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- (71) Applicant: **AKZO NOBEL N.V.** [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL).
- (72) Inventors: **BRADY, Mike**; 4248 Rhodes Avenue, Studio City, CA 91604 (US). **LAHEIJ, Erik, Jeroen**; Graaf Aelbrechtlaan 14, NL-1181 SW Amstelveen (NL). **O'CONNOR, Paul**; Hogebrinkerweg 9, NL-3871 KM Hoevelaken (NL). **STAMIREES, Dennis**; 1300 Colony Plaza, Newport Beach, CA 92660 (US).
- (74) Agent: **SCHALKWIJK, Pieter, Cornelis**; Akzo Nobel N.V., Intellectual Property Department (Dept. AIP), P.O. Box 9300, NL-6800 SB Arnhem (NL).
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(54) Title: PROCESS FOR THE PREPARATION OF DOPED PENTASIL-TYPE ZEOLITE USING DOPED SEEDS

(57) Abstract: The present invention relates to a process for the preparation of doped pentasiltype zeolite, which process comprises the steps of: a) preparing an aqueous precursor mixture from a silicon source, an aluminium source, and doped non-zeolitic seeds, and b) thermally treating the precursor mixture to form a doped pentasil-type zeolite. The term "non-zeolitic seeds" includes seeds made from materials selected from the group consisting of (i) X-ray amorphous materials, (ii) milled crystalline materials, such as milled zeolites, that have a relative crystallinity of not more than 75%, and (iii) crystalline materials other than zeolites, such as clays (e.g. bentonite and kaolin) and (low) crystalline aluminas.

PROCESS FOR THE PREPARATION OF DOPED PENTASIL-TYPE ZEOLITE USING DOPED SEEDS

The present invention relates to the preparation of doped pentasil-type zeolites
5 using doped seeds.

US 5,232,675 discloses a process for the preparation of rare earth metal (RE)-
doped pentasil-type zeolites using RE-doped faujasite seeds. This process
leads to the crystallisation of pentasil-type zeolite on the faujasite-type seeds.
10 Hence, the product consists of two types of zeolites one within the other: a core
of RE-doped faujasite and a shell of pentasil-type zeolite. So, the RE-ions are
located in the core and not (or at least not significantly) in the pentasil-type
shell. This will hinder the RE-ions from improving the activity, selectivity, and
stability of the pentasil-type zeolite.

15 Furthermore, upon thermal treatment (e.g. during calcination, steaming, or use
in an FCC unit), the RE-ions move to the very small sodalite cages of the
faujasite zeolite, thereby further decreasing their influence on the activity,
selectivity, and stability of the pentasil-type zeolite.

20 The present invention offers a process for the preparation of doped pentasil-
type zeolites in which the dopant is not only located in the core.

This process involves the steps of:

- a) preparing an aqueous precursor mixture from a silicon source, an aluminium
source, and doped non-zeolitic seeds, and
- 25 b) thermally treating the precursor mixture to form a doped pentasil-type zeolite.

The process requires the use of doped non-zeolitic seeds.

The term "non-zeolitic seeds" includes seeds made from materials selected
from the group consisting of

- 30 (a) X-ray amorphous materials – i.e. materials which are either amorphous, or
containing crystallites too small to be detected by X-ray diffraction - such as

an amorphous aluminosilicate nucleating gel according to, e.g., US 4,606,900, US 4,166,099, and Kasahara et al. in "Studies of Surface Science and Catalysis," *Proceedings of the 7th International Conference on Zeolites* 1986, pp. 185-192,

- 5 (b) milled crystalline materials, such as milled zeolites, that have a relative crystallinity of not more than 75%, and
- (c) crystalline materials other than zeolites, such as clays (e.g. bentonite, sepiolites, smectites, kaolins, etc.) and (low) crystalline aluminas.
- 10 The relative crystallinity of the milled crystalline materials according to group b) preferably is not more than 60%, more preferably not more than 55%, and most preferably not more than 50%.

The relative crystallinity of the materials is determined by Powder X-ray
15 diffraction using copper K-alpha radiation, thereby comparing the total net integrated intensity of one or more strong reflections of the seeding material with that of the same material but having 100% crystallinity (i.e. having no amorphous phases).

For instance, the relative crystallinity of milled sodium Y-zeolite is measured by
20 determining the total net integrated intensity of the reflections covering the interplanar spacing range of 0.62 to 0.25 nm and comparing it with the intensity of a standard sodium Y-zeolite with a crystallinity of 100%.

The term "doped non-zeolitic seeds" refers to non-zeolitic seeds containing an
25 additive (also called dopant). Suitable additives include compounds comprising rare earth metals such as Ce or La, alkaline earth metals such as Mg, Ca, and Ba, transition metals such as Mn, Fe, Ti, Zr, Cu, Ni, Zn, Mo, W, V, and Sn, actinides, noble metals such as Pt and Pd, gallium, boron, and/or phosphorus. Suitable compounds are the oxides, hydroxides, carbonates, hydroxy-
30 carbonates, chlorides, nitrates, sulfates, and phosphates of the above elements.

The dopant is present in the doped non-zeolitic seed in amounts of 1-30 wt%, preferably 2-10 wt%, and more preferably 3-7 wt%, calculated as oxide and based on the dry weight of the doped non-zeolitic seeds.

5 Seeds can be doped by, e.g., ion-exchange, preparation of the seed in the presence of an additive, impregnation, or solid state exchange. For example, clay or amorphous Si-Al cogel can be ion-exchanged, resulting in a doped clay or cogel, which can serve as doped non-zeolitic seed in the process according to the invention.

10 A doped non-zeolitic seed according to the above definition can also be prepared by milling a doped seed (e.g. RE-Y) until its relative crystallinity is 60% or less.

15 Without wishing to be bound by theory, it is assumed that during the process of the invention the non-zeolitic seeds will (re-)crystallise, thereby breaking down their original structure and releasing the dopant. This in contrast to the highly ordered doped faujasite seeds according to US 5,232,675, which retain their original structure containing the dopant.

20 The pentasil-type zeolite resulting from the process according to the invention preferably has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 25-90. Typical examples of pentasil-type zeolites are ZSM-type zeolites, such as ZSM-5, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, zeolite beta, or zeolite boron beta. The doped pentasil-type zeolite preferably contains 0.1-10 wt% of dopant, more preferably 0.1-3 wt%, and most preferably 0.5-2.5 wt%, calculated as oxide and based on
25 the dry weight of the doped pentasil-type zeolite.

The first step of the process according to the invention involves the preparation of an aqueous precursor mixture comprising a silicon source, an aluminium source, and the doped non-zeolitic seeds. Preferably, the precursor mixture
30 comprises 1-10 wt% of doped non-zeolitic seeds, based on the total solids

content. More than one type of doped non-zeolitic seeds can be used in the process according to the invention.

The amount of aluminium and silicon source present in the precursor mixture depends on the desired SAR of the resulting pentasil-type zeolite.

5

It is possible for the precursor mixture to also contain an organic directing template. However, such templates are expensive and - as a result of their decomposition - environmentally harmful compounds are released upon heating of the so-prepared zeolites. Hence, it is preferred not to use a template in the process according to the invention.

10

Suitable aluminium sources include aluminium salts, such as $\text{Al}_2(\text{SO}_4)_3$, AlCl_3 , AlPO_4 , $\text{Al}_2(\text{HPO}_4)_3$, and $\text{Al}(\text{H}_2\text{PO}_4)_3$, and water-insoluble aluminium compounds, e.g. aluminium trihydrate ($\text{Al}(\text{OH})_3$) such as gibbsite and bauxite ore concentrate (BOC), thermally treated aluminium trihydrate such as flash-calcined aluminium trihydrate, (pseudo)boehmite, aluminium chlorohydrate, aluminium nitrohydrate. Also mixtures of one or more of these aluminium sources can be used.

15

Alternatively, doped aluminium sources can be used. Examples of such doped aluminium sources are doped (pseudo)boehmite, doped aluminium trihydrate, and doped flash-calcined aluminium trihydrate.

20

Doped aluminium sources can be prepared by preparation of the aluminium source in the presence of the dopant, impregnation of the aluminium source with the dopant, or ion-exchanging the aluminium source with the dopant.

25

Doped (pseudo)boehmite, for instance, can be prepared by hydrolysis of aluminium alkoxide in the presence of a dopant, hydrolysis and precipitation of aluminium salts in the presence of a dopant, or by aging a slurry of (thermally treated) aluminium trihydrate, amorphous gel alumina, or less crystalline (pseudo)boehmite in the presence of a dopant. For more information concerning the preparation of doped (pseudo)boehmite reference is made to

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International Patent Application Nos. WO 01/12551, WO 01/12552, and WO 01/12554.

Suitable silicon sources include sodium silicate, sodium meta-silicate, stabilised
5 silica sols, silica gels, polysilicic acid, tetra ethylortho silicate, fumed silicas, precipitated silicas, and mixtures thereof.

Also doped silicon sources can be used. Doped silicon sources can be obtained by preparing the silicon source in the presence of the dopant, impregnating the silicon source with the dopant, or ion-exchanging the silicon source with the
10 dopant.

Doped silica sol, for instance, can be obtained by preparing a silica sol from water glass and acid (e.g. sulfuric acid), and exchanging the sodium ions with the desired dopant. Alternatively, water glass, acid (e.g. sulfuric acid), and dopant are coprecipitated to form a doped silica sol.

15

Suitable dopants for the aluminium and/or the silicon source include compounds comprising rare earth metals such as Ce or La, alkaline earth metals such as Mg, Ca, and Ba, transition metals such as Zr, Mn, Fe, Ti, Zr, Cu, Ni, Zn, Mo, W, V, and Sn, actinides, noble metals such as Pt and Pd, gallium, boron and/or
20 phosphorus. The optional dopant(s) present in the silicon and/or aluminium source and the dopant in the doped non-zeolitic seeds can be the same or different.

If so desired, several other compounds may be added to the precursor mixture,
25 such as templates or non-doped seeds (e.g. ZSM-5 seeds, zeolite beta seeds), metal (hydr)oxides, sols, gels, pore regulating agents (sugars, surfactants), clays, metal salts, acids, bases, etc.

Furthermore, it is possible to mill the precursor mixture.

30 If so desired, the precursor mixture may be shaped to form shaped bodies. Suitable shaping methods include spray-drying, pelletising, extrusion (optionally

combined with kneading), beading, or any other conventional shaping method used in the catalyst and absorbent fields or combinations thereof. The amount of liquid present in the precursor mixture should be adapted to the specific shaping step to be conducted. It might be advisable to partially remove the liquid used in the precursor mixture and/or add an additional or another liquid, and/or to change the pH of the precursor mixture to make the mixture gellable and thus suitable for shaping. Additives commonly used in the different shaping methods, e.g. extrusion additives, may be added to the precursor mixture used for shaping.

10

The second step of the process involves thermal treatment of the precursor mixture at temperatures preferably ranging from 130 to 200°C, more preferably 150-180°C, for 3-60 hrs. During this step, the doped pentasil-type zeolite is formed by crystallisation.

15

The thermal treatment can be conducted in one or a series of at least two reaction vessels. If more than one such vessel is used, the process is preferably conducted in a continuous mode. Using more than one reaction vessel further allows the aqueous precursor mixture to be prepared either by adding all ingredients to the first vessel, or by spreading the addition of (part of the total amount of) the ingredients over the reaction vessels.

20

If so desired, the resulting doped pentasil-zeolite may be calcined and optionally ion-exchanged.

25

The so-formed doped pentasil-type zeolite can be used in or as a catalyst composition or catalyst additive composition for, e.g. hydrogenation, dehydrogenation, catalytic cracking (FCC), and alkylation reactions.

EXAMPLES

Example 1

5 A 29.8 wt% aluminium sulfate solution (484 g) and a 30.3 wt% H₂SO₄ solution (597 g) were added to a stirred 30-litre vessel containing 3,026 g water. To this solution, 3,084 g of water glass were slowly added in 15 minutes. A gel was formed during the addition.

10 A first seeding slurry was prepared by milling an aqueous slurry (Loss on Ignition at 1,000°C = 27.7 wt%) of Na- and RE-exchanged zeolite Y using a KD-03 mill (bead size 1 mm). The relative crystallinity of the resulting seeds was 49%.

This relative crystallinity was determined by X-ray-diffraction using Cu K-alpha radiation. The peak areas for the sample's faujasite peaks within the scan range
15 14-36° 2-theta were determined using the Bruker profile fitting program Topasp. The pattern of a curved background was fitted according to the multiple background method and then subtracted from the measured faujasite pattern. The so-obtained total net integrated intensity of the sample's reflections covering the interplanar spacing range of 0.62 to 0.25 nm, relative to that of a
20 standard sodium Y-zeolite with a crystallinity of 100%, was the relative crystallinity.

A second seeding slurry (Loss on Ignition at 1,000°C = 14.1 wt%) was prepared by mixing a commercial ZSM-5 and water. The slurry was milled until the ZSM-5
25 had an average particle size of 0.89 µm.

104 g of the first seeding slurry were mixed with 205 g of the second seeding slurry. The resulting seeding slurry was slowly added to the aluminium sulfate/water glass mixture under vehement stirring for 10 minutes. The slurry was autoclaved for 5 hours at 170°C and dried overnight in a stove at 120°C.

The PXRD pattern of the sample showed the formation of ZSM-5. No separate La_2O_3 , $\text{La}(\text{OH})_3$, or Ce_2O_3 phases were detected, meaning that the rare earth metal dopant was not precipitated as a separate phase.

XPS and SEM/EDAX showed that the rare earth metal was present in the entire
5 zeolite structure; not only in its core.

Example 2

A 29.8 wt% aluminium sulfate solution (530 g) and a 30.3 wt% H_2SO_4 solution (616 g) were added to a stirred 30-litre vessel containing 2,879 g water. To this
10 solution, 3,084 g of water glass were slowly added in 15 minutes. A gel was formed during the addition.

La-doped amorphous seeds were prepared by adding $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to an amorphous aluminosilicate nucleating gel. The gel was milled while diluting with water. The resulting first seeding slurry had a Loss on Ignition (LOI) at 1,000°C
15 of 22.1 wt%; the La-concentration was 20 wt% (calculated as La_2O_3 and based on the dry weight of the doped seeds after heating at 1,000°C).

A second seeding slurry (LOI at 1,000°C = 14.1 wt%) was prepared by mixing a commercial ZSM-5 and water. The slurry was milled until the ZSM-5 had an average particle size of 0.89 μm .

20 152 g of the first seeding slurry were mixed with 240 g of the second seeding slurry. The resulting seeding slurry was slowly added to the aluminium sulfate/water glass mixture under vehement stirring for 10 minutes. The slurry was autoclaved for 5 hours at 170°C and dried overnight in a stove at 120°C.

25 The PXRD pattern of the sample showed the formation of ZSM-5. No separate La_2O_3 or $\text{La}(\text{OH})_3$ phases were detected, meaning that the La-dopant was not precipitated as a separate phase.

XPS and SEM/EDAX showed that the rare earth metal was present in the entire zeolite structure; not only in its core.

CLAIMS

1. Process for the preparation of doped pentasil-type zeolite, which process comprises the steps of:
 - 5 a) preparing an aqueous precursor mixture from a silicon source, an aluminium source, and doped non-zeolitic seeds, and
 - b) thermally treating the precursor mixture to form a doped pentasil-type zeolite.
- 10 2. A process according to claim 1 wherein the doped pentasil-type zeolite is doped ZSM-5.
3. A process according to claim 1 or 2 wherein the non-zeolitic seeds are X-ray amorphous.
- 15 4. A process according to claim 1 or 2 wherein the non-zeolitic seeds are milled crystalline materials that have a relative crystallinity of not more than 75%.
- 20 5. A process according to claim 4 wherein the milled crystalline materials have a relative crystallinity of not more than 60%.
6. A process according to claim 5 wherein the milled crystalline materials have a relative crystallinity of not more than 50%.
- 25 7. A process according to claim 1 or 2 wherein the non-zeolitic seeds are crystalline materials other than zeolites.
8. A process according to any one of the preceding claims wherein the non-zeolitic seeds are doped with a dopant selected from the group
- 30

consisting of Ce, La, Zr, Mn, Fe, Ti, Cu, Ni, Zn, Mo, W, V, Sn, Pt, Pd, Ga, B, and P.

- 5 9. A process according to any one of the preceding claims wherein the silicon source is selected from the group consisting of sodium (meta)silicate, stabilised silica sols, silica gels, polysilicic acid, tetra ethylortho silicate, fumed silicas, precipitated silicas, and mixtures thereof.
- 10 10. A process according to any one of the preceding claims wherein the aluminium source is selected from the group consisting of $\text{Al}_2(\text{SO}_4)_3$, AlCl_3 , AlPO_4 , $\text{Al}_2(\text{HPO}_4)_3$, $\text{Al}(\text{H}_2\text{PO}_4)_3$, aluminium trihydrate ($\text{Al}(\text{OH})_3$), thermally treated aluminium trihydrate, (pseudo)boehmite, aluminium chlorohydrol, aluminium nitrohydrol, and mixtures thereof.
- 15 11. A process according to any one of the preceding claims wherein a shaping step is performed between steps a) and b).

INTERNATIONAL SEARCH REPORT

PCT/EP 03/09187

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C01B39/36 C01B39/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; MEGED, N. F. ET AL: "Synthesis of pentasil -type zeolite with introduction of amorphous seeds" retrieved from STN Database accession no. 117:114588 CA XP002261039 abstract & KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL (1992), (2), 13-14 , 1992, --- -/--	1-7,9,10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Rigondaud, B

INTERNATIONAL SEARCH REPORT

PCT/EP 03/09187

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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