

Process for the preparation of crystalline microporous and mesoporous metal silicates, products obtainable by said process and their use ✓

- 5 The invention relates to a process for the preparation of crystalline microporous and mesoporous metal silicates composed of silicon dioxide and one or more metal oxides, to products obtainable by said process and to their use.
- 10 A variety of crystalline microporous and mesoporous metal silicates are known. According to the JUPAC [sic] definition, micropores are understood as meaning pores with a diameter of less than 2 nm and mesopores are understood as meaning pores with a diameter of 2 to 50 nm.
- 15 Some crystalline metal silicates with regular micropores or mesopores are extremely effective catalysts in a very wide variety of applications. In particular, microporous products of the composition $(\text{SiO}_2)_{1-x}(\text{TiO}_2)_x$, in which
- 20 titanium atoms replace some of the silicon atoms in the crystal lattice, have achieved industrial importance as oxidation catalysts. The structures of these metal silicates differ according to the starting materials and conditions of preparation: Thus, for example, so-called
- 25 titanium silicalite-1, titanium silicalite-2 and titanium beta-zeolite have the MFI, MEL and BEA crystal structures respectively. Crystal structure types of known zeolites and silicalites are described in W.M. Meier, D.H. Olson, Atlas of Zeolite Structure Types, Butterworth-Heinemann,
- 30 1993. Known structures with regular mesopores are the MCM-41 and MCM-48 structures described in C.T. Kresge et

al., Nature, 359 (1992) 710 - 712. A survey of structures with regular mesopores is also given in S. Behrens, Angew. Chemie, 1996, 108 (5), 561 - 564.

- 5 It is known that the catalytic efficacy of generic metal silicates is substantially dependent on their phase purity and the morphology and hence on the conditions of preparation. For example, the catalytic activity of titanium silicalite is reduced by other titanium-
10 containing phases, for instance TiO_2 , and by an increase in the crystal size - see B. Notari in (a) Catal. Today 18 (1993), 163 and (b) Stud. Surf. Sci. Catal. 67 (1991), 243.
- 15 Generic metal silicates, for instance titanium silicalite-1, can be prepared by hydrothermal synthesis: In the first step a silicon source and a titanium source, conventionally tetraalkyl orthosilicate and tetraalkyl orthotitanate, and water are condensed to a gel in the
20 presence of a structure-determining quaternary ammonium cation, usually used in the form of the quaternary ammonium hydroxide, and the gel is then crystallized under hydrothermal conditions, usually above 100°C and under autogenous pressure; the solid formed is separated off,
25 washed, dried and calcined above 300°C . The way in which the Ti component is introduced is liable to cause problems, it often being impossible to exclude contamination of the product by TiO_2 as a foreign phase - loc. cit. B. Notari (b). According to EP 543 247 the
30 quaternary ammonium hydroxide can be replaced as the template with a combination of a quaternary ammonium salt

and a base such as ammonia, although the crystals obtained are relatively large. According to US patent 5,198,203 a mesoporous titanium silicate of the MCM-41 structure can be prepared with cetyltrimethylammonium hydroxide as the
5 template.

Another known silicon source is pyrogenic silicic acid: According to R. Kumar et al. in Stud. Surf. Sci. Catal. 84 (1994) 109, titanium silicalite-1 can be obtained by
10 hydrothermal synthesis from pyrogenic silicic acid and tetrabutyl orthotitanate. The use of a tetraalkyl orthotitanate carries the risk of obtaining a product of insufficient phase purity.

15 According to EP 0 311 983 titanium silicalites are prepared by impregnating a coprecipitated porous TiO_2 - SiO_2 material, which can be amorphous or crystalline, with a template compound and then subjecting the product to hydrothermal synthesis. Suggestions of using
20 coprecipitates with other metals, or pyrogenic mixed oxides, are not to be found in said document.

In known synthesis processes the generic microporous metal silicates are formed as crystallites with a size usually
25 of less than one micrometre, which can only be separated from a liquid at considerable expense. For many industrial applications the fine material is therefore coarsened by a subsequent agglomeration step. According to EP 0 265 018 the agglomeration is effected using
30 oligomeric SiO_2 as a binder.

According to EP 0 299 430 a preformed amorphous SiO_2 matrix is impregnated with an aqueous solution containing a soluble titanium compound and a suitable template, and crystallized under hydrothermal conditions, the shape and size of the SiO_2 matrix remaining essentially unchanged. This process again has the disadvantage that the use of a soluble titanium compound carries the risk of reducing the phase purity and hence the catalytic activity.

The object of the invention consists in providing another process for producing generic metal silicates of high phase purity and high catalytic activity. The process should be suitable not only for the preparation of products based on $(\text{SiO}_2)_{1-x}(\text{TiO}_2)_x$, but also for the preparation of products in which titanium is replaced with one or more other metals in the crystal lattice. Finally, according to a particular embodiment, the process should also be capable of being carried out in such a way that binder-free shaped objects of the crystalline microporous and mesoporous metal silicates can be obtained directly, i.e. without a subsequent agglomeration step.

A process for the preparation of microporous and mesoporous metal silicates, comprising the hydrothermal reaction of a silicon source in the presence of a metal source and a template, has now been found which is characterized in that a pyrogenic metal-silicon mixed oxide is used as the silicon and metal source.

The general composition of the pyrogenic mixed oxides and hence also of the crystalline microporous and mesoporous metal silicates to be prepared is conventionally



5 A and A' are a metal of valency p from the group comprising B, Al, Ga, In, Ge, Sn and Pb or from subgroups 3 to 8.

m and m' and n and n' are the number of atoms, where $m \cdot p = 2n$ and $m' \cdot p = 2n'$.

10

x is a number between 0.0001 and 0.25, preferably between 0.001 and 0.2 and especially between 0.005 and 0.1.

15 y in formula (Ib) is a number greater than 0 and less than 1.

Apart from SiO_2 , pyrogenic mixed oxides which are preferably to be used contain one or more oxides from the group comprising Al_2O_3 , B_2O_3 , TiO_2 , ZrO_2 , V_2O_5 , Cr_2O_3 and Fe_2O_3 . Oxides of the subgroup elements are optionally present not only in the highest oxidation state but also in a lower oxidation state. Generic metal silicates which are to be used as oxidation catalysts are prepared with mixed oxides which are free of aluminium oxide, the process according to the invention giving metal silicalites in this case. Generic metal silicates of the general composition



30

are prepared using mixed oxides of general composition (Ia). M in composition (II) is a cation of valency q from the group comprising alkali metals, alkaline earth metals, H^+ , NH_4^+ and $N(alkyl)_4^+$; $m \cdot p + r \cdot q = 2n$ in (II). In the process according to the invention, M is introduced into the metal silicate either via the template or via alkali metal or alkaline earth metal hydroxide or ammonia present in the hydrothermal synthesis. After the calcination of a generic metal silicate of composition (II), M is a proton or an alkali metal or alkaline earth metal ion. However, said cations M or other cations can also be incorporated into the microporous and mesoporous metal silicates at a later stage by means of conventional ion exchange reactions.

15.

The pyrogenic mixed oxides to be used in the process according to the invention can be prepared in a manner known per se from a mixture of a volatile silicon compound and one or more volatile metal compounds (compounds of A and/or A'), for example by flame hydrolysis or the luminous arc process. The process according to the invention is preferably carried out using pyrogenic mixed oxides of silicon which have been prepared by flame hydrolysis, for example those known from Ullmann's Encyklopädie der technischen Chemie (Ullmann's Encyclopaedia of Chemical Technology), 4th edition, volume 21, pages 464 to 465 (1982), and DE-A 36 11 449.

The process according to the invention can be carried out using both the pulverulent pyrogenic mixed oxides and shaped objects thereof.

The shaped objects of the metal-silicon mixed oxide can be produced by known processes, for example spray granulation, fluidized bed granulation, extrusion, pelleting or tableting. In a preferred embodiment of the invention the shaped objects can be produced by means of spray granulation, as described for example in DE-A 36 11 449.

In the process according to the invention the pyrogenic metal/silicon mixed oxide, in powder form or in the form of a binder-free shaped object produced therefrom, is brought into contact with an aqueous solution of a suitable template; when using coarser shaped objects of mixed oxide, for instance extrudates, this is conventionally an impregnation process. After intermediate drying, if appropriate, this step is followed by the hydrothermal reaction to convert the pyrogenic metal-silicon mixed oxide to the crystalline microporous or mesoporous metal silicate according to the invention. After the hydrothermal reaction the template is removed from the metal silicate in a manner known per se - conventionally by extraction or, preferably, by calcination.

Suitable template compounds are amines having one or more amino groups, amino alcohols or tetrasubstituted ammonium compounds. Tetraalkylammonium compounds are particularly suitable, especially tetraalkylammonium hydroxide. The nature of the alkyl groups in said tetraalkylammonium compounds is significant in terms of the pore structure: The tetraalkylammonium compounds used to prepare

microporous metal silicates according to the invention are preferably those in which alkyl is ethyl, propyl and butyl, preferably n-propyl. Thus, for example, metal silicates according to the invention of the MFI, MEL and BEA structure can be prepared using tetra-n-propylammonium, tetra-n-butylammonium and tetraethylammonium compounds respectively. The tetraalkylammonium compounds used to prepare mesoporous metal silicates according to the invention are preferably those which have surfactant properties; accordingly these compounds contain an alkyl group or an alkenyl group having at least 7 C atoms in the longest chain. Particularly preferred ammonium compounds are those of the general formula $\text{RNR}'_3\text{X}^-$, in which R contains 12 to 18 C atoms and is preferably unbranched and saturated, R' has 1 or 2 C atoms and X is the anion, conventionally hydroxide or halide. Cetyltrimethylammonium chloride or bromide and lauryltrimethylammonium chloride or bromide are particularly suitable for the preparation of mesoporous structures. When using tetraalkylammonium halides as the template, a base, such as ammonia, a primary, secondary or tertiary amine or an alkali metal or alkaline earth metal hydroxide, is added to the template solution used for the contacting/impregnation process.

The template compound is conventionally used in a molar ratio of template to SiO_2 of 0.05 to 2.0. For the preparation of microporous metal silicates, a molar ratio of template to SiO_2 of between 0.05 and 1.0, especially of between 0.10 and 0.45, is preferred. For the preparation of mesoporous metal silicates according to the invention of the MCM-41 or MCM-48 structure, a molar ratio of

template to SiO_2 of between 0.05 and 2.0, especially of between 0.1 and 0.8, is preferred.

The molar ratio OH^-/SiO_2 is generally between 0.05 and 2.0 and preferably between 0.1 and 1.0. In the hydrothermal reaction the molar ratio $\text{H}_2\text{O}/\text{SiO}_2$ is between 1 and 200 and preferably between 4 and 100. Seed crystals of the same structural type can be added to the reaction mixture if necessary. The molar ratio $\text{H}_2\text{O}/\text{SiO}_2$ is generally lower when using shaped objects of pyrogenic mixed oxides than when using pyrogenic mixed oxides as obtained directly by flame hydrolysis.

In the process according to the invention for the preparation of microporous metal silicates, the hydrothermal reaction is conventionally carried out under autogenous pressure at a temperature between 100 and 220°C and preferably between 150 and 190°C. Mesoporous metal silicates according to the invention can also be prepared at lower temperature, the conventional temperature range being between 25 and 200°C, preferably between 50 and 175°C and especially between 70 and 150°C. The hydrothermal reaction is carried out until the pyrogenic mixed oxide used has been completely converted to the crystalline microporous or mesoporous metal silicate according to the invention at the given reaction temperature. The degree of completion of the reaction can be determined by known methods of structural analysis. Under optimized conditions the reaction time is conventionally between 1 and 50 hours.

To separate the template compound from the solid obtained in the hydrothermal reaction, said solid is usually calcined at between 300 and 1000°C, optionally after a prior washing process, it being possible for the
5 calcination step to include a shaping process at the same time. In the case of the mesoporous metal silicates according to the invention, at least some of the template compound can also be removed by extraction with an organic solvent.

10

In one particular embodiment of the process according to the invention, the pyrogenic metal-silicon mixed oxide, for instance as obtained by flame hydrolysis, is suspended in an aqueous template solution. The molar ratios used
15 here can be the same as those indicated above. This suspension is spray-dried and the resulting granules containing the template are treated in an autoclave at elevated temperature, for example at 175°C, optionally in a steam atmosphere. Said spray drying is advantageously
20 carried out by setting the temperature of the drying air in the range 100 to 500°C so that the resulting granules have a water content of 5 to 50 wt.%. After the hydrothermal reaction the shaped objects obtained are calcined at a temperature of 300 to 1000°C, preferably of
25 400 to 800°C, to remove the template.

The process according to the invention can be carried out reproducibly and is easy to control. The use of the pyrogenic mixed oxides avoids problems due to the presence
30 of foreign phases of the metal oxides in question. A high catalytic activity is a characteristic feature of the

crystalline microporous and mesoporous metal silicates obtainable by the process according to the invention. The generic metal silicates can moreover be obtained not only in the form of very finely powdered materials but also in the form of different shaped objects. When using shaped objects of pyrogenic mixed oxides or forming such shaped objects directly before the hydrothermal reaction, a subsequent agglomeration step is not necessary. The addition of catalytically inactive binders is also superfluous. A further advantage of shaped objects of crystalline microporous and mesoporous metal silicates obtainable according to the invention is that they can be more easily separated from liquids by filtration than can unshaped catalysts, thereby facilitating their use as suspension catalysts. As pyrogenic mixed oxides are easy to shape, for instance into spheres, extrudates, pellets or tablets, and the shape remains essentially unchanged in the process according to the invention, said process directly produces suitable shaped objects for use as catalysts in fixed bed reactors.

Although it is known from EP 0 311 983 B that coprecipitated TiO_2 - SiO_2 material can be used for the preparation of titanium silicalites, the coprecipitates to be used are very porous products. It was therefore surprising that crystalline microporous and mesoporous metal silicates are easily obtainable by using pore-free pyrogenic mixed oxides such as those used in the process according to the invention.

As such, preferably in the form of shaped objects, the crystalline microporous and mesoporous metal silicates obtainable according to the invention are used as catalysts. Titanium silicalites and other aluminium-free products are particularly suitable as catalysts for oxidation reactions with hydrogen peroxide or organic hydroperoxides. Examples are the use of titanium silicalite-1 as a catalyst for the reaction of olefins, i.e. propene, with hydrogen peroxide to give epoxides (EP 100 119), the reaction of aromatics with hydrogen peroxide to give hydroxyaromatics (DE 31 35 559), the reaction of aliphatic hydrocarbons with hydrogen peroxide to give alcohols and ketones (EP 376 453) and the reaction of cyclohexanone with hydrogen peroxide and ammonia to give cyclohexanone oxime (EP 208 311). Titanium silicalite-2 is used as a catalyst for the hydroxylation of phenol (J.S. Reddy, S. Sivasanker, P. Ratnasamy, J. Mol. Catal. 71 (1992) 373) and for the reaction of cyclohexanone with hydrogen peroxide and ammonia to give cyclohexanone oxime (J.S. Reddy, S. Sivasanker, P. Ratnasamy, J. Mol. Catal. 71 (1992) 383). Titanium beta-zeolite can be used as a catalyst for the reaction of olefins with hydrogen peroxide or organic hydroperoxides to give epoxides (A. Corma, P. Esteve, A. Martinez, S. Valencia, J. Catal. 152 (1995) 18 and EP 659 685).

Example 1: Preparation of a titanium silicalite-1 powder

137.0 g of tetrapropylammonium hydroxide solution (40 wt.%) and 434.2 g of deionized water are placed in a polyethylene beaker and 111.1 g of a pyrogenic silicon-titanium mixed oxide containing 3.0 wt.% of TiO_2 are added, with stirring. The resulting synthetic gel is first aged for four hours at 80°C, with stirring, and then crystallized in an autoclave for 24 hours at 175°C. The solid obtained is separated from the mother liquor by centrifugation, washed with three times 250 ml of deionized water, dried at 90°C and calcined in an air atmosphere for four hours at 550°C. The yield is 98.3 g.

The X-ray diffraction diagram of the catalyst prepared in this way shows the diffraction pattern typical of the MFI structure and the IR spectrum shows the band at 960 cm^{-1} characteristic of titanium-containing molecular sieves. Wet chemical analysis gives a titanium content of 2.3 wt.% of TiO_2 . The DR-UV-Vis spectrum also shows that the sample is free of titanium dioxide.

Example 2: Application Example of the epoxidation of propylene with hydrogen peroxide

25

1.0 g of the catalyst prepared according to Example 1 in 300 ml of methanol is placed in a thermostated laboratory autoclave with gas dispersion stirrer, at 40°C under a propylene atmosphere, and the solvent is saturated with propylene under an excess pressure of 3 bar. 13.1 g of

30

30 wt.% aqueous hydrogen peroxide solution are then added all at once, with stirring, and the reaction mixture is kept at 40°C and 3 bar, additional propylene being metered in via a pressure regulator in order to make up the
5 quantity consumed by the reaction. Samples are taken at regular intervals on a filter and the hydrogen peroxide content of the reaction mixture is determined by redox titration with cerium(IV) sulphate solution. The plot of $\ln(c/c_0)$ against the time t , c being the measured H_2O_2
10 concentration at time t and c_0 being the calculated H_2O_2 concentration at the start of the reaction, gives a straight line. An activity coefficient k of 25.4 min^{-1} is determined from the gradient of the lines by means of the relationship $dc/dt = -k \cdot c \cdot c_{cat}$, where c_{cat} is the catalyst
15 concentration in kg of catalyst per kg of reaction mixture.

Example 3: Preparation of titanium silicalite-1 microgranules

20

800 g of deionized water and 30 g of acetic acid are placed in a polyethylene beaker and 200 g of a pyrogenic silicon-titanium mixed oxide containing 3.6 wt.% of TiO_2 are added, with stirring. This mixture is sheared for
25 five minutes in an Ultraturax [sic] stirrer. The resulting suspension is dried by means of a spray dryer (NIRO-Atomizer model 1638; inlet temperature 380°C; outlet temperature 102°C; speed of rotation of the spray disk $15,000 \text{ min}^{-1}$). 20 g of the resulting microgranules, with a
30 mean particle diameter of 30 μm , are impregnated with a mixture of 20 g of tetrapropylammonium hydroxide solution

(40 wt.%) and 20 g of deionized water. The impregnated microgranules are charged into an autoclave with a Teflon inliner and crystallized for 24 hours at 175°C under static conditions. The solid obtained is separated from the
5 mother liquor by centrifugation, washed with three times 100 ml of deionized water, dried at 90°C and calcined in an air atmosphere for four hours at 550°C. The yield is 17 g.

The catalyst prepared in this way consists of titanium
10 silicalite-1 microgranules.

Example 4: Preparation of titanium silicalite-1 microgranules

15 720.7 g of deionized water and 179.3 g of tetrapropylammonium hydroxide solution (40 wt.%) are placed in a polyethylene beaker and 100 g of a pyrogenic silicon-titanium mixed oxide containing 3.6 wt.% of TiO_2 are added, with stirring. This mixture is sheared for
20 five minutes in an Ultraturax [sic] stirrer. The resulting suspension is dried by means of a spray dryer (NIRO-Atomizer model 1638; inlet temperature 380°C; outlet temperature 90°C; speed of rotation of the spray disk 15,000 min^{-1}). 20 g of the resulting microgranules, with a
25 mean particle diameter of 30 μm , a loss on drying of 23 wt.% (10 h at 105°C; corresponds to the water content) and a loss on calcination of 43 wt.% (5 h at 550°C; corresponds to the water and template content), are charged into an autoclave with a Teflon inliner and crystallized for 4
30 days at 180°C under static conditions. The solid is then

dried at 90°C and calcined in an air atmosphere for four hours at 550°C.

The catalyst prepared in this way consists of titanium
5 silicalite-1 microgranules.

Example 5: Preparation of a titanium beta-zeolite powder

435.3 g of tetraethylammonium hydroxide solution (35 wt.%)
10 and 236.3 g of deionized water are placed in a
polyethylene beaker and 109.6 g of a pyrogenic silicon-
titanium mixed oxide containing 3.0 wt.% of TiO_2 are added.
The resulting mixture is aged for four hours at 80°C and,
after cooling to room temperature, 12 g of beta-zeolite
15 seed crystals with an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 27 are added.
This synthetic gel is crystallized in an autoclave for 3
days at 150°C, with stirring.

The solid obtained is separated from the mother liquor by
20 centrifugation, washed three times, each time with 250 ml
of deionized water, dried at 90°C and calcined in an air
atmosphere for four hours at 550°C.

The X-ray diffraction diagram of the catalyst prepared in
25 this way shows the diffraction pattern typical of the BEA
structure. Wet chemical analysis gives a titanium content
of 1.8 wt.% of TiO_2 .

Example 6: Preparation of a mesoporous titanium silicate
30 of the MCM-41 structure

114.2 g of tetramethylammonium hydroxide solution (10 wt.%) are placed in a polyethylene beaker and 30.0 g of a pyrogenic silicon-titanium mixed oxide containing 3.6 wt.% of TiO_2 are added, with stirring. This mixture is stirred for one hour. A suspension of 29.1 g of cetyltrimethylammonium bromide ($\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$) in 109.2 g of deionized water is then added, with stirring, and stirring is continued for 10 minutes. The resulting synthetic gel (molar composition: SiO_2 : 0.17 $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$: 0.26 Me_4NOH : 25 H_2O) is crystallized in an autoclave for 48 hours at 140°C under static conditions. The solid obtained is filtered off and washed with deionized water until the filtrate is neutral. The solid is dried at 90°C and then calcined in an air atmosphere for four hours at 640°C . The yield is 28 g.

The X-ray diffraction diagram of the catalyst prepared in this way shows the diffraction pattern typical of MCM-41 materials, with a d_{100} reflection at 3.60 nm. Examination by sorption analysis with nitrogen at 77 K shows a mean pore diameter of 3.16 nm, a BET specific surface area of $1040 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of 0.89 g ml^{-1} [sic]. Wet chemical analysis gives a titanium content of 4.6 wt.% of TiO_2 . The material is catalytically active in the epoxidation of propene with hydrogen peroxide.

Example 7: Preparation of a mesoporous titanium silicate of the MCM-48 structure

114.2 g of tetramethylammonium hydroxide solution (10 wt.%) are placed in a polyethylene beaker and 30.0 g of a pyrogenic silicon-titanium mixed oxide containing 3.6 wt.% of TiO_2 are added, with stirring. This mixture is stirred
5 for one hour. A suspension of 114.2 g of cetyltrimethylammonium bromide ($\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$) in 435.2 g of deionized water is then added, with stirring, and stirring is continued for 10 minutes. The resulting synthetic gel (molar composition: SiO_2 : 0.65 $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$
10 : 0.26 Me_4NOH : 62 H_2O) is crystallized in an autoclave for 48 hours at 140°C under static conditions. The solid obtained is filtered off and washed with deionized water until the filtrate is neutral. The solid is dried at 90°C and then calcined in an air atmosphere for four hours at
15 640°C .

The catalyst prepared in this way consists of Ti-MCM-48.

Example 8: Preparation of a boron pentasil zeolite

20

800 g of aqueous hexamethylenediamine solution (50 wt.%) are placed in a polyethylene beaker and 70.7 g of a pyrogenic silicon-boron mixed oxide containing 9.5 wt.% of B_2O_3 are added, with stirring. This mixture is stirred for
25 half an hour and then crystallized in an autoclave for five days at 170°C . The solid obtained is separated from the mother liquor by centrifugation, washed with three times 250 ml of deionized water, dried at 90°C and calcined in an air atmosphere for six hours at 550°C .

30

The X-ray diffraction diagram of the catalyst prepared in this way shows the diffraction pattern typical of the MFI structure. Wet chemical analysis gives a B_2O_3 content of 2.4 wt.%.

5

Example 9: Preparation of a boron silicate of the MCM-41 structure

157.6 g of tetramethylammonium hydroxide solution (10 wt.%) are placed in a polyethylene beaker and 42.3 g of a pyrogenic silicon-boron mixed oxide containing 5.5 wt.% of B_2O_3 are added, with stirring. This mixture is stirred for one hour. A suspension of 65.5 g of cetyltrimethylammonium bromide ($C_{16}H_{33}(CH_3)_3NBr$) in 576.5 g of deionized water is then added, with stirring, and stirring is continued for 10 minutes. The pH is adjusted to 11.5 by the addition of dilute sulphuric acid. The resulting synthetic gel is crystallized in an autoclave for 48 hours at $140^\circ C$ under static conditions. The solid obtained is filtered off and washed with deionized water until the filtrate is neutral. The solid is dried at $90^\circ C$ and then calcined in an air atmosphere for four hours at $540^\circ C$.

25 The X-ray diffraction diagram of the catalyst obtained shows the diffraction pattern typical of MCM-41 materials. Examination by sorption analysis with nitrogen at $77^\circ K$ shows a mean pore diameter of 2.83 nm, a BET specific surface area of $1060 \text{ m}^2/\text{g}$ and a pore volume of 0.89 ml/g.

Example 10: Preparation of a zirconium silicalite-1 powder

62.4 g of tetrapropylammonium hydroxide solution (40 wt.%)
and 229.8 g of deionized water are placed in a
5 polyethylene beaker and 57.4 g of a pyrogenic silicon-
zirconium mixed oxide containing 3.0 wt.% of ZrO_2 are
added, with stirring. The resulting synthetic gel is then
crystallized in an autoclave for 24 hours at 175°C. The
solid obtained is separated from the mother liquor by
10 centrifugation, washed with three times 250 ml of
deionized water, dried at 90°C and calcined in an air
atmosphere for four hours at 550°C.

The X-ray diffraction diagram of the catalyst obtained
15 shows the diffraction pattern typical of the MFI
structure. X-ray fluorescence analysis gives a ZrO_2
content of 1.0 wt.%.

Example 11: Preparation of a zirconium silicate of the
20 MCM-41 structure

114.2 g of tetramethylammonium hydroxide solution (10
wt.%) are placed in a polyethylene beaker and 30.0 g of a
pyrogenic silicon-zirconium mixed oxide containing 3.0
25 wt.% of ZrO_2 are added, with stirring. This mixture is
stirred for one hour. A suspension of 29.1 g of
cetyltrimethylammonium bromide ($\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$) in 109.2 g
of deionized water is then added, with stirring, and
stirring is continued for 10 minutes. The resulting
30 synthetic gel is crystallized in an autoclave for 48 hours
at 140°C under static conditions. The solid obtained is

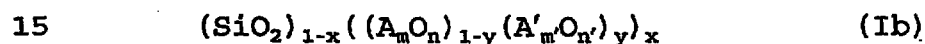
filtered off and washed with deionized water until the filtrate is neutral. The solid is dried at 90°C and then calcined in an air atmosphere for four hours at 640°C.

- 5 The X-ray diffraction diagram of the catalyst obtained shows the diffraction pattern typical of MCM-41 materials, with a d_{100} value of 3.25 nm. Examination by sorption analysis with nitrogen at 77 K shows a mean pore diameter of 2.4 nm, a BET specific surface area of 860 m²/g and a
- 10 pore volume of 0.59 ml/g.



Patent claims

1. A process for the preparation of microporous and mesoporous metal silicates, comprising the hydrothermal
5 reaction of a silicon and metal source in the presence of a template, characterized in that a pyrogenic metal-silicon mixed oxide is used as the silicon and metal source.
- 10 2. A process according to Claim 1 for the preparation of crystalline microporous and mesoporous metal silicates of the general composition



or



in which:

- x is a number between 0.0001 and 0.25;
- 20 y is a number greater than 0 and less than 1;
- A and A' are a metal of valency p from the group comprising B, Al, Ga, In, Ge, Sn and Pb or from subgroups 3 to 8;
- M is a cation of valency q from the group
25 comprising alkali metals, alkaline earth metals, H^+ , NH_4^+ and $N(alkyl)_4^+$; and
- m, m', n, n', n'' and r are the number of atoms, where:

$$m \cdot p = 2n \text{ and } m' \cdot p = 2n'$$

$$\text{and } m \cdot p + r \cdot q = 2n'',$$



- characterized in that a pyrogenic mixed oxide of composition (Ia) or (Ib) is used and the cation M of formula (II) is incorporated via the template or via alkali metal or alkaline earth metal hydroxide present in the hydrothermal synthesis.
3. A process according to Claim 1 or 2, characterized in that a pyrogenic metal-silicon mixed oxide prepared by flame hydrolysis is used.
4. A process according to one of Claims 1 to 3, characterized in that a pyrogenic mixed oxide from the group comprising $(\text{SiO}_2)_{1-x}(\text{TiO}_2)_x$, $(\text{SiO}_2)_{1-x}(\text{Al}_2\text{O}_3)_x$, $(\text{SiO}_2)_{1-x}(\text{B}_2\text{O}_3)_x$, $(\text{SiO}_2)_{1-x}(\text{V}_2\text{O}_5)_x$ and $(\text{SiO}_2)_{1-x}(\text{ZrO}_2)_x$ is used.
5. A process according to one of Claims 1 to 4, characterized in that the template is used in an amount of 0.05 to 2.0 mol per mol of SiO_2 in the mixed oxide.
6. A process according to one of Claims 1 to 5, characterized in that the hydrothermal reaction in the preparation of microporous metal silicates is carried out at a temperature between 100 and 220°C, preferably between 150 and 190°C, and in the preparation of mesoporous metal silicates is carried out at between 50 and 175°C, preferably between 70 and 150°C, under at least autogenous pressure.
7. A process according to one of Claims 1 to 6, characterized in that the pyrogenic mixed oxide is brought into contact with an aqueous template solution containing



hydroxyl ions, the molar ratio of OH^- to SiO_2 being between 0.05 and 2.0.

8. A process according to one of Claims 1 to 7,
5 characterized in that the pyrogenic silicon-metal mixed oxide is used in the form of a shaped object, the size and shape of the shaped objects remaining essentially unchanged in the hydrothermal reaction to give microporous and mesoporous metal silicates.
- 10 9. Binder-free shaped objects of microporous and mesoporous metal silicates, obtainable by the process of Claim 8.
- 15 10. Use of the shaped objects according to Claim 9 as a catalyst in oxidation reactions, the composition of said shaped objects corresponding to an Al-free metal silicalite.
- 20 11. Use of the metal silicates prepared by the process according to Claims 1 to 8 as catalysts in the oxidation of olefins, e.g. propene, with hydrogen peroxide to give the corresponding epoxides.