the crystalline galloaluminosilicate and deposited, probably in the form of gallium oxide, on the surface and in the pores thereof.

Both crystalline galloaluminosilicates and steam-modified galloaluminosilicates may be used as catalysts and catalyst supports, in for example, the conversion of synthesis gas to hydrocarbons and/or oxygenated derivatives thereof and the conversion of hydrocarbons to aromatic hydrocarbons. In particular, the steam-modified galloaluminosilicates are useful as catalysts in the dehydrocyclo-oligomerisation of hydrocarbons to condensable hydrocarbon fractions containing mononuclear aromatics such as benzene, toluene and xylene.

Accordingly, the present invention in another aspect provides a process for the production of aromatic hydrocarbons which process comprises contacting in the vapor phase a C_2 to C_{12} hydrocarbon feedstock at elevated temperature with a steam-modified crystalline galloaluminosilicate as hereinbefore described.

By C_2 to C_{12} hydrocarbon feedstock is meant a feedstock containing either a single hydrocarbon component or a mixture of saturated and/or unsaturated C_2 to C_{12} hydrocarbons. The feedstock is suitably one or more saturated and/or unsaturated C_2 to C_8 hydrocarbons. Hydrocarbon feedstocks containing

either ethane and/or ethylene, or propane and/or propylene, or isobutane and/or isobutene are particularly useful in the process of the invention.

The hydrocarbon feedstock may be contacted with the catalyst at a temperature suitably in the range from 400 to 700°C, preferably from 500 to 600°C.

Further details relating to process conditions may be found in for example, GB 1561590 and European patent publication No. 55021 (BP Case No. 5012), to which the reader is referred.

The invention will now be described by reference to the following Examples.

A. Preparation of crystalline galloaluminosilicates

Example 1

Crystalline galloaluminosilicate (a).

1.08 g of sodium hydroxide and 1.31 g of sodium aluminate were dissolved in 35.6 g of water. 1.25 g of gallium nitrate were then added and the mixture stirred for 15 minutes. A second solution was made by adding 4.84 g of 0.91 SG aqueous ammonia (ca 25% by wt NH_3) to 37.5 g of Ludox AS40 colloidal silica. After 25 minutes had elapsed, the second solution was added to the first with vigorous stirring over ca 5 minutes. At the end of this time the mixture was stirred for a further 5 minutes until the gel formed a uniform white paste.

The gel was transferred to a stainless steel 200 ml pressure vessel, the vessel sealed, and the mixture heated to 170°C with slow agitation. After 72 hours at this temperature, the vessel was cooled and opened. The solid contents of the vessel were separated by filtration and washed with distilled water. The X-ray pattern of the solid product after drying was identical with that of an MFI zeolite.

Examples 2 to 4

Crystalline galloaluminosilicates (b)–(d)

The method described in Example 1 of preparing galloaluminosilicate (a) was used but for each experiment the weights of materials used were those given in Table 1. In each case the solid product recovered after 72 hours crystallisation at 170°C was identical with that of an MFI-type zeolite.

TABLE 1

Ex.	Gallo-alumino-silicate	Wt of reactant in grams						
		Ludox AS40	H ₂ O	NaOH	NaAlO ₂	Ga(NO ₃) ₃	NH ₃	Product
2	(b)	37.5	35.6	1.25	1.31	1.25	1.04	MFI-type zeolite
3	(c)	37.5	35.6	0.7	1.31	1.25	3.4	MFI-type zeolite
4	(d)	37.5	35.6	0.9	1.31	1.25	6.5	MFI-type zeolite

The products obtained from these four preparations indicate that mixed galloaluminosilicates can be produced using aqueous ammonia over a range of chemical conditions.

Example 5—Crystalline galloaluminosilicate (e)

6,000 g of Ludox AS40 colloidal silica (40% by wt SiO_2) was mixed with 2,030 g of a 20% by weight solution of tetrapropylammonium hydroxide. A second mixture consisting of a solution of 255 g of sodium aluminate (ca 40% Al_2O_3 by weight), 103.8 g of gallium nitrate and 48 g of sodium hydroxide in 4,072 g of water was prepared. The two solutions were mixed and stirred vigorously for 30 minutes.

The mixture was transferred to a 4 gallon autoclave and heated to 170°C with stirring. After 72 hours the mixture was cooled and the solid product isolated by filtration. X-ray diffraction showed that the solid product had a powder pattern similar to ZSM-5. Analysis of the product revealed a $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 33.9 and a %wt gallium content of 0.74.

B. Preparation of catalysts derived from galloaluminosilicates

Example 6

A sample of the MFI-galloaluminosilicate (a) (Example 1) was converted to the ammonium form by

ion-exchange (twice) with 1M ammonium chloride solution for 2 hours at 100°C. The ammonium exchanged form of the product was carefully dried at 200°C and then heated to 500°C in dry air over a period of two hours. The catalyst was then heated for a further 18 hours at 500°C in dry air. The catalyst will hereinafter be referred to as catalyst A.

Example 7

The procedure of Example 6 was followed using MFI-galloaluminosilicate (a) (Example 1). However, on reaching 500°C dry air was replaced for 2 hours by a feed consisting of 20% steam in air. Using this steam treatment the catalyst was further heated to 550°C. After 2 hours had elapsed the steamed catalyst was cooled to 500°C and calcined for a further 18 hours in dry air. The catalyst will hereinafter be referred to as Catalyst B.

Example 8

The MFI-galloaluminosilicate (b) (Example 2) was treated in identical manner to the MFI-galloaluminosilicate (a), as described in Example 6. The catalyst will hereinafter be referred to as Catalyst E.

Example 9

The procedure of Example 7 was used except that MFI-galloaluminosilicate (b) was used in place of MFI-galloaluminosilicate (a). The catalyst will hereinafter be referred to as Catalyst F.

Example 10

A sample of the MFI-galloaluminosilicate (e) obtained in Example 5 was calcined at 500°C in dry air for 60 hours and then converted to the ammonium form by ion-exchange (twice) with 1M ammonium chloride solution for 2 hours at 100°C. The product was calcined in dry air at 500°C, followed by calcination in air containing 20% steam at 550°C for 2 hours.

The catalyst will hereinafter be referred to as Catalyst G.

C. Preparation of catalysts derived from MFI-type aluminosilicates

Comparison test 1

The method used to prepare Catalyst A was followed, but in place of the MFI galloaluminosilicate an MFI-type aluminosilicate was used (prepared by the method described in Example 1 of our European patent publication No. 30811). The catalyst was calcined for 18 hours in dry air at 500°C. The catalyst will hereinafter be referred to as Catalyst C.

Comparison test 2

A sample of Catalyst C was steamed using the method described in Example 7. After 2 hours at 550°C in a feed of 20% steam in air, the catalyst was cooled to 500°C and calcined in dry air for 18 hours. The catalyst will hereinafter be referred to as Catalyst D.

Comparison Tests 1 and 2 are not Examples according to the invention and are included only for the purpose of comparison.

D. Testing of catalysts

Examples 11 and 12

Catalysts A and B were tested individually in isothermal reactors for the conversion of propane into aromatics. The conditions used in each case were identical and were as follows:

Reaction temperature	=535°C
Contact time	=6 secs (NTP)
Feed	=Propane
Duration of test	=6 hours
Pressure	=1 Atm

Comparison tests 3 and 4

The procedure of Examples 11 and 12 was repeated using Catalysts C and D respectively in place of Catalysts A and B.

The results of Examples 11 and 12 and Comparison Tests 3 and 4 are illustrated graphically in Figures 1 to 4 which are as follows:

Figure 1 (Example 11)	—Catalyst A of Example 6.
Figure 2 (Example 12)	—Catalyst B of Example 7.
Figure 3 (Comparative Test 3)	—Catalyst C of Comparison Test 1.
Figure 4 (Comparative Test 4)	—Catalyst D of Comparison Test 2.

The results shown in Figures 1 to 4 clearly demonstrate the advantages of using a steamed galloaluminosilicate as catalyst in the conversion of propane to aromatics. The activity of the steamed

galloaluminosilicate (Figure 2) is very much higher than the unsteamed galloaluminosilicate (Figure 1) and both the steamed and unsteamed MFI-aluminosilicates in the hydrogen form (Figures 3 and 4). Furthermore, the selectivity to aromatics (47 to 55%) for the steamed galloaluminosilicate (Figure 2) is higher than for the unsteamed galloaluminosilicate (Figure 1) which in turn is higher than the MFI-aluminosilicates (Figures 3 and 4) and is in fact similar to that obtained for a gallium impregnated and/or exchanged aluminosilicate.

Examples 13 and 14

The procedure of Examples 11 and 12 was repeated except that Catalysts A and B were replaced by Catalysts E and F respectively.

The results are given in Table 2.

TABLE 2

Example	Hours on stream							
	0.5		2		4		6	
	C ₃ H ₈ conversion (%)	S _A *	C ₃ H ₈ conversion (%)	S _A *	C ₃ H ₈ conversion (%)	S _A *	C ₃ H ₈ conversion (%)	S _A *
13	55	13.7	53	21.9	49	20.2	49	17.9
14	86	46.2	84	42.6	81	52.0	77	48.4

*S_A=% by wt selectivity to aromatics.

The results in Table 2 demonstrate that steaming the crystalline galloaluminosilicate improves both the activity and the selectivity of the material as a catalyst in the DHCD of propane to aromatics.

Example 15

Catalyst G of Example 10 was activated for 4 hours in dry air at 550°C.

The activated catalyst was then tested for DHCD of butane under the following conditions:—

Temperature = 540°C
 Contact time = 16 secs (NTP)
 Feed = butane
 Pressure = 6 Atm
 Duration of test = 93 hours

The results obtained are shown in Table 3.

TABLE 3

HOS	4	25	49	73	93
% C ₄ Conv.	99.3	98.6	98.1	94.7	89.1
% (C ₃ +C ₄) Conv.	85.7	79.8	72.4	66.1	59.8
% Aromatics					
Yield	44.4	42.6	40.3	38.2	34.4
Selectivity	51.8	53.3	55.7	57.7	57.4

Claims

1. A process for the production of a steam modified crystalline galloaluminosilicate which comprises crystallising at elevated temperature a gel comprising (i) a source of silica (SiO₂), (ii) a source of alumina (Al₂O₃), (iii) a source of gallia (Ga₂O₃), (iv) a mineralising agent selected from oxides, hydroxides and salts of alkali and alkaline earth metals, (v) an organic base (B) and (vi) ROH wherein R is H and/or lower alkyl, in the following molar proportions:—

SiO₂:M₂O₃ (wherein M₂O₃ is defined as total molar Al₂O₃+Ga₂O₃)=greater than 12:1,

SiO₂:X_{2/n}O=1000:1 to 50:1 (wherein X is the alkali metal or alkaline earth metal of the mineralising agent and n is the valency of X),

galloaluminosilicate (Figure 2) is very much higher than the unsteamed galloaluminosilicate (Figure 1) and both the steamed and unsteamed MFI-aluminosilicates in the hydrogen form (Figures 3 and 4). Furthermore, the selectivity to aromatics (47 to 55%) for the steamed galloaluminosilicate (Figure 2) is higher than for the unsteamed galloaluminosilicate (Figure 1) which in turn is higher than the MFI-aluminosilicates (Figures 3 and 4) and is in fact similar to that obtained for a gallium impregnated and/or exchanged aluminosilicate.

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% (C ₃ +C ₄) Conv.	85.7	79.8	72.4	66.1	59.8
% Aromatics Yield	44.4	42.6	40.3	38.2	34.4
Selectivity	51.8	53.3	55.7	57.7	57.4

Claims

1. A process for the production of a steam modified crystalline galloaluminosilicate which comprises crystallising at elevated temperature a gel comprising (i) a source of silica (SiO₂), (ii) a source of alumina (Al₂O₃), (iii) a source of gallia (Ga₂O₃), (iv) a mineralising agent selected from oxides, hydroxides and salts of alkali and alkaline earth metals, (v) an organic base (B) and (vi) ROH wherein R is H and/or lower alkyl, in the following molar proportions:—

SiO₂:M₂O₃ (wherein M₂O₃ is defined as total molar Al₂O₃+Ga₂O₃)=greater than 12:1,

SiO₂:X_{2/n}O=1000:1 to 50:1 (wherein X is the alkali metal or alkaline earth metal of the mineralising agent and n is the valency of X),



$\text{SiO}_2:\text{B}=50:1$ to $1:20$,

$\text{SiO}_2:\text{ROH}=\text{less than } 1:10$.

$\text{Al}_2\text{O}_3:\text{Ga}_2\text{O}_3=500:1$ to $1:100$

to form a crystalline galloaluminosilicate having an X-ray pattern substantially the same as that of an MFI-zeolite and a composition in terms of mole ratios of oxides as follows:



wherein M is a cation, n is the valence of the cation, a has a value between 0.0001 and 2, b has a value of at least 12 and z has a value of from 0 to 40, converting said galloaluminosilicate to substantially the hydrogen or ammonium form, and steam modifying said galloaluminosilicate by heating the galloaluminosilicate substantially in the hydrogen-form or the ammonium form with steam at a temperature in the range from 400 to 700°C for a period of at least 0.5 hour.

2. A process according to Claim 1 wherein the cation M is H^+ , NH_4^+ , a metallic cation or an organic nitrogen cation or a mixture of at least two such cations.

3. A process according to Claim 2 wherein M is a metallic cation which is a cation of a rare earth metal, aluminium, gallium or a Group VIII metal.

4. A process according to any one of Claims 1 to 3 wherein z in the compositional formula is zero.

5. A process for the production of a galloaluminosilicate comprising a process as claimed in Claim 1 subject to the modification that instead of the organic base (B) there is used a source of ammonium ions.

6. The hydrogen-form or ammonium-form of a crystalline galloaluminosilicate having an X-ray diffraction pattern substantially the same as that of an MFI-type zeolite and a composition in terms of mole ratios of oxides as follows:



wherein M is a cation, n is the valence of the cation, a has a value between 0.0001 and 2, b has a value of at least 12 and z has a value of from 0 to 40, modified by heating with steam at a temperature of from 400 to 700°C for a period of at least 0.5 hours.

7. The use as a catalyst or a catalyst support of a steam modified galloaluminosilicate as claimed in Claim 6.

8. A process for the production of aromatic hydrocarbons which process comprises contacting in the vapour phase a C_2 to C_{12} hydrocarbon feedstock at elevated temperature with a steam-modified crystalline galloaluminosilicate as claimed in Claim 6.

Patentansprüche

1. Verfahren zur Herstellung eines wasserdampf-modifizierten kristallinen Galliumaluminiumsilicats, umfassend bei höherer Temperatur das Kristallisieren eines Gels, umfassend

(i) eine Quelle für Siliciumdioxid (SiO_2)

(ii) eine Quelle für Aluminiumoxid (Al_2O_3),

(iii) eine Quelle für Galliumoxid (Ga_2O_3),

(iv) ein mineralisierendes Mittel, das aus Oxiden, Hydroxiden und Salzen von Alkali- und Erdalkalimetallen ausgewählt ist,

(v) eine organische Base (B) und

(vi) ROH, worin R H und/oder Niederalkyl ist, in den folgenden Stoffmengen-Verhältnissen ("Mol-Verhältnissen"):

$\text{SiO}_2:\text{M}_2\text{O}_3$ (worin M_2O_3 als die Gesamt-Stoffmenge von $\text{Al}_2\text{O}_3 + \text{Ga}_2\text{O}_3$ definiert ist) = größer als 12:1,

$\text{SiO}_2:\text{X}_{2/n}\text{O}=1000:1$ bis 50:1 (worin X das Alkalimetall oder Erdalkalimetall des mineralisierenden Mittels und n die Wertigkeit von X ist),

$\text{SiO}_2:\text{B}=50:1$ bis 1:20,

$\text{SiO}_2:\text{ROH}=\text{kleiner als } 1:10$,

$\text{Al}_2\text{O}_3:\text{Ga}_2\text{O}_3=500:1$ bis 1:100,

zur Bildung eines kristallinen Galliumaluminiumsilicats mit einem Röntgendiagramm, das im wesentlichen das gleiche ist wie dasjenige eines MFI-Zeoliths, und einer Zusammensetzung, angegeben als Stoffmengen-Verhältnisse ("Mol-Verhältnisse") der Oxide, wie folgt:



worin M ein Kation ist, n die Wertigkeit des Kations ist, a einen Wert zwischen 0,0001 und 2 hat, b einen Wert von wenigstens 12 hat und z einen Wert von 0 bis 40 hat,

das Überführen dieses Galliumaluminiumsilicats im wesentlichen in die Wasserstoff- oder Ammonium-Form, und das Modifizieren dieses Galliumaluminiumsilicats mit Wasserdampf durch Erhitzen des im wesentlichen in der Wasserstoff- oder Ammonium-Form vorliegenden Galliumaluminiumsilicats



mit Wasserdampf während einer Zeitdauer von wenigstens 0,5 h auf eine Temperatur im Bereich von 400°C bis 700°C.

2. Verfahren nach Anspruch 1, worin das Kation M H^+ , NH_4^+ , ein metallisches Kation oder ein organisches Stickstoff-Kation oder eine Mischung aus wenigstens zwei solcher Kationen ist.

3. Verfahren nach Anspruch 2, worin M ein metallisches Kation ist, das ein Kation von einem Seltenerdmetall, Aluminium, Gallium oder einem Metall der Gruppe VIII ist.

4. Verfahren nach irgendeinem der Ansprüche 1 bis 3, worin z in der Formel der Zusammensetzung Null ist.

5. Verfahren zur Herstellung eines Galliumaluminiumsilicats, umfassend ein Verfahren nach Anspruch 1, das dahingehend modifiziert ist, daß an Stelle der organischen Base (B) eine Quelle für Ammonium-Ionen verwendet wird.

6. Wasserstoff-Form oder Ammonium-Form eines kristallinen Galliumaluminiumsilicats mit einem Röntgenbeugungsdiagramm, das im wesentlichen das gleiche ist wie dasjenige eines MFI-Zeoliths, und einer Zusammensetzung, angegeben als Stoffmengen-Verhältnisse ("Mol-Verhältnisse") der Oxide, wie folgt:



worin M ein Kation ist, n die Wertigkeit des Kations ist, a einen Wert zwischen 0,0001 und 2 hat, b einen Wert von wenigstens 12 hat und z einen Wert von 0 bis 40 hat, modifiziert durch Erhitzen mit Wasserdampf während einer Zeitdauer von wenigstens 0,5 h auf eine Temperatur von 400°C bis 700°C.

7. Verwendung des wasserdampf-modifizierten Galliumaluminiumsilicats nach Anspruch 6 als Katalysator oder Katalysator-Träger.

8. Verfahren zur Herstellung aromatischer Kohlenwasserstoffe, umfassend das In-Berührung-Bringen der Dampfphase eines C_2 — C_{12} -Kohlenwasserstoff-Einsatzmaterials bei höherer Temperatur mit einem wasserdampf-modifizierten kristallinen Galliumaluminiumsilicat nach Anspruch 6.

Revendications

1. Procédé de production d'un gallo-aluminosilicate cristallin, modifié par traitement à la vapeur d'eau, qui comprend la cristallisation, à une température élevée, d'un gel comprenant (i) une source de silice (SiO_2), (ii) une source d'alumine (Al_2O_3), (iii) une source d'oxyde de gallium (Ga_2O_3), (iv) un agent de minéralisation, choisi parmi des oxydes, hydroxydes et sels de métaux alcalins et de métaux alcalino-terreux, (v) une base organique (B) et (vi) ROH, où R représente H et/ou un groupe alkyle inférieur, selon les proportions molaires suivantes:

rapport $SiO_2:M_2^nO_3$ (où $M_2^nO_3$) est défini comme représentant le total molaire $Al_2O_3 + Ga_2O_3$ = supérieur à 12:1, rapport $SiO_2:X_{2/n}O = 1000:1$ à 50:1 (où X représente le métal alcalin ou le métal alcalino-terreux de l'agent de minéralisation, et n est la valence de X),

rapport $SiO_2:B = 50:1$ à 1:20,

rapport $SiO_2:ROH$ = inférieur à 1:10,

rapport $Al_2O_3:Ga_2O_3 = 500:1$ à 1:100,

pour former un gallo-aluminosilicate cristallin ayant un spectre de diffraction des rayons X sensiblement identique à celui d'une zéolite de type MFI et ayant une composition, en termes des rapports molaires des oxydes, comme suit:



où M représente un cation, n est la valence du cation, a vaut de 0,0001 à 2, b vaut au moins 12 et z vaut de 0 à 40, la conversion dudit gallo-aluminosilicate sous forme sensiblement complète hydrogène ou ammonium, et la modification, par traitement à la vapeur d'eau, dudit gallo-aluminosilicate par chauffage du gallo-aluminosilicate, sensiblement sous forme hydrogène ou sous forme ammonium, avec de la vapeur d'eau à une température comprise entre 400 et 700°C pendant une période d'au moins une demi-heure.

2. Procédé selon la revendication 1, dans lequel le cation M représente H^+ , NH_4^+ , un cation métallique ou un cation azoté organique ou un mélange d'au moins deux de ces cations.

3. Procédé selon la revendication 2, dans lequel M est un cation métallique qui est un cation d'un métal des terres rares, l'aluminium, le gallium, ou un métal du groupe VIII.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel z est nul dans la formule de composition.

5. Procédé pour la production d'un gallo-aluminosilicate, comprenant un procédé tel que revendiqué à la revendication 1, avec la modification qu'au lieu de la base organique (B), on utilise une source d'ions ammonium.

6. Forme hydrogène ou forme ammonium d'un gallo-aluminosilicate cristallin ayant un spectre de diffraction des rayons X sensiblement identique à celui d'une zéolite de type MFI et ayant une composition, en termes des rapports molaires des oxydes, comme suit:



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où M est un cation, n est la valence du cation, a vaut entre 0,0001 et 2, b vaut au moins 12 et z vaut de 0 à 40, forme modifiée par chauffage avec de la vapeur d'eau à une température de 400 à 700°C pendant une période d'au moins une demi-heure.

7. Utilisation, à titre de catalyseur ou de support de catalyseur, d'un gallo-aluminosilicate, modifié par traitement à la vapeur d'eau, tel que revendiqué à la revendication 6.

8. Procédé pour la production d'hydrocarbures aromatiques, ce procédé comprenant la mise en contact en phase vapeur, d'une charge hydrocarbonée d'alimentation en C₂ à C₁₂, à température élevée, avec un gallo-aluminosilicate cristallin, modifié par traitement à la vapeur d'eau, tel que revendiqué à la revendication 6.

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