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⑤④ **Catalyst composition and a process for the preparation therewith of hydrocarbons from synthesis gas.**

⑤⑦ A catalyst composition which contains at least one metal from Group 2b and at least one metal from Group 6b of the Periodic Table of the Elements or compounds thereof and a crystalline trivalent metal (e.g. iron or gallium) silicate which is obtainable by maintaining an aqueous alkaline starting mixture comprising at least one trivalent metal (A) compound, at least one silicon compound, at least one compound of a metal from Group 1a of the Periodic Table of the Elements (MX) and organic nitrogen compounds at an elevated temperature until crystalline metal silicate has formed and subsequently separating crystalline metal silicate from the mother liquor, in which starting mixture the various compounds are present within the following molar ratios:

$RN : R_4NY = 1 - 1000,$

$SiO_2 : R_4NY = 10 - 5000,$

$SiO_2 : A_2O_3 = 50 - 300,$

$SiO_2 : MX < 15,$ and

$H_2O : SiO_2 = 5 - 100,$

EP 0 251 358 A2 RN representing a pyridine and R_4NY representing an organic quaternary ammonium compound. The catalyst composition can be used in a process for the preparation of hydrocarbons from synthesis gas.

**CATALYST COMPOSITION AND A PROCESS FOR THE PREPARATION THEREWITH OF HYDROCARBONS
FROM SYNTHESIS GAS**

The invention relates to a catalyst composition which is suitable for use in a process for the preparation of hydrocarbons from synthesis gas.

Catalyst compositions containing zinc and chromium as metals from Groups 2b and 6b, respectively, of the Periodic Table of the Elements in combination with a crystalline aluminium silicate are known to possess catalytic activity for the conversion of synthesis gas into hydrocarbons.

However, a disadvantage associated with the use of said catalyst compositions is the relatively high durene production observed during the preparation of hydrocarbons therewith. In view of the relatively high melting point of durene, the presence thereof in considerable quantities in synthesized hydrocarbons which are to be further processed, or applied as gasoline, is high undesirable. Moreover, the stability of the aforementioned catalyst composition is in some cases lower than would be desirable for the application thereof on a commercial scale.

Surprisingly, it has now been found that catalyst compositions having excellent properties for use in various processes can be reproducibly prepared from particular crystalline trivalent metal silicates, provided that the various compounds required for hydrothermally synthesizing said silicates are present in the starting mixture in specific molar ratio ranges.

The invention therefore relates to a catalyst composition which contains at least one metal from Group 2b and at least one metal from Group 6b of the Periodic Table of the Elements or compounds thereof and a crystalline trivalent metal silicate which is obtainable by maintaining an aqueous alkaline starting mixture comprising at least one silicon compound, at least one trivalent metal (A) compound, at least one compound of a metal from Group 1a of the Periodic Table of the Elements (MX) and organic nitrogen compounds at an elevated temperature until crystalline metal silicate has formed and subsequently separating crystalline metal silicate from the mother liquor, in which starting mixture the various compounds are present within the following molar ratios:

RN : R₄NY = 1 - 1000,

SiO₂ : R₄NY = 10 - 5000,

SiO₂ : A₂O₃ = 50 - 300,

SiO₂ : MX < 15, and

H₂O : SiO₂ = 5 - 100,

RN representing a pyridine and R₄NY representing an organic quaternary ammonium compound.

The Periodic Table of the Elements referred to is stated in the "Handbook of Chemistry and Physics", 55th edition, CRC Press, Ohio, USA (1975).

Suitably RN represents a compound selected from the group consisting of pyridine, alkyl pyridines and (substituted alkyl) pyridines, wherein the alkyl-groups preferably comprise from 1-4 carbon atoms, and amino pyridines; most preferably RN represents pyridine.

The groups R in R₄NY suitably comprise four of the same or different alkyl-groups and/or substituted alkyl-groups, e.g. alkyl-groups comprising a hydroxy-and/or a halogen (e.g. bromine)-substituent; these alkyl-groups generally comprise from 1-20, preferably from 1-4 carbon atoms. The symbol Y in R₄NY suitably represents an anion of a mineral acid or a hydroxyl ion. Preferably R₄NY represents tetrapropyl ammonium hydroxide, a suitable alternative therefore being tetraethyl ammonium bromide.

The above-defined organic nitrogen compounds RN and R₄NY are preferably present in the starting mixture in a molar ratio from 5-200, and most preferably from 10-75, which means that the molar quantity of compound R₄NY is preferably substantially smaller than the employed molar quantity of compound RN. The molar ratio in which SiO₂ and R₄NY are present in the starting mixture is preferably from 20-400, and most preferably from 30-300.

The compound MX in the starting mixture preferably represents at least one of M_nZ and at least one of MOH in which M represents an alkali metal ion and Zⁿ⁻ represents an anion of a mineral acid (n satisfying the electroneutrality of the compound M_nZ); most preferably M represents a sodium ion. The compounds SiO₂ and MOH are suitably present in the starting mixture in a molar ratio of from 5.2-7.8, preferably of from 5.6-7.0. In any case the aqueous starting mixture has an alkaline character which means that the pH of the starting mixture is greater than 7.

The trivalent metal which is present in the crystal lattice of the silicate is preferably selected from Groups 3a, 3b and 8 of the Periodic Table of the Elements; aluminium is a suitable Group 3a metal for the present purpose. However, in order to even further improve the stability and/or the selectivity for the preparation of normally liquid hydrocarbons from synthesis gas with a catalyst composition according to the invention, most preferably iron and/or gallium are present in the crystal lattice of the trivalent metal silicate.

The compounds SiO_2 , Al_2O_3 and H_2O are preferably present in the starting mixture in the following molar ratios: $\text{SiO}_2:\text{Al}_2\text{O}_3 = 65-200$, and $\text{H}_2\text{O}:\text{SiO}_2 = 8-60$.

In the starting mixture used in the preparation of a crystalline aluminium silicate for a catalyst composition according to the present invention various silicon-and aluminium compounds may be present. Suitable silicon compounds include water glass and amorphous silica, while suitable aluminium compounds include aluminium sulphate and sodium aluminate. Suitable alkali metal salts of mineral acids include sulphates, nitrates and phosphates. It is not necessary, however, that the above-mentioned compounds are added to the aqueous starting mixture in that form. They may also be formed from other reaction components, for instance from water glass and sulphuric acid. A very suitable starting mixture comprises amorphous silica, aluminium sulphate, sodium hydroxide, sodium sulphate, pyridine, water and either tetrapropyl ammonium hydroxide or tetraethyl ammonium bromide.

The gel-like starting mixture is preferably stirred for a period of 1-24 hours prior to the hydrothermal synthesis of the crystalline metal silicate, in case it is desired to prepare such silicates which contain substantial amounts of two different co-synthesized crystalline metal (e.g. aluminium) silicates; the formation said co-synthesized silicates can be enhanced even further by adding the organic nitrogen compounds to the starting mixture at a later stage, just prior to the hydrothermal synthesis step.

The crystalline metal silicates are suitably prepared in the manner as described hereinbefore by maintaining the starting mixture, usually under autogenous pressure, at an elevated temperature, preferably from 100-250 °C, for 24-190 hours, preferably from 30-120 hours, under stirred or stagnant conditions, until the appropriate crystalline metal silicate has formed and subsequently separating crystalline metal silicate from the mother liquor (e.g. by means of filtration or centrifugation), washing the crystalline metal silicate thus obtained and drying (suitably at a temperature from 100-200 °C), optionally followed by calcining at a temperature from 200-600 °C, preferably from 300-500 °C.

By maintaining the starting mixture under stagnant conditions during the hydrothermal synthesis step, it has been found that platelet-shaped crystals of cosynthesized metal silicates can be prepared in addition to elongated (e.g. needle)-shaped crystals.

The present invention relates in particular to a catalyst composition which contains at least one metal from Group 2b and at least one metal from Group 6b of the Periodic Table of the Elements or compounds thereof and a crystalline aluminium silicate having a characteristic X-ray diffraction pattern substantially as shown in Table A and discussed hereinafter.

The crystalline metal silicates as synthesized contain alkali metal. An alkali metal content of more than 0.1% by weight is undesirable, however, when catalyst compositions containing the crystalline metal silicates are to be used in a process for the preparation of hydrocarbons by contacting synthesis gas at hydrocarbon synthesis conditions with said catalyst composition, to which process the present invention also relates. In order to reduce the alkali metal content of the silicates to less than 0.1% by weight and in particular to less than 0.01% by weight, the metal silicates are suitably contacted once or several times with an aqueous solution which comprises ammonium ions. From the NH_4^+ metal silicates obtained in this manner the H^+ metal silicates can be prepared by calcination.

The catalyst composition according to the invention preferably contains zinc together with chromium as metals from Groups 2b and 6b, respectively, in particular in the form of their oxides ZnO and Cr_2O_3 . Preferably, a $\text{ZnO}/\text{Cr}_2\text{O}_3$ catalyst component is prepared by means of continuous precipitation. The weight ratio of zinc and chromium (calculated on the basis of the sum of said oxides) to crystalline metal silicate is preferably from 0.1-10, and in particular from 0.2-7. The molar percentage of zinc, based on the sum of zinc and chromium is preferably from 50-95%, and in particular from 60-80%.

The catalyst composition according to the invention may be a macro-or a micro-mixture. In the first case the composition comprises at least two kinds of macro-particles, of which one kind consists of Groups 2b and 6b metals or compounds thereof and the other kind consists of crystalline metal silicate, and, optionally, a binder material. In the second case the composition comprises one kind of macroparticles, each macroparticle being built up from a substantial number of microparticles of each of said metals (or compounds thereof) and of the metal silicate. Catalyst compositions in the form of macromixtures may be

prepared e.g. by thoroughly mixing a fine powder of oxides of the metals in question with a fine powder of the metal silicate and shaping the resulting mixture into larger particles (preferably having a diameter from 0.2-5 mm) e.g. by extruding or tableting. Catalyst compositions in the form of physical micromixtures are preferred for use in the hydrocarbon synthesis process according to the present invention.

5 During shaping the catalyst compositions may be combined with a binder material, suitably in a weight ratio from 1-10 catalyst to binder; preferably a binder material such as alumina is used which contains no or only very little alkali metal. The binder material may also exert catalytic activity if so desired. Catalytically active metals can be suitably deposited on the binder material (e.g. by means of ion exchange) before combining it with the afore-described catalyst composition. However, it is also possible to impregnate an
10 extrudate of the catalyst composition and a binder material with a metal (compound) in order to prepare catalysts.

It has furthermore been found that the catalyst compositions according to the present invention can be improved (in particular with respect to their stability and to a further decrease in durene formation in a hydrocarbon synthesis process) by using them simultaneously as carrier for at least one additional metal
15 from Groups 1a, 2a, 2b, 4b, 5b, 6b, 7b and 8 of the Periodic Table of the Elements or a compound thereof. Preferred metals are cesium, calcium, magnesium, titanium, zinc and in particular manganese (optionally in combination with cesium) because it appears that the presence thereof in the catalyst composition leads to a shift in product distribution towards lower boiling aromatic compounds and simultaneously to a reduction of the undesired formation of durene in a hydrocarbon synthesis process to such an extent that further
20 upgrading of the hydrocarbons-containing product is no longer necessary, in particular when the gasoline fraction of said product is to be used as motor fuel. Furthermore, it appears that the addition of cesium, in particular from 0.05-0.8% by weight, calculated on basis of the catalyst composition without cesium, results in less C₁-C₄ alkane formation. The metals or their compounds may be deposited on the catalyst compositions or on the crystalline metal silicates as such by means of any process for the preparation of
25 catalysts known in the art, such as (pre-)impregnation, ion-exchange, precipitation or co-mulling. It is preferred to incorporate said additional metal(s) into the metal silicates by means of pre-impregnation with an aqueous solution of a salt (e.g. the nitrate) thereof followed by drying and, optionally, calcining of the metal-loaded silicates and combining the silicates thus obtained with Group 2b and 6b metals or compounds thereof.

30 The metal-loaded catalyst compositions preferably contain from 0.1-10% by weight, in particular from 1-5% by weight, of manganese, calculated on the basis of the catalyst composition without manganese.

The process for the preparation of hydrocarbons starts from synthesis gas containing as major components hydrogen and carbon monoxide; in addition the synthesis gas feed may contain carbon dioxide, water, nitrogen, argon and minor amounts of compounds having 1-4 carbon atoms per molecule
35 such as methane, methanol or ethene.

The synthesis gas feed can be prepared in any manner known in the art e.g. by means of steam gasification of a hydrocarbonaceous material such as brown coal, anthracite, coke, crude mineral oil and fractions thereof, and oil recovered from tar sand and bituminous shale. Alternatively, steam methane reforming and/or catalytic partial oxidation of a hydrocarbonaceous material with an oxygen-containing gas
40 can be applied to produce synthesis gas suitable for use in the hydrocarbon synthesis process according to the invention.

A process for the preparation of hydrocarbons from synthesis gas with the catalyst composition according to the present invention is preferably carried out at a temperature from 200-500 °C, a total pressure from 1-200 bar abs., a space velocity from 200-3000 l (S.T.P.) synthesis gas/kg catalyst/hour and a H₂/CO molar feed ratio from 0.3-5. Particularly preferred process conditions include a temperature from
45 300-450 °C, a pressure from 5-100 bar abs., a space velocity from 400-2000 l (S.T.P.) synthesis gas/kg catalyst/hour and a H₂/CO molar feed ratio from 0.4-2. The expression "S.T.P." as referred to hereinbefore means Standard Temperature (of 0 °C) and Pressure (1 bar abs.).

Furthermore, the present invention relates to hydrocarbon-containing mixtures (suitably containing
50 aromatic-, naphthenic-and/or acyclic-compounds which may further contain oxygen and/or light olefins) whenever prepared according to a process as described hereinbefore.

EXAMPLE 1

(a) Preparation of crystalline aluminium silicates A and B.

5 An aqueous alkaline starting mixture was prepared by adding to water the following compounds: amorphous silica, aluminium sulphate, sodium sulphate, sodium hydroxide, pyridine and tetrapropyl ammonium hydroxide in such quantities that the starting mixture had the following molar composition: 93.5 SiO₂-1 Al₂O₃-30 C₅H₅N-0.5 (C₃H₇)₄NOH-7.4 Na₂O-19.6 Na₂SO₄-1938 H₂O.

10 Aluminium silicate A was prepared by maintaining the starting mixture at 150 °C for 72 hours with stirring in an autoclave under autogenous pressure. After cooling the reaction mixture crystalline aluminium silicate was filtered off, washed with water until the pH of the wash water was about 8 and dried at 120 °C for 16 hours; the dried crystalline aluminium silicate was calcined in air at 538 °C for two hours followed by an ammonium-exchange treatment and subsequently calcining in air at 500 °C for one hour to obtain the aluminium silicate in the H⁺ form. The so obtained aluminium silicate A had the characteristic X-ray diffraction pattern given in Table A, in which "D-space" represents the interplanar spacing (in Å) calculated from the measured theta (Bragg angle) by using the Bragg equation and "I/I_{max},%" represents the intensity of a peak, expressed as a percentage of the intensity of the main peak.

TABLE A

| D-space | I/I _{max} , % |
|---------|------------------------|
| 11.04 | 57 |
| 9.96 | 30 |
| 9.93 | 31 |
| 3.84 | 100 |
| 3.81 | 68 |
| 3.74 | 33 |
| 3.71 | 59 |
| 3.43 | 12 |
| 3.39 | 9 |
| 3.34 | 11 |
| 3.12 | 82 |
| 1.92 | 51 |

45 Chemical analysis of crystalline aluminium silicate A showed that its aluminium content was 1.2% by weight.

Aluminium silicate B was prepared by using a similar starting mixture as used for aluminium silicate A, except that the molar amount of (C₃H₇)₄NOH was increased from 0.5 to 1.0. The starting mixture was maintained at 150 °C for 72 hours with stirring in an autoclave under autogenous pressure and treated further as described hereinabove for the preparation of aluminium silicate A.

50 The aluminium silicate B thus obtained gave a similar characteristic X-ray diffraction pattern as shown in Table A.

The aluminium content of aluminium silicate B was 1.2% by weight.

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(b) Preparation of catalyst compositions 1 and 2.

From crystalline aluminium silicates A and B catalyst compositions 1 and 2, respectively, were prepared by mixing a combination of ZnO and Cr₂O₃ having a Zn : Cr atomic ratio of 66 : 34 with the respective crystalline aluminium silicates in a weight ratio of 5 : 1 (calculated on the basis of said zinc-and chromium-oxides).

(c) Preparation of catalyst compositions 3 and 4 containing manganese.

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18 grams each of catalyst compositions 1 and 2 were impregnated with 10 ml of a solution containing 0.93 mol manganese nitrate/l at a temperature of 25 °C, dried at a temperature of 120 °C for 2 hours and then calcined at a temperature of 450 °C for 1 hour. The resulting catalyst compositions 3 and 4, respectively, both contained 2.8% by weight of manganese, calculated on the basis of the catalyst compositions without manganese.

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EXAMPLE 2

20 (a) Preparation of crystalline aluminium silicate C.

Aluminium silicate C was prepared using a similar starting mixture as used for aluminium silicate A, except that the molar amount of (C₃H₇)₄NOH was decreased from 0.5 to 0.28. The starting mixture was maintained at 150 °C for 75 hours with stirring in an autoclave under autogenous pressure and treated

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further as described hereinbefore for the preparation of aluminium silicates A and B. The aluminium silicate C thus obtained showed a X-ray diffraction pattern as given in the following Table B.

TABLE B

30

| | <u>D-space</u> | <u>I/I max, %</u> |
|----|----------------|-------------------|
| | 11.22 | 41 |
| 35 | 10.09 | 22 |
| | 9.79 | 11 |
| | 3.98 | 13 |
| 40 | 3.86 | 100 |
| | 3.83 | 71 |
| | 3.75 | 44 |
| | 3.73 | 56 |
| 45 | 3.65 | 37 |
| | 3.54 | 15 |
| | 3.43 | 22 |
| 50 | 3.36 | 11 |
| | 3.31 | 19 |
| | 3.05 | 13 |
| | 2.99 | 14 |
| 55 | 2.98 | 15 |

Chemical analysis of composite crystalline aluminium silicate C showed that its aluminium content was 2.7% by weight. Composite aluminium silicate C comprises a crystalline material containing two different crystalline aluminium silicates including a major amount of aluminium silicate A.

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(b) Preparation of crystalline aluminium silicate E.

Aluminium silicate E was prepared using a similar starting mixture as used for aluminium silicate C, except that the molar amounts of $0.28 (C_3H_7)_4NOH$ and $30C_5H_5-N$ were not added until after the starting gel had been mixed by stirring for 16 hours at ambient temperature; the starting mixture was subsequently treated further as described hereinbefore for the preparation of silicate C, except that the hydrothermal synthesis was carried out under stagnant conditions. The composite crystalline aluminium silicate E thus obtained comprises a crystalline material containing about equal fractions of aluminium silicate A and ferrierite.

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(c) Preparation of catalyst composition 5.

From composite aluminium silicate C catalyst composition 5 was prepared in a similar manner as described for catalyst compositions 1 and 2 in Example 1b).

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(d) Catalyst composition 6 which contained 2.8% by weight of manganese, calculated on the basis of catalyst composition 5, was prepared from the latter composition in a similar manner as described hereinbefore in Example 1c for catalyst compositions 3 and 4.

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COMPARATIVE EXAMPLE

a) Crystalline aluminium silicate D was prepared in a similar manner as aluminium silicate A by using an aqueous alkaline starting mixture having the following molar composition:

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$93.5 SiO_2 - 1.25 Al_2O_3 - 33.6 (C_3H_7)_4NOH - 1.25 Na_2O - 1938 H_2O$. The characteristic X-ray diffraction pattern of crystalline aluminium silicate D is given in the following Table C.

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TABLE C

| D-space | I/I _{max} , % |
|---------|------------------------|
| 11.03 | 74 |
| 9.90 | 40 |
| 3.84 | 100 |
| 3.80 | 70 |
| 3.73 | 40 |
| 3.70 | 62 |
| 3.42 | 10 |
| 3.39 | 4 |
| 3.34 | 8 |
| 3.13 | 75 |
| 1.92 | 48 |

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Aluminium silicate D, which is not a compound of a catalyst composition in accordance with the present invention, comprised a crystalline aluminium silicate with a similar chemical composition as aluminium silicate A. However, by comprising the characteristic X-ray diffraction patterns as shown in Tables A and C it will be clear that aluminium silicate D is different from aluminium silicate A or C.

5 b) Catalyst composition 7 was prepared from aluminium silicate D in a similar manner as described in Example 1b) for catalyst compositions 1 and 2.

EXAMPLE 3

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Hydrocarbon synthesis experiments.

Synthesis gas containing hydrogen and carbon monoxide in a molar ratio of 0.5 led with a space velocity of 850 l (S.T.P.)/kg catalyst/hour through a microflow reactor containing catalyst compositions 1, 2, 15 5 and 7, respectively, with a particle size of 0.2-0.6 mm at a temperature of 375 °C and a pressure of 60 bar abs. The normally liquid product thus obtained contained 4.0% by weight of durene when catalyst composition 1 or 2 was employed whereas the composition 5 a durene-content of only 1.5 %w was attained. The liquid product obtained with comparative catalyst composition 7 contained 9.6 %w durene, thus showing a shift in product distribution to undesirably high boiling aromatic compounds compared to 20 catalyst compositions 1 and 2.

Further hydrocarbon synthesis experiments were carried out under similar conditions as described hereinbefore using manganese-containing catalyst compositions 3, 4 and 6 and equivalent catalyst compositions 1, 2 and 5, respectively, which did not contain manganese. The results of said experiments are given in the following Table D.

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| | TABLE D | | | |
|-------------------------|---------|--------|-----|-----|
| Catalyst composition | 1 or 2 | 3 or 4 | 5 | 6 |
| durene, %w on aromatics | 9.8 | 6.2 | 7.9 | 5.2 |
| life time, h | 220 | 550 | 100 | 340 |

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35 The expression "life time" as used hereinbefore represents the period (in hours) in which the initial conversion of CO and H₂ feed (in % by volume) has been halved divided by ln 2. The expression "durene, %w on aromatics" represents the weight percentage of durene based on the amount of aromatic compounds present in the normally liquid product fraction.

40 From the results given in Table D it will be clear that the incorporation of a relatively small amount (2.8% by weight) of manganese into the catalyst compositions according to the invention leads to a substantial increase in the life time of said compositions, while the formation of durene is even further suppressed.

45 Claims

1. A catalyst composition which contains at least one metal from Group 2b and at least one metal from Group 6b of the Periodic Table of the Elements or compounds thereof and a crystalline trivalent metal silicate which is obtainable by maintaining an aqueous alkaline starting mixture comprising at least one 50 silicon compound, at least one trivalent metal (A) compound, at least one compound of a metal from Group 1a of the Periodic Table of the Elements (MX) and organic nitrogen compounds at an elevated temperature until crystalline metal silicate has formed and subsequently separating crystalline metal silicate from the mother liquor, in which starting mixture the various compounds are present within the following molar ratios:

55 RN : R₄NY = 1 - 1000,
SiO₂ : R₄NY = 10 - 5000,
SiO₂ : A₂O₃ = 50 - 300,

SiO₂ : MX < 15, and
H₂O : SiO₂ = 5 - 100,

RN representing a pyridine and R₄NY representing an organic quaternary ammonium compound.

2. A catalyst composition according to claim 1 wherein RN represents a compound selected from the group consisting of pyridine, alkyl pyridines and (substituted alkyl) pyridines.
3. A catalyst composition according to claim 1 or 2 wherein the groups R in R₄NY comprise four alkyl-groups and/or substituted alkyl-groups and Y represents an anion.
4. A catalyst composition according to any one of the preceding claims wherein the trivalent metal (A) represents iron and/or gallium.
5. A catalyst composition which contains at least one metal from Group 2b and at least one metal from Group 6b of the Periodic Table of the Elements or compounds thereof and a crystalline aluminium silicate having a X-ray diffraction pattern substantially as shown in Table A.
6. A catalyst composition according to any one of the preceding claims which contains zinc as metal from Group 2b and chromium as metal from Group 6b.
7. A catalyst composition according to any one of the preceding claims which additionally contains at least one metal from Groups 1a, 2a, 2b, 4b, 5b, 6b, 7b and 8 of the Periodic Table of the Elements or a compound thereof.
8. A catalyst composition according to claim 7 which contains from 0.1-10%, and in particular from 1-5%, by weight of manganese, calculated on the basis of the catalyst composition without manganese.
9. A process for the preparation of hydrocarbons from synthesis gas wherein said synthesis gas is contacted at hydrocarbon synthesis conditions with a catalyst composition according to any one of the preceding claims.
10. A process according to claim 9 which is carried out at a temperature from 200-500 °C, a total pressure from 1-200 bar abs., a space velocity from 200-3000 l (S.T.P.) synthesis gas/kg catalyst/hour and a H₂/CO molar feed ratio from 0.3-5.
11. Hydrocarbon-containing mixtures whenever prepared by a process according to claim 9 or 10.

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