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(54) Benævnelse: **KATALYSATORSAMMENSÆTNING OMFATTENDE MODIFICERET KRYSTALLINSK ALUMINOSILIKAT TIL DEHYDRERING AF ALKOHOLER**

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DESCRIPTION

TECHNICAL FIELD

[0001] The present invention relates generally to the field of dehydration and skeletal isomerization of alcohols on acidic catalysts to make corresponding olefins, preferably of alcohols having at least four carbon atoms for the production of olefins having the same number of carbon atoms as the alcohols. The present invention relates to a catalyst composition comprising a modified crystalline aluminosilicate preferably of the group FER (Framework Type FER) or SZR, and a silica binder; and to a process for the preparation thereof. The present invention also relates to the use of said catalyst composition in a dehydration process of alcohols and to the use of the olefins so-produced in various subsequent processes.

BACKGROUND OF THE INVENTION

[0002] The dehydration reactions of alcohols to produce alkenes have been known for a long time. Solid acid catalysts are widely used for alcohol dehydration and the conversion of alcohols therewith is nearly complete. However, in view of the potential downstream applications of olefins, it is of particular importance to limit the amount of secondary products and ensure a stable catalyst performance to gain in process efficiency and to save expensive steps of downstream separation/purification as well as to recover the catalyst activity by regeneration. Zeolites-based catalysts are particularly interesting for alcohols dehydration due to their high-activity, high-yield of corresponding olefins, and a possibility to operate under high-pressure conditions, which offers the best energy efficiency solutions for the technology.

[0003] Dehydration of ethanol on zeolites was described in WO2011/089235. The process for the dehydration of ethanol to ethylene was carried out in presence of zeolite catalysts and provides an alternative route to ethylene from biobased products if ethanol is obtained by fermentation of carbohydrates.

[0004] Dehydration of isobutanol to the corresponding olefins brings a perspective route to produce the renewable feedstock for petrochemicals and refining applications. Unfortunately, the direct conversion of isobutanol over a conventional dehydration catalyst, for example on alumina, leads to a product rich in isobutene. Selective production of linear butenes from iBuOH requires again a zeolite-based catalyst. The cut that is rich in linear butenes is often interesting as feedstock for metathesis, sulfuric acid catalyzed alkylation, oligomerization, oxidative dehydrogenation to butadiene, for the use as a copolymer. Therefore, the efficient catalyst for one-pot process converting isobutanol to the effluent rich in the linear butenes is sought.

[0005] While many skeletal isomerization catalysts for the conversion of n-butenes into isobutene have been developed, the reverse skeletal isomerization of isobutene into n-butenes has been rarely mentioned. Among the catalysts being active and selective, there are mostly unidirectional 10-membered ring zeolites. WO2011/113834 relates to the simultaneous dehydration and skeletal isomerization of isobutanol on acid catalysts. The process discloses the contact of a stream comprising isobutanol with a catalyst able to make such reaction. The catalyst was a crystalline silicate, a dealuminated crystalline silicate, or phosphorus modified crystalline silicate having Si/Al higher than 10, or silicoaluminaphosphate molecular sieve, or a silicated, zirconated or titanated or fluorinated alumina. The conversion of isobutanol was almost complete with selectivity in butenes ranging from 95 wt% to 98 wt%. The selectivity in isobutene was around 41-43%. This document indicates that steaming at temperatures above 400°C leads to a modification of the acidity of the catalyst and to the removal of aluminium from the crystalline silicate framework. Subsequently, it is necessary to treat the catalyst via a leaching to remove the aluminium and to increase the ratio Si/Al. The steps of steaming and leaching are associated in this document.

[0006] However, crystalline silicate catalysts deactivate fast and have limited regenerability. Hence, there is still a need for selective catalysts towards linear olefins and having improved regenerability.

[0007] In catalysis letters 41 (1996) 189-194, Gon Seo et al. studied the impact of coke deposits on ferrierite zeolites for the reaction of skeletal isomerization of 1-butene. The ferrierite studied was calcined at 500°C for 16h without any other particular treatment aiming at modifying its acidity. This ferrierite has a Si/Al ratio of 21 and it is further covered with coke using a plasma deposition before the reaction of skeletal isomerization of 1-butene is studied.

[0008] In WO2013/014081, SUZ-4 is studied for the methanol to olefin reaction. This document discloses the possibility of steaming the catalyst at a temperature of at least 400°C followed by a leaching, i.e. a washing, of the steamed solid with an aqueous acid solution. Such treatment is said to increase the Si/Al ratio.

[0009] In Applied Catalysis A: General 208 (2001) 153-161, Rutenbeck et al. studied the skeletal isomerization of n-butenes to isobutene. The catalyst studied was a ferrierite having a Si/Al ratio in the range of 20-70. A treatment of the ferrierite with the inorganic acid HCl was performed to obtain the protonic form of the ferrierite.

[0010] In the Journal of Catalysis 163, 232-244 (1996), Wen-Qing Xu et al. studied the modification ferrierite for the skeletal isomerization of n-butene. The ferrrierite used presents a Si/Al ratio of 8.8. Treatment of the ferrierite also includes steaming at a temperature of at least 550°C and acidic treatment with HCl or HNO_3.

[0011] In EP2348005, the use of a ferrierite based catalyst for the dehydration of isobutanol is described. It is disclosed that the ferrierite may be used directly without further treatment or that it may be used once being steamed and dealuminated with an acidic treatment.

[0012] In Applied Catalysis A: General 403 (2011) 1-11, Dazhi Zhang et al. the use of a ferrierite for the conversion of n-butanol to isobutene is described. Such ferrierite was calcined at 550°C but did not undergo any further treatment.

[0013] In US5523510, the use of an acid wash ferrierite based catalyst for the skeletal isomerization of n-olefins to iso-olefins is described. Such acid wash is performed with HCl. In all the examples, the ferrierite is firstly steamed above 400°C at atmospheric pressure before being acid washed. In EP 0 134 333, a method of preparation of a cracking catalyst comprising a zeolite with a Si/Al ratio of at least 250 with a binder is described. In EP 0 034 444, a method for increasing the catalytic of acid zeolite catalyst is described.

[0014] To summarize, zeolite-based catalysts are important for alcohols dehydration, skeletal isomerization of butenes, MTO and many other reactions. To tune the Si/Al ratio of zeolite, dealumination via steaming at a temperature above 400°C under atmospheric pressure followed by a leaching is usually performed. However, such treatment leads to the formation of extra framework aluminium and partial destruction of the zeolite framework that induce different diffusion properties. Consequently, the selectivity of a catalyst prepared with a steamed and leached zeolite is generally impacted by the steaming. In the particular case of FER and SZR (SUZ-4), steaming followed by leaching has an even stronger impact on the selectivity due to the plate-shaped crystal morphology of those frameworks. However, FER and SZR are interesting because of their very high selectivity. Additionally, those structure types are particularly difficult to synthesize with a Si/Al atomic ratio above 35. Tuning of the acidity is consequently not easy albeit necessary. The present invention aims at providing catalyst compositions that address the above-discussed drawbacks of the prior art and solve the problem.

SUMMARY OF THE INVENTION

[0015] In particular, it is an object of the present invention to provide a catalyst composition comprising a crystalline aluminosilicate and a binder, wherein the crystalline aluminosilicate is a modified crystalline aluminosilicate or zeolite (both terms are equivalent) being preferably of the Framework Type FER or SZR and having a Si/Al framework molar ratio greater than 10. The catalyst composition according to the invention exhibits substantially complete once-through conversion of the C2-C7 alcohols to the corresponding olefins.

[0016] In a preferred mode, the present invention provides a catalyst composition showing good to excellent selectivity to linear olefins, above thermodynamic equilibrium, in simultaneous dehydration and skeletal isomerization reaction of alcohols having at least four carbon atoms.

[0017] In one aspect, the present invention provides a process for preparing a catalyst composition containing a modified a crystalline aluminosilicate as well as the catalyst

composition obtained by said process. The use of a modified crystalline aluminosilicate is for instance useful for the preparation of a catalyst composition that can be used in the conversion of the C2-C7 alcohols to the corresponding olefins. In a preferred mode said catalyst composition comprising a modified crystalline aluminosilicate is particularly useful for the simultaneous dehydration and skeletal isomerization of a mono-alcohol having at least four carbon atoms into olefins having the same number of carbons. In a most preferred application, said mono-alcohol is isobutanol, i.e. 2 methyl propan-1-ol.

[0018] The invention provides a process for preparing a catalyst composition containing a modified crystalline aluminosilicate and a binder, wherein the catalyst composition comprises from 5 to 95 % by weight of crystalline aluminosilicate as based on the total weight of the catalyst composition, the process being remarkable in that it comprises the following steps:

1. a) providing a crystalline aluminosilicate having a Si/Al framework molar ratio greater than 10;
2. b) optionally calcining said crystalline aluminosilicate;
3. c) steaming said crystalline aluminosilicate:
    - at a temperature ranging from 100 °C to 380 °C ;
    - under a gas phase atmosphere, without liquid, containing from 5 wt % to 100 wt % of steam, the rest being one or more gas selected from N_2, CO_2, Ar, He, CH_4, air, or any mixture of thereof; with preference air is selected from air and depleted air containing below 10 wt% of oxygen as based on the total weight of the depleted air, preferably below 5 wt%, more preferably below 1 wt% ;
    - at a pressure ranging from 2 to 200 bars ;
    - at a partial pressure of H_2O ranging from 2 to 200 bars ; and
    - said steaming being performed during at least 30 min and up to 144 h ;

and in that the process comprises a step of shaping, or of extruding, the crystalline aluminosilicate with a binder, wherein the binder is selected to comprise at least 85 wt % of silica as based on the total weight of the binder, and less than 1000 ppm by weight as based on the total weight of the binder of aluminium, gallium, boron, iron and/or chromium.
The content of steam in wt% is based on the total weight of the gas phase atmosphere.

[0019] The process for modifying a crystalline aluminosilicate by steaming avoids the formation of the defects in the crystalline aluminosilicate. Indeed, the process avoids blocking the porosity simultaneously to a decrease of the effective number of the acid sites. It has been discovered that a mild steaming (i.e. steaming performed at a maximum temperature of 380°C) and under pressure (i.e. a pressure higher than the atmospheric pressure) is particularly beneficial for the activity, selectivity and regenerability of the catalyst composition prepared with said modified crystalline aluminosilicate. It has been discovered that modified crystalline aluminosilicate being prepared according to the above mentioned recipe presents acidic properties that are particularly suitable for the dehydration of mono-alcohol having 2 to 7 carbon atoms as well as for the simultaneous dehydration and skeletal isomerization of a mono-alcohol into olefins having the same number of carbons. Such modified crystalline

aluminosilicate has a sufficient acidity to perform the dehydration reaction with a good activity while not being too acidic thereby maintaining a suitable selectivity toward normal olefins. Said modified crystalline aluminosilicate is therefore particularly useful for instance for the preparation of a catalyst composition that can be used for alcohol(s) dehydration into corresponding olefins having the same number of carbons said mono-alcohol being preferably ethanol, isobutanol, i.e. 2 methyl propan-1-ol.

[0020] With preference, one or more of the following features can be used to better define the inventive process for modifying a crystalline aluminosilicate:

- The step c) of steaming said crystalline aluminosilicate is performed at a temperature of at least 200°C, preferably at least 250°C.
- The step c) of steaming said crystalline aluminosilicate is performed at a temperature up to a maximum temperature of 350°C.
- The step c) of steaming said crystalline aluminosilicate is performed at a pressure ranging from 2 to 20 bars, more preferably ranging from 2 to 15 bars.
- The step c) of steaming said crystalline aluminosilicate is performed at a partial pressure of H_2O from 3 to 10 bars.
- The binder contains at least 90 wt % of silica as based on the total weight of the binder, preferably at least 95 wt %, more preferably at least 99 wt%, and even more preferably at least 99.5 wt%.
- The binder comprises less than 500 ppm by weight as based on the total weight of the binder of aluminium, gallium, boron, iron and/or chromium, preferably less than 200 ppm.
- No any leaching treatment is performed either before step a) or after step c) in order to maintain constant the concentration of aluminium in the modified crystalline aluminosilicate.
- A step of washing or ion exchange with an alkali metal or NH_4 salts is performed after step c) or before step b).
- A calcination step of the product obtained after step c) or before step b) is performed.
- A step of recovering said modified crystalline aluminosilicate is performed after step c) or after any of the other optional steps.
- The crystalline aluminosilicate is a 10 membered ring zeolite preferably of the Framework Type FER, MWW, EUO, MFS, ZSM-48, MTT, MFI, MEL, TON or SZR and is preferably chosen among ferrierite, FU-9, ISI-6, NU-23, Sr-D, ZSM-35, ZSM-57 or SUZ-4 or any mixture thereof.
- The step of shaping, or of extruding, the crystalline aluminosilicate with a binder is performed prior to any of steps a) to c), so the step of steaming said crystalline aluminosilicate is conducted on a crystalline aluminosilicate shaped with, or extruded with, a binder; preferably the step of shaping, or of extruding, the crystalline aluminosilicate with a binder is a step of extruding in quadrilobes the crystalline aluminosilicate with a binder.
- The step of shaping, or of extruding, the crystalline aluminosilicate with a binder is performed on the product obtained after step c), preferably the step of shaping, or of

extruding, the crystalline aluminosilicate with a binder is a step of extruding in quadrilobes the product obtained after step c) with a binder.

- The step of shaping, or of extruding, the crystalline aluminosilicate with a binder is conducted with a binder containing at least 99.5 wt % of SiO_2.
- Neither any steaming at a temperature higher than 380 °C nor any leaching has been performed on said crystalline aluminosilicate prior to step a) and wherein neither any steaming at a temperature higher than 380 °C nor any leaching is further performed on said modified aluminosilicate after step c).
- The modified crystalline aluminosilicate has Si/Al framework molar ratio ranging from 10 to 100, preferably ranging from 10 to 65, more preferably 20 to 50, and even more preferably ranging from 21 to 30.
- The modified crystalline aluminosilicate has a content in transition metals or cations thereof lower than 1000 ppm wt, as measured by the method ASTM UOP961-12, said transition metals belonging to any of the columns 3 to 12 of the Periodic Table. Indeed transition metals or cations thereof are particularly detrimental for the catalyst composition selectivity because they catalyze the formation of heavy hydrocarbons.
- The process for modifying a crystalline aluminosilicate is remarkable in that said crystalline aluminosilicate is shaped (μ-spheres by spray-drying or droplet, tablets, extrudates: trilobes, quadrilobes, cylinders) preferably in quadrilobes extrudates prior to any of steps a) to c) with said binder being preferably pure SiO_2 (i.e. silica) for instance. said binder contains at least 99.5 wt % of SiO_2.
- The process for preparing a catalyst composition is further remarkable in that said steaming of step c) is performed on said shaped or extruded crystalline alumino silicate in situ prior to the use of the catalyst composition.
- The process for modifying a crystalline aluminosilicate is remarkable in that preferably after step c) a further step of shaping or extrusion, preferably in quadrilobes is performed with a binder being preferably pure SiO_2, i.e. said binder contains at least 99.5 wt % of SiO_2.
- The process for modifying a crystalline aluminosilicate is further remarkable in that preferably neither any steaming at a temperature higher than 380 °C nor any leaching has been performed on said crystalline aluminosilicate prior to being used in the dehydration of a mono-alcohol into olefins having the same number of carbons.
- The process for modifying a crystalline aluminosilicate is further remarkable in that it is a versatile process: it can be performed in situ or ex situ. Said process for modifying a crystalline aluminosilicate can preferably be performed on a catalyst composition comprising the crystalline aluminosilicate to be modified. Said process for modifying a crystalline aluminosilicate can more preferably be performed on a catalyst composition comprising the crystalline aluminosilicate to be modified already loaded and prior to its use in a process for dehydration of a mono-alcohol. Alternatively, said process for modifying a crystalline aluminosilicate can be performed on the crystalline aluminosilicate to be modified prior to its incorporation and/or prior to the shaping into a catalyst composition.

[0021] In a second aspect, the present invention provides a process for dehydration of a mono-alcohol, or of a mixture of at least two mono-alcohols, having at least 2 carbon atoms and at most 7 carbon atoms into olefins having the same number of carbons; the process being remarkable in that it comprises the following steps:

1. i. providing catalyst composition comprising a modified crystalline aluminosilicate, wherein the catalyst composition is prepared according to the first aspect;
2. ii. providing a feed (A) comprising said mono-alcohols, optionally water, optionally an inert component;
3. iii. contacting said feed (A) with said catalyst composition at conditions effective to dehydrate at least a portion of said mono-alcohol;
4. iv. recovering an effluent (B) and removing water, the inert component if any and unconverted alcohols if any to get said olefins having the same number of carbons as said mono-alcohol.

With preference, the catalyst composition containing a modified crystalline aluminosilicate and a binder, wherein the catalyst composition comprises from 5 to 95 % by weight of crystalline aluminosilicate as based on the total weight of the catalyst composition, is prepared by a process for modifying a crystalline aluminosilicate comprising the following steps:

1. a) providing a crystalline aluminosilicate, preferably of the FER or SZR structure type, having a Si/Al framework molar ratio greater than 10;
2. b) optionally shaping and/or calcination said crystalline aluminosilicate;
3. c) steaming said crystalline aluminosilicate or said optionally shaped and/or calcined crystalline aluminosilicate:
   - at a temperature of at least 100 °C preferably 200 °C more preferably 250 °C up to a maximum temperature of 380 °C preferably 350 °C; and
   - under a gas phase atmosphere (i.e. without liquid) containing from 5 wt % to 100 wt % of steam the rest being one or more gas selected from N_2, CO_2, Ar, He, CH_4, air, or any mixture of thereof; with preference air is selected from air and depleted air containing below 10 wt% of oxygen as based on the total weight of the depleted air or preferably below 5 wt % or even below 1 wt % of oxygen ; and
   - at a pressure ranging from 2 bars up to 200 bars preferably up to 20 more preferably up to 15 bars ; and
   - at a partial pressure of H_2O from 2 bars to 200 bars more preferably from 3 to 10 bars; and
   - said steaming being performed during at least 30 min and up to 144h;
   - optionally the steaming being performed in a flow reactor;

   wherein the binder is selected to comprise at least 85 wt % of silica as based on the total weight of the binder, and less than 1000 ppm by weight as based on the total weight of the binder of aluminium, gallium, boron, iron and/or chromium.

[0022] In a third aspect, the present invention provides a process for dehydration of a mono-alcohol, or of a mixture of at least two mono-alcohols, having at least 2 carbon atoms and at most 7 carbon atoms into olefins having the same number of carbons; the process being conducted in a dehydration reactor or in a dehydration and skeletal isomerization reactor, and being remarkable in that it comprises the following steps:

1. i. providing a catalyst composition comprising a crystalline aluminosilicate shaped with, or extruded with, a binder; wherein the catalyst composition comprises from 5 to 95 % by weight of crystalline aluminosilicate as based on the total weight of the catalyst composition, and steaming said catalyst composition in situ in the dehydration reactor or in the dehydration and skeletal isomerization reactor:
   - at a temperature ranging from 100 °C to 380 °C ;
   - under a gas phase atmosphere, without liquid, containing from 5 wt % to 100 wt % of steam, the rest being one or more gas selected from N_2, CO_2, Ar, He, CH_4, air, or any mixture of thereof; with preference air is selected from air and depleted air containing below 10 wt% of oxygen as based on the total weight of the depleted air, preferably below 5 wt%, more preferably below 1 wt% ;
   - at a pressure ranging from 2 to 200 bars ;
   - at a partial pressure of H_2O ranging from 2 to 200 bars ; and
   - said steaming being performed during at least 30 min and up to 144h ;

   wherein the crystalline aluminosilicate having a Si/Al framework molar ratio greater than 10;

   wherein the binder is selected to comprise at least 85 wt % of silica as based on the total weight of the binder, and less than 1000 ppm by weight as based on the total weight of the binder of aluminium, gallium, boron, iron and/or chromium ; and

   wherein the step of steaming the catalyst composition comprising a crystalline aluminosilicate results in a catalyst composition comprising a modified crystalline aluminosilicate ;
2. ii. providing a feed (A) comprising said mono-alcohols, optionally water, optionally an inert component;
3. iii. contacting said feed (A) with said catalyst composition at conditions effective to dehydrate at least a portion of said mono-alcohol;
4. iv. recovering an effluent (B) and removing water, the inert component if any and unconverted alcohols if any to get said olefins having the same number of carbons as said mono-alcohol.

[0023] With preference, one or more of the following features can be used to better define the inventive process according to the second or to the third aspect for the simultaneous dehydration and skeletal isomerization:

- No any leaching treatment is performed either before step a) or after step c) in order to maintain constant the concentration of aluminium in the modified crystalline aluminosilicate;

- A step of washing or ion exchange with an alkali metal or NH_4 salts is performed after step c) or before step a).
- An optionally calcination step of the product obtained after step c) or before step b) is performed.
- A step of recovering said modified crystalline aluminosilicate is performed after step c) or after any of the other optional steps.
- The crystalline aluminosilicate, or the modified crystalline aluminosilicate, is a 10 membered ring zeolite preferably of the Framework Type FER, MWW, EUO, MFS, ZSM-48, MTT, MFI, MEL, TON or SZR and is preferably chosen among ferrierite, FU-9, ISI-6, NU-23, Sr-D, ZSM-35, ZSM-57 or SUZ-4 or any mixture thereof
- The modified crystalline aluminosilicate has Si/Al framework molar ratio ranging from 10 to 100, preferably ranging from 10 to 65, more preferably from 20 to 50, and even more preferably ranging from 21 to 30.
- The modified crystalline aluminosilicate has a content in transition metals or cations thereof lower than 1000 ppmwt, preferably measured by the method ASTM UOP961-12, said transition metals belonging to any of the columns 3 to 12 of the Periodic Table.
- The process for modifying a crystalline aluminosilicate is remarkable in that said crystalline aluminosilicate is shaped (μ-spheres by spray-drying or droplet, tablets, extrudates: trilobes, quadrilobes, cylinders) preferably in quadrilobes extrudates prior to any of steps a) to c) with said binder pure being SiO_2, i.e. said binder contains at least 99.5 wt % of SiO_2.
- The process for modifying a crystalline aluminosilicate is remarkable in that after step c) a further step of shaping or extruded preferably in quadrilobes is performed with said being pure SiO_2, i.e. said binder contains at least 99.5 wt % of SiO_2.
- The process for modifying a crystalline aluminosilicate is further remarkable in that neither any steaming at a temperature higher than 380 °C nor any leaching has been performed on said crystalline aluminosilicate prior to step before being used for the dehydration of a mono-alcohol(s) into olefins having the same number of carbons.
- The process for modifying a crystalline aluminosilicate is further remarkable said steaming of step c) is performed on said shaped or extrudated crystalline aluminosilicate in situ prior to the direct use of the catalyst composition.
- The process for modifying a crystalline aluminosilicate is further remarkable in that it is a versatile process: it can be performed in situ or ex situ. Said process for modifying a crystalline aluminosilicate can preferably be performed on a catalyst composition containing the crystalline aluminosilicate to be modified. Said process for modifying a crystalline aluminosilicate can more preferably be performed on a catalyst composition containing the crystalline aluminosilicate to be modified already loaded and prior to its use in a process for dehydration of a mono-alcohol. Alternatively said process for modifying a crystalline aluminosilicate can be performed on the crystalline aluminosilicate to be modified prior to its incorporation and/or prior to the shaping into a catalyst composition.
- The process for dehydrating a mono-alcohol is further remarkable in that said conditions effective to the simultaneous dehydration and skeletal isomerization of a mono-alcohol,

or of a mixture of at least two mono-alcohols, into olefins having the same number of carbons are any combinations of:

- adiabatic or isotherm operating conditions or any of intermediate conditions in between the adiabatic and the isotherm including partial heat compensation or intermediate re heating; and/or
- an inlet temperature ranging from 200°C to 500°C, preferably 225°C to 450°C, most preferably 250°C to 400°C, and/or
- a pressure ranging from 0.5 bar to 15 bars absolute (50 kPa to 1.5 MPa) preferably 0.5 bar to 10 bars absolute (50 kPa to 1.0 MPa) most preferably 1.2 to 9 bars absolute (0.12 MPa to 0.9 MPa) ; and/or
- a Weight Hourly Space Velocity (WHSV) ranging from 1 to 30 h^{-1} preferably from 2 to 21 h^{-1}, more preferably from 3 to 9 h^{-1}, wherein the WHSV represents the weight flow rate of said mono-alcohol at the inlet of the reactor divided by the mass of the catalyst composition in said reactor; and/or
- said feed (A) having a partial pressure of alcohols from 0.1 to 15 bars absolute (0.01 MPa to 1.5 MPa), more preferably from 0.5 to 9 bars absolute (0.05 MPa to 0.9 MPa).

- the process for dehydrating a mono-alcohol, or of a mixture of at least two mono-alcohols, is further remarkable in that said mono-alcohol(s) has at least four carbon atoms and at most five carbon atoms and in that said dehydration of a mono-alcohol is performed together with a skeletal isomerization
- the process for dehydrating a mono-alcohol is further remarkable in that said mono-alcohol is isobutanol, i.e. 2 methyl propan-1-ol, that is converted into n-butenes and isobutene.
- The catalyst composition comprising a crystalline aluminosilicate shaped with, or extruded with, a binder, is selected to have a modified crystalline aluminosilicate having an acidity between 350 and 500 µmol/g, preferably between 350 and 450 µmol/g as measured by temperature programmed desorption of ammonia.

[0024] It has been discovered that catalyst composition comprising said modified aluminosilicate are particularly suitable for the dehydration of alcohols or of a mixture of at least two mono-alcohols. In particular, the above described ranges of acidity are perfectly well suited for having a sufficient catalyst activity while maintaining the selectivity at a sufficient level.

[0025] The process for modifying a crystalline aluminosilicate is particularly versatile. The steaming can be applied directly after the synthesis of the crystalline aluminosilicate or it can be applied once the catalyst composition has been shaped or extruded with a binder. Said process for modifying a crystalline aluminosilicate can also be performed in situ, i.e. once the catalyst composition comprising a modified crystalline aluminosilicate is loaded in a dehydration reactor or in the dehydration and skeletal isomerization reactor, i.e. prior to its use. In this latter case, there is no need to have a dedicated unit to perform the steaming under

pressure. Catalyst manufacturers do not necessarily have the facilities to perform a steaming under pressure, but it is still possible to prepare said modified crystalline aluminosilicate in situ of the dehydration and optionally isomerization unit.
Additionally, it has been discovered that the process for modifying an aluminosilicate leads to improved properties. Without willing to be bound by any theory, it is assumed that a low temperature steaming associated with an increase partial pressure during the steaming and the absence of any leaching is particularly beneficial for the activity and selectivity of the modified crystalline aluminosilicate. Therefore, to maintain the good activity and selectivity, any further steaming at a high temperature or any further leaching should be avoided.

DETAILED DESCRIPTION OF THE INVENTION

[0026] In a preferred embodiment, the crystalline aluminosilicate or the modified crystalline aluminosilicate of the Framework Type FER is a crystalline aluminosilicate containing advantageously at least one 10 members ring into the structure based on T-atoms, i.e. on the Al and Si atoms contained in said ring. The family of Framework Type FER includes Ferrierite, [B-Si-O]-FER, [Ga-Si-O]-FER, [Si-O]-FER, [Si-O]-FER, FU-9, ISI-6, Monoclinic ferrierite, NU-23, Sr-D, ZSM-35, and SUZ-4. Preferably, the modified crystalline aluminosilicate of the Framework Type FER is Ferrierite. The process for modifying a crystalline aluminosilicate does not change the Framework Type FER.

[0027] The Si/Al framework molar ratio of the modified crystalline aluminosilicate may be at least 11, preferably at least 15, more preferably at least 20, even more preferably at least 21, most preferably at least 22, and even most preferably at least 25. Preferably, the Si/Al framework molar ratio of the modified crystalline aluminosilicate may be at most 150, preferably at most 100, more preferably at most 75, even more preferably at most 65, most preferably at most 55 and even most preferably at most 35. In a preferred embodiment, the Si/Al framework molar ratio of the modified crystalline aluminosilicate may range from 11 to 150, preferably from 15 to 100, more preferably from 20 to 100, even more preferably from 20 to 75, and in particular from 25 to 35. In a preferred embodiment, the Si/Al framework molar ratio of the modified crystalline aluminosilicate is ranging from 10 to 65. Advantageously, the modified crystalline aluminosilicate shows a high crystallinity of its zeolite phase, said crystallinity being similar to the crystallinity of the parent zeolite before modification, i.e. said crystallinity is similar to the crystallinity of the crystalline aluminosilicate before being modified. A similar crystallinity is evidenced via the X ray diffraction patterns (less than 20% of difference measured on the area below the X ray curves), i.e. the X ray diffraction pattern of the crystalline aluminosilicate (before being modified) is the same as the crystallinity of the modified crystalline aluminosilicate.

[0028] In a preferred embodiment, said modified crystalline aluminosilicate has content in redox transition metals or cations thereof lower than 1000 ppmwt, said transition metals belonging to one of the columns 3 to 12 of the Periodic Table. Preferably, said metals are Fe, Co, Ni, Cu, Mo, Mn, Ti, Zn, V, Cr, Ru, Rh, Cd, Pt, Pd, Au, Zr. Preferably, said modified

crystalline aluminosilicate has content in metals or cations thereof as defined above lower than 500 ppm wt, more preferably lower than 200 ppm wt, most preferably lower than 100 ppm wt, in particular lower than 50 ppm wt being measured by the method ASTM UOP961-12.

[0029] According to the invention, the catalyst composition comprising a modified crystalline aluminosilicate comprises a binder, preferably an inorganic binder. The catalyst composition comprises from 5 to 95 wt% as based on the total weight of the catalyst of crystalline aluminosilicate, preferably from 10 to 90 wt%, more preferably at least 20 to 80 wt% even more preferably from 30 to 70 wt%.
The binder is selected so as to be resistant to the temperature and other conditions employed in the dehydration process of the invention. The binder is an inorganic material containing at least 85 wt% of silica as based on the total weight of the binder, preferably 90 wt%, more preferably 95 wt % of silica, even more preferably at least 97 wt%, most preferably at least 99 wt%, and even most preferably at least 99.5 wt%. The binder has a concentration of aluminium, gallium, boron, iron and/or chromium of at most 1000 ppm wt, preferably at most 500 ppm wt, more preferably at most 200 ppm. It is desirable to provide a catalyst having good crush strength. This is because in commercial use, it is desirable to prevent the catalyst from breaking down into powder-like materials. A particularly preferred binder for the catalyst composition of the present invention is silica. The relative proportions of the finely divided modified crystalline aluminosilicate material and the inorganic oxide matrix of the binder can vary widely. Typically, the binder content may range from 5 to 95% by weight, more typically from 20 to 85% by weight, based on the weight of the catalyst composition. By adding a binder to the catalyst composition, this latter may be formulated into pellets, extruded into other shapes, or formed into spheres or a spray-dried powder.

[0030] The modified crystalline aluminosilicate may be in H-form. The H-form of a modified crystalline aluminosilicate of the Framework Type FER means that it comprises oxygen atoms bonded to one aluminium atom and one silicon atom, and which is protonated with a hydrogen atom, resulting in the following sequence -[-Al-O(H)-Si-]-. In the present invention, the modified crystalline aluminosilicate may be essentially under H-form, which means containing less than 1000 ppmwt of the total amount of the alkali ions and the alkaline earth ions. In another embodiment, the modified crystalline aluminosilicate is partly under H-form. It means that in said modified crystalline aluminosilicate part of the hydrogen atoms bonded to oxygen atoms in the following sequence -[-Al-O(H)-Si-]- is substituted by metallic ions, preferably alkali ions, alkaline earth ions or silver ions. Preferably, the alkali ions or alkaline earth ions may be Na, K, Cs, Li, Mg or Ca being measured via chemical analysis with the method ASTM UOP961-12.

[0031] Said process for modifying a crystalline aluminosilicate is particularly remarkable in that no preferably leaching is performed. The term leaching shall encompass any treatment of a solid with an acidic medium (inorganic or organic) or complexing agent able to remove aluminium from the crystalline aluminosilicate framework or preferably extra framework aluminium (EFAL).

[0032] As non-limiting example, said acidic medium and/or said complexing agent used in

leaching treatment shall encompass citric acid, formic acid, oxalic acid, tartaric acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, phthalic acid, isophthalic acid, fumaric acid, nitrilotriacetic acid, hydroxyl ethylene diamine triacetic acid, ethylene diamine tetraacetic acid, trichloroacetic acid, trifluoroacetic acid, methanesulfonic or a salt of such an acid (e.g. the sodium salt) or a mixture of two or more of such acids or salts. Inorganic acids, such as nitric acids or halogenic acids, are also encompassed in the meaning of acidic medium. Complexing agent shall encompass any organic molecule able to form a complex with aluminium and preferably forms a water-soluble complex with aluminium in order to remove aluminium and preferably extra framework aluminium (EFAL). A particularly preferred complexing agent may comprise an amine, preferably ethylene diamine tetraacetic acid (EDTA) or a salt thereof, in particular the sodium salt thereof. The term complexing agent shall encompass also organic acidic medium but not only. The man skilled in the art can recognize the organic medium able to remove the aluminium or EFAL from a crystalline aluminosilicate. As a guidance, it may be put forward that said organic medium refers to organic molecule able to form a complex with aluminium and preferably forms a water-soluble complex with aluminium in order to remove aluminium or EFAL, i.e. in order to remove at least 5 wt %, preferably 10 wt % of the aluminium or EFAL present on the crystalline aluminosilicate. It shall also be clear that said modified crystalline aluminosilicate is not preferably further leached prior to its use for instance in the process for dehydrating mono-alcohols.

[0033] In an optional embodiment, the process for modifying a crystalline aluminosilicate encompasses an optional calcinations. Said calcinations are performed to burn organic component that may be present on the crystalline aluminosilicate but under conditions avoiding the formation of pentahedral aluminium. In particular, at the inlet of the calcinations reactor, the calcination gas should contain less than 1000 ppm vol of water. Therefore, even if the crystalline aluminosilicate contains interstitial water, the presence of water inside the calcinations reactor is low enough to avoid a partial steaming of the crystalline aluminosilicate. During the optional calcinations, the crystalline aluminosilicate may be under the NH_4 form, the Na, K or H - forms. The calcinations can be performed under atmospheric pressure or alternatively at a pressure up to 9 bars. The calcination gas may contain inert components such as for instance N_2, Ar, He, CO_2, or other species such as for instance natural gas components or CO, N_2O which are not inert under the calcination conditions but do not lead to the deposition of any molecules such as coke on the crystalline aluminosilicate. The calcinations may be alternatively be performed under depleted air or the calcination gas may contains below 10 wt% of oxygen or preferably below 5 wt % or even below 1 wt % of oxygen in order to avoid the thermal runaway when organic molecules are burnt during calcinations. In depleted air the content of oxygen is based on the total weight of said depleted air. The optional calcinations can be performed at a temperature not higher than 600 °C preferably 550 °C, most preferably 500 °C and with a temperature increase of less than 10 °C/min, preferably less than 1 °C/min, the most preferably at 0.5 °C/min, for a period of at least 30 min, preferably at least 2 h and at most 48 h and under a gas flow containing at most 1000 ppm volume of water measured at the inlet of the calcination reactor. The optional calcinations can either be performed in situ or ex situ, i.e. calcinations can be applied directly after the synthesis of the crystalline aluminosilicate or after the process for modifying the crystalline aluminosilicate or it

can be applied once the catalyst composition has been shaped or extruded with a binder. Said optional calcinations can also be performed in situ, i.e. once the catalyst composition comprising a crystalline aluminosilicate or a modified crystalline aluminosilicate is loaded in a dehydration reactor or in the dehydration and skeletal isomerization reactor, i.e. prior to its use in a process for dehydrating.

[0034] Preferably, the mono-alcohol or the mixture of at least two mono-alcohols has at least four carbon atoms and at most five carbon atoms. Said mono-alcohol is preferentially a primary mono-alcohol substituted by an alkyl group in position 2. Preferably, the mono-alcohols are provided from biomass fermentation or biomass gasification to syngas followed by a modified Fischer-Tropsch synthesis.

[0035] Preferably, the alcohol may be 1-butanol, 2-butanol, isobutanol, pentan-1-ol, 3-Methylbutan-1-ol, 2-Methylbutan-1-ol, 2,2-Dimethylpropan-1-ol, pentan-3-ol, Pentan-2-ol, 3-Methylbutan-2-ol, 2-Methylbutan-2-ol, or mixture thereof with the proviso that the mixture contains alcohols having the same number of carbon atoms or optionally presenting a different number of carbon atoms. For example, a mixture of butanol comprises two or more of the following alcohols: 1-butanol, 2-butanol, isobutanol. A mixture of pentanol comprises two or more of the following alcohols: pentan-1-ol, 3-methylbutan-1-ol, 2-methylbutan-1-ol, 2,2-dimethylpropan-1-ol, pentan-3-ol, pentan-2-ol, 3-methylbutan-2-ol, 2-methylbutan-2-ol. More preferably, the alcohol may be selected from C2-C4 alkyl substituted by one hydroxyl group or mixture thereof with the proviso that the alcohols contained in the mixture have the same number of carbon atoms. Advantageously, the invention is of interest for 1-butanol, 2-butanol, isobutanol or mixture thereof with the proviso that the mixture contains alcohols having the same number of carbon atoms. In particular, a mixture of butanol is used, preferably isobutanol is used.

[0036] The dehydration reactor can be a fixed bed reactor (radial, isothermal, adiabatic etc), a moving bed reactor, multitubular or a fluidized bed reactor. A typical fluid bed reactor is one of the FCC type used for fluidized-bed catalytic cracking in the oil refinery. A typical moving bed reactor is of the continuous catalytic reforming type. The dehydration may be performed continuously in a fixed bed reactor configuration using several reactors in series of equal or different sizes or a pair of parallel "swing" reactors. The various preferred catalyst compositions of the present invention have been found to exhibit high stability. This enables the dehydration process to be performed continuously in two parallel "swing" reactors wherein when one reactor is operating, the other reactor is undergoing catalyst regeneration. The catalyst composition of the present invention also can be regenerated several times.

[0037] As preferred embodiment, the process for dehydration of a mono-alcohol or of a mixture of at least two mono-alcohols may be performed at a pressure ranging from 0.5 to 30 bars absolute (50kPa to 3 MPa), advantageously from 0.5 to 15 bars absolute (50kPa to 1.5 MPa), advantageously from 0.5 to 10 bars absolute (50kPa to 1 MPa). Advantageously, the partial pressure of the alcohol is lower than 5 bars absolute (0.5 MPa) and more advantageously from 0.5 to 9 bars absolute (0.05 MPa to 0.9 MPa), preferably lower than 8

bars absolute (0.8 MPa) and more preferably lower than 7 bars absolute (0.7 MPa).

[0038] As preferred embodiment, the process for dehydration of a mono-alcohol or of a mixture of at least two mono-alcohols may be performed at a temperature ranging from 200 °C to 500 °C, more advantageously from 225 °C to 450 °C and preferably from 250 °C to 400 °C. These reaction temperatures refer mainly to the inlet temperature. Dehydration is an endothermic reaction and requires the input of reaction heat in order to maintain catalyst activity sufficiently high and shift the thermodynamic equilibrium to sufficiently high conversion levels. In case of fluidised bed reactors: (i) for stationary fluidised beds without catalyst circulation, the reaction temperature is substantially homogeneous throughout the catalyst bed; (ii) in case of circulating fluidised beds where catalyst circulates between a converting reaction section and a catalyst regeneration section, depending on the degree of catalyst back mixing the temperature in the catalyst bed approaches homogeneous conditions (a lot of back mixing) or approaches plug flow conditions (nearly no back mixing) and hence a decreasing temperature profile will install as the conversion proceeds. In case of fixed bed or moving bed reactors, a decreasing temperature profile will install as the conversion of the alcohol proceeds. In order to compensate for temperature drop and consequently decreasing catalyst activity or approach to thermodynamic equilibrium, reaction heat can be introduced by using several catalyst beds in series with inter heating of the reactor effluent from the first bed to higher temperatures and introducing the heated effluent in a second catalyst bed, etc. When fixed bed reactors are used, a multitubular reactor can be used where the catalyst composition is loaded in small-diameter tubes that are installed in a reactor shell. At the shell side, a heating medium is introduced that provides the required reaction heat by heat-transfer through the wall of the reactor tubes to the catalyst composition.

[0039] As preferred embodiment, the process for dehydration of a mono-alcohol or of a mixture of at least two mono-alcohols may be performed with a weight hour space velocity ranging from 0.1 h^{-1} to 20 h^{-1}, preferably from 0.5 h^{-1} to 10 h^{-1}, more preferably from 1 h^{-1} to 9 h^{-1}. The WHSV represents the weight flow rate of the mono-alcohol at the inlet of the reactor divided by the mass of the catalyst composition in said reactor.

[0040] The effluent of the process for the simultaneous dehydration and skeletal isomerization comprises essentially water, olefin, an inert component (if any) and unconverted mono-alcohol. Said unconverted mono-alcohol is supposed to be as low as possible. The olefin is recovered by usual fractionation means. Advantageously, the inert component, if any, is recycled in the feed (A) as well as the unconverted alcohol, if any.

[0041] The inert component, if any, is any component provided that there is no adverse effect on the catalyst composition comprising the modified crystalline aluminosilicate. Dehydration of a mono-alcohol is an endothermic reaction; the inert component can be used to bring energy to the reactor. For instance, the inert component can be selected among water, saturated hydrocarbons having up to 10 carbon atoms, naphthenes, nitrogen and CO_2. An example of inert component can be any individual saturated compound, a synthetic mixture of individual

saturated compounds as well as some equilibrated refinery streams like straight naphtha, butanes etc. Advantageously, it is a saturated hydrocarbon or a mixture of saturated hydrocarbons having from 3 to 7 carbon atoms, more advantageously having from 4 to 6 carbon atoms and preferably pentane. The weight proportions of respectively alcohols, water and inert component are, for instance, 5-100/0-95/0-95 the total being 100.

[0042] In a preferred embodiment, said process for dehydration of a mono-alcohol or of a mixture of at least two mono-alcohols may further comprises a step of recovering and regenerating the catalyst.

[0043] In a preferred embodiment, at least 80% wt of the olefins obtained in said process for dehydration of a mono-alcohol have the same number of carbon atoms as the mono-alcohol, preferably at least 85% wt, more preferably at least 90% wt, in particular at least 95% wt.

[0044] In a preferred embodiment, the present process for dehydrating is carried out with a mixture of butanol as mono-alcohol, preferably isobutanol, and the mixture of olefins produced comprises at least 80% wt of butene and isomers thereof, preferably at least 90%, more preferably at least 95% wt, most preferably at least 98% wt. In addition, the selectivity in n-butenes may be at least 65% wt based on the total amount of butene and isomers thereof contained in the mixture of olefins produced, preferably at least 70% wt.

[0045] In another aspect of the present invention, the mixture of olefins produced by the process for dehydration of a mono-alcohol may be used as starting material for subsequent reactions such as the production of propylene via metathesis process, the production of butadiene via dehydrogenation, oligomerization, as well as for the production of transportation fuels, monomers and fuel additives. The mixture of olefins produced according to the present process may also replace the use of raffinate as defined in US4282389 in the refinery or petrochemical plants. The most typical application of a mixture containing isobutene is the conversion of the said isobutene into ethers (MTBE and ETBE), into t-butylalcohol (TBA) or oligomers (e.g. di/tri-iso-butenes), all being gasoline components. The higher oligomers of isobutene can be used for jet fuel applications. High purity isobutene can further be made by the decomposition of ethers (backcracking) or TBA (dehydration). High purity isobutene finds applications in the production of butyl-rubber, poly-isobutene, methylmethacrylate, isoprene, hydrocarbons resins, t-butyl-amine, alkyl-phenols and t-butyl-mercaptan. When the mixture of olefins contains n-butenes which have not reacted during the production of ethers or TBA and substantially not or only to a limited extent during the oligomerisation, said n-butenes have applications in the production of sec-butanol, alkylate (addition of isobutane to butenes), polygasoline, oxo-alcohols and propylene (metathesis with ethylene or self-metathesis between but-1-ene and but-2-ene). By means of super fractionation or extractive distillation or absorptive separation but-1-ene can be isolated from the n-butenes mixture. But-1-ene is used as comonomer for the production of polyethylenes, for polybut-1-ene and n-butyl-mercaptan. This involves an isomerization catalyst that is located in the distillation column and continuously converts the but-1-ene into but-2-ene, being a heavier component than but-1-ene. Doing so, a bottom product rich in but-2-ene and a top product poor in but-1-ene and rich in isobutene is

produced. The bottom product can be used as described above. One main application of such but-2-ene rich stream is the metathesis with ethylene in order to produce propylene. If high purity isobutene is desired the top product can be further super fractionated into substantially pure isobutene and pure but-1-ene or the isobutene can be isolated via formation of ethers or TBA that is subsequently decomposed into pure isobutene. The n-butenes rich stream may be used for the production of butadiene via dehydrogenation or oxidative dehydrogenation or send to alkylation unit to produce bio-alkylate. The mixture of isobutene and butenes can be sent to a catalytic cracking which is selective towards light olefins in the effluent, the process comprising contacting said isobutene and butenes mixture with an appropriate catalyst composition to produce an effluent with an olefin content of lower molecular weight than that of the feedstock. Said cracking catalyst can be a silicalite (MFI or MEL type) or a P- ZSM5.

ANALYTICAL METHODS

[0046] Measure of the acidity of the crystalline aluminosilicate or of the modified aluminosilicate can be performed by temperature desorption of ammonia. Methods known in the art suitable to quantify the acidic sites can be used. For instance, the method described in the procedure ASTM D4824-13 can be used. The amount of ammonia then determined via this method in cubic centimetre per grams can then be easily converted into µmol/g.

[0047] Alternative measure of the amount of acid sites can for instance be done by temperature-programmed desorption of ammonia according to the following method. The temperature-programmed desorption of ammonia is performed in a Pyrex®™ cell containing about 0.4 g of sample in form of the fraction 35-45 mesh. The cell is placed in an oven of the AUTOCHEM II 2920 equipped with TCD detector and the following steps are carried out:

Activation: this step is performed under a flow rate of dried (over molecular sieve e.g. 3A or 4A) He of 50 cm^3/min (<0.001 % of water). The temperature is increased from room temperature to 600°C with a rate of 10°C/min. The temperature is then maintained at 600°C during 1h. The temperature is then decreased to 100°C with a rate of 10°C/min.

Saturation: this step is performed at 100°C. During a first hour, the solid is put in contact with a flow of 30 cm^3/min of a dried (over molecular sieve e.g. 3A or 4A, <0.001 % of water) mixture of 10 weight % of NH_3 diluted in He. Then, during the next 2h, the solid is put in contact with a flow rate of 50 cm^3/min of dried (over molecular sieve e.g. 3A or 4A, <0.001 % of water) He to remove the physisorbed NH_3.

Analysis: this step is performed under a flow of 50 cm^3/min of dried (over molecular sieve e.g. 3A or 4A, <0.001 % of water) He. The temperature is increased to 600°C with a rate of 10°C/min. Once the temperature of 600°C has been reached, it is maintained for 1h. The cell is then cooled down and weighted.

Calculation: The amount of NH_3 desorbed from the solid is referenced to the weight of the

sample by integrating the surface below the TCD curve and reporting to a calibration curve. The amount of NH_3 desorbed from the solid gives the acidity of the solid in µmol/g.

[0048] Measure of the content of transition metals and determination of the Si/Al framework molar ratio in the catalyst, in the modified crystalline aluminosilicate or in the crystalline aluminosilicate can be done by any suitable technique known in the art. For instance, it can be done using the method ASTM UOP961-12.

[0049] Alternatively measure of the Si/Al framework molar ratio in the catalyst, in the modified crystalline aluminosilicate or in the crystalline aluminosilicate can be determined using solid-state ^{29}Si MAS NMR. All solid state ^{29}Si MAS MAS NMR spectra were recorded on a Bruker DRX500 spectrometer (Pulse 45°, Relaxation delay 7 sec, rotor 4mm). For a low defect zeolite samples, an aluminium atom will always be surrounded by four Silicones. The ^{29}Si MAS NMR spectra of aluminosilicate zeolites give typically a series of peaks which correspond to SiO_4 tetrahedra in five different possible environments corresponding to different numbers of AlO_4 tetrahedra connected to the silicon via oxygen. For simplicity, these sites will be denoted ignoring the oxygen atoms as Si (4-nAl), where n is a number of Si in the tetrahedral: Si(0Al), Si(1Al), Si(2Al), Si(3Al), Si(4Al). The intensity of a silicon resonance is proportional to the number of associated silicon atoms. The number of Al atoms is proportional to a sum of the each corresponding peak multiplied by a number of Al (4-n) and divide by 4. The intensity of each resonance is determined by deconvolution: Si(0Al), Si(1Al), Si(2Al), Si(3Al), Si(4Al).
The Si/Al ratio is then given by the following equation:
Si/Al = 4*Si total area / [Area Si(1Al) + 2*Area Si(2Al) + 3*Area Si(3Al) + 4*Area Si(4Al)]

EXAMPLES

[0050] The Si/Al framework molar ratio was determined using solid-state ^{29}Si MAS NMR measurement method described above.

[0051] The acidity was measured using the temperature-programmed desorption of ammonia method as described in the analytical methods above.

[0052] General procedure for dehydration process of alcohols is done as follows:
A stainless-steel reactor tube having an internal diameter of 10mm is used. 10ml of the catalyst composition, as pellets of 35-45 mesh, is loaded in the tubular reactor. The void spaces, before and after the catalyst composition, are filled with SiC granulates of 2mm. The temperature profile is monitored with the aid of a thermocouple well placed inside the reactor at the top of the catalyst bed. Before the reaction, the catalyst was pretreated in a nitrogen flow

at 550°C for 2h (heating rate 60°C/h) followed by cooling down to the reaction temperature. The nitrogen is then replaced by the feed at the indicated operating conditions. The catalytic tests are performed down-flow, in a pressure range from 1.5 to 11 bars, in a temperature range of 100-500°C and with an alcohol weight hour space velocity varying from 0.1- 20 h^{-1} (kg of product/ hours X kg of catalyst). Analysis of the products is performed by using an on-line gas chromatography.

Example 1

[0053] Sample A is made of FER55 (CP914 from Zeolyst international) extruded with SiO_2 (FER/SiO_2: 70/30). It is characterized by having a Si/Al in the zeolite framework of 28 and an acidity of 750 µmol/g.

Example 2

[0054] Sample B has been obtained by steaming sample A with deionized water at 300°C at 8.8 bars during 24h hours with a weight hour speed velocity (whsv) of 7.9 h^{-1} and under an atmosphere containing 100% of steam (i.e. at a partial pressure of H_2O of 8.8 bars). Sample B is characterized by having an acidity of 500 µmol/g.

Example 3

[0055] Sample C has been obtained by steaming sample A with deionized water at 300°C at 8.8 bars during 6 days with a weight hour speed velocity (whsv) of 7.9 h^{-1} and under an atmosphere containing 100% of steam (i.e. at a partial pressure of H_2O of 8.8 bars). Sample C is characterized by having an acidity of 400 µmol/g.

Example 4

[0056] Sample D has been obtained by steaming sample A with deionized water at 350 °C at 8.8 bars during 24 hours with a weight hour speed velocity (whsv) of 7.9 h^{-1} and under an atmosphere containing 100% of steam (i.e. at a partial pressure of H_2O of 8.8 bars). Sample C is characterized by having an acidity of 425 µmol/g.

Example 5

[0057] Sample E has been obtained by steaming sample A according to a standard procedure: steaming with deionized water at 600 °C under atmospheric pressure during 6 hours with a weight hour speed velocity (whsv) of 0.5 h^{-1} and under an atmosphere containing 100% of steam. Sample E is characterized by having an acidity of 300µmol/g.

Example 6

[0058] Sample F has been obtained by steaming sample A according to a standard procedure: steaming with deionized water at 300 °C under atmospheric pressure during 24 hours with a weight hour speed velocity (whsv) of 7.9 h^{-1} and under an atmosphere containing 100% of steam. Sample F is characterized by having an acidity of 550 µmol/g.

Example 7 (comparison)

[0059] The catalysts described in the examples 1 to 5 have been crushed and sieved (35-45 mesh) for loading 10 mL in a fixed bed reactor. The catalysts are then subjected to isobutanol dehydration testing. The testing conditions are a pressure of 3 bars, a temperature between 250 and 350 °C (isothermal) and an isobutanol weight hour space velocity (WHSV) of 7 h^{-1}. Isobutanol was diluted with H_2O, the ratio iBuOH/H_2O = 95/5. The results obtained at 300 °C and 350 °C are presented in Table 1.

Table 1 - Isobutanol dehydration test results under isothermal conditions.

	Reaction Temp.: 300°C			**Reaction Temp.: 350°C**		
	iBuOH conv.	**C4= sel.**	**nC4= sel.**	**iBuOH conv.**	**C4= sel.**	**nC4= sel.**
Sample A (base)	100 %	97.5 %	80.5 %	100 %	97.0 %	73.0 %
Sample B (invention)	100 %	98.5 %	82.0 %	100 %	97.5 %	77.0 %
Sample C (invention)	100 %	99.0 %	83.5 %	100 %	98.5 %	80.5 %
Sample D (invention)	100 %	99.0 %	86.0 %	100 %	99.0 %	80.0 %
Sample E (comparative)	87.0 %	99.0 %	75.0 %	100 %	98.0 %	65.5 %
Sample F (comparative)	100 %	97.0 %	80.5 %	100 %	97.0 %	65.5 %

[0060] At a reaction temperature of 300 °C (Table 1), the catalysts treated according to the present invention have similar isobutanol conversion but improved selectivity towards linear

butenes compared to base catalyst (Sample A). The comparative sample E has lower conversion and lower selectivity while comparative sample F is similar to base catalyst (Sample A).
At a reaction temperature of 350 °C (Table 1), the catalysts treated according to the present invention have similar isobutanol conversion but improved selectivity towards linear butenes compared to base catalyst (Sample A) while the comparative samples E and F are much less selective.

Example 8 (comparison)

[0061] Sample A and sample B have been tested under adiabatic condition. The testing conditions are a pressure of 8.8 bars, an entrance temperature of 350 °C (adiabatic) and an isobutanol weight hour space velocity (WHSV) of 7 h^{-1}. For this test, 200 mL of extruded catalysts which were blended with 200 ml of SiC are placed in 2 reactors (100 mL of catalyst per reactor). The reactors were installed in a series with an intermediate reheating. The results obtained after 100 h on stream are presented in Table 2.
Table 2 - Isobutanol dehydration test results under adiabatic conditions.

	iBuOH conv.	**C4= sel.**	**nC4= sel.**
Sample A (base)	99.5 %	99.0 %	78.0 %
Sample B (invention)	99.5 %	99.0 %	83.5 %

[0062] According to testing results under adiabatic conditions (Table 2), the catalysts treated according to the present invention have similar isobutanol conversion but improved selectivity towards linear butenes compared to base catalyst (Sample A).

Example 9 (Comparison)

[0063] Samples A, B and D have been loaded, in a 3 parallel fixed beds reactors (316 L stainless steel, 13 mm internal diameter, downflow operating). 1.5 g of extrudated catalysts are diluted with 200 µm SiC. The catalyst is activated under air (6 NL/h) at 450 °C (10 °C/min) during 1 h. The catalysts are then subjected to isobutanol dehydration testing under these conditions: a pressure of 8.8 bars, a temperature of 300°C (isothermal) and an isobutanol weight hour space velocity (WHSV) of 7 h-1. Isobutanol was diluted with H_2O, the ratio iBuOH/H_2O = 95/5 w/w. The results obtained in these conditions, after 50h and after 300 h on stream, are presented here below (Table 3).
Table 3 - Isobutanol dehydration test results under isothermal conditions (300 °C) at different times on stream.

	Time on stream: 50h			Time on stream: 300h		
	iBuOH conv.	C4= sel.	nC4= sel.	iBuOH conv.	C4= sel.	nC4= sel.
Sample A (base)	100 %	98.5 %	83.5 %	87.0 %	99.5 %	84.0 %
Sample B (invention)	100 %	99.0 %	85.0 %	99.0 %	99.5 %	85.0 %
Sample D (invention)	100 %	99.0 %	85.0 %	99.0 %	99.5 %	85.0 %

[0064] At a reaction temperature of 300°C, after 50 h on stream (Table 3, left part), the catalysts treated according to the present invention have similar isobutanol conversion but improved selectivity towards linear butenes compared to base catalyst (Sample A). At longer reaction time, at 300 °C (Table 3, right part), the isobutanol conversion obtained with base catalyst (Sample A) drops while samples prepared according to the invention maintain high conversion. Furthermore, the catalysts treated according to the present invention retain better selectivity towards linear butenes and better stability compared to base catalyst (Sample A).

[0065] As shown in the present examples, the catalysts according to the present invention have several advantages compared to the catalysts known in the art.

REFERENCES CITED IN THE DESCRIPTION

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KATALYSATORSAMMENSÆTNING OMFATTENDE MODIFICERET KRYSTALLINSK ALUMINOSILIKAT TIL DEHYDRERING AF ALKOHOLER

PATENTKRAV

1. Fremgangsmåde til fremstilling af en katalysatorsammensætning indeholdende et modificeret krystallinsk aluminosilikat og et bindemiddel, hvor katalysatorsammensætningen omfatter fra 5 til 95 vægt-% krystallinsk aluminosilikat baseret på den samlede vægt af katalysatorsammensætningen, hvilken fremgangsmåde er kendetegnet ved, at den omfatter følgende trin:

a) tilvejebringelse af et krystallinsk aluminosilikat med et Si-/Al-rammemolforhold, der er større end 10;

b) eventuelt kalcinering af det krystallinske aluminosilikat;

c) dampning af det krystallinske aluminosilikat:

- ved en temperatur fra 100 °C til 380 °C, og
- under en gasfaseatmosfære uden væske indeholdende fra 5 vægt-% til 100 vægt-% damp, idet resten er en eller flere gasser valgt blandt N_2, CO_2, Ar, He, CH_4, luft eller enhver blanding af deraf, idet luft fortrinsvis er valgt blandt luft og udtømt luft indeholdende under 10 vægt-% oxygen baseret på den samlede vægt af den udtømte luft, fortrinsvis under 5 vægt-%, mere fortrinsvis under 1 vægt-%, og
- ved et tryk fra 2 til 200 bar;
- ved et delvist tryk af H_2O fra 2 til 200 bar, og
- hvilken damping udføres i mindst 30 minutter og op til 144 timer;

og ved at fremgangsmåden omfatter et trin med formning eller ekstrudering af det krystallinske aluminosilikat med et bindemiddel, hvor bindemidlet er valgt til at omfatte:

- mindst 85 vægt-% silika baseret på den samlede vægt af bindemidlet, og
- mindre end 1000 vægt-ppm baseret på den samlede vægt af bindemidlet af aluminium, gallium, bor, jern og/eller krom.

2. Fremgangsmåde til fremstilling af en katalysatorsammensætning ifølge krav 1, kendetegnet ved, at:

- bindemidlet indeholder mindst 90 vægt-% silika baseret på den samlede vægt af bindemidlet, fortrinsvis mindst 95 vægt-%, mere fortrinsvis mindst 99,5 vægt-% og/eller
- bindemidlet omfatter mindre end 500 vægt-ppm baseret på den samlede vægt af

bindemidlet af aluminium, gallium, bor, jern og/eller krom, fortrinsvis mindre end 200 ppm.

3. Fremgangsmåde til fremstilling af en katalysatorsammensætning ifølge krav 1 eller 2, kendetegnet ved, at fremgangsmåden yderligere omfatter følgende trin:

- ingen udførelse af nogen udvaskningsbehandling hverken før trin b) eller efter trin c) for at holde koncentrationen af aluminium i det modificerede krystallinske aluminosilikat konstant;
- udførelse af et valgfrit trin med vask eller ionbytning med et alkalimetal eller NH_4-salte efter trin c) eller før trin b);
- udførelse af et valgfrit kalcineringstrin af det opnåede produkt efter trin c) eller før trin b);
- udførelse af et valgfrit trin med genvinding af det modificerede krystallinske aluminosilikat efter trin c).

4. Fremgangsmåde til fremstilling af en katalysatorsammensætning ifølge et hvilket som helst af kravene 1 til 3, kendetegnet ved, at det krystallinske aluminosilikat er en 10-leddet ringzeolit af rammetypen FER, MWW, EUO, MFS, ZSM-48, MTT, MFI, MEL, TON eller SZR og fortrinsvis er valgt blandt ferrierit, FU-9, ISI-6, NU-23, Sr-D, ZSM-35, ZSM-57 eller SUZ-4 eller en hvilken som helst blanding deraf.

5. Fremgangsmåde til fremstilling af en katalysatorsammensætning ifølge et hvilket som helst af kravene 1 til 4, kendetegnet ved, at trinnet med formning eller ekstrudering af det krystallinske aluminosilikat med et bindemiddel udføres før et hvilket som helst af trinnene a) til c), så trinnet med dampning af det krystallinske aluminosilikat udføres på et krystallinsk aluminosilikat formet med, eller ekstruderet med, et bindemiddel, fortrinsvis at trinnet med formning eller ekstrudering af det krystallinske aluminosilikat med et bindemiddel er et trin med ekstrudering af det krystallinske aluminosilikat i quadrilober med et bindemiddel.

6. Fremgangsmåde til fremstilling af en katalysatorsammensætning ifølge et hvilket som helst af kravene 1 til 4, kendetegnet ved, at trinnet med formning eller ekstrudering af det krystallinske aluminosilikat med et bindemiddel udføres på det opnåede produkt efter trin c), fortrinsvis at trinnet med formning, eller ekstrudering, af det krystallinske aluminosilikat med et bindemiddel er et trin med ekstrudering af det opnåede produkt i quadrilober efter

trin c) med et bindemiddel.

7. Fremgangsmåde til fremstilling af en katalysatorsammensætning ifølge et hvilket som helst af kravene 1 til 6, kendetegnet ved, at hverken nogen dampning ved en temperatur over 380 °C eller nogen udvaskning er blevet udført på det krystallinske aluminosilikat før trin a), og hvor hverken nogen dampning ved en temperatur over 380 °C eller nogen udvaskning yderligere udføres på det modificerede aluminosilikat efter trin c).

8. Fremgangsmåde til fremstilling af en katalysatorsammensætning ifølge et hvilket som helst af kravene 1 til 7, kendetegnet ved, at det modificerede krystallinske aluminosilikat har Si-/Al-rammemolforhold fra 10 til 65.

9. Fremgangsmåde til fremstilling af en katalysatorsammensætning ifølge et hvilket som helst af kravene 1 til 8, kendetegnet ved, at det modificerede krystallinske aluminosilikat har et indhold i overgangsmetaller eller kationer deraf under 1000 vægt-ppm som målt ved fremgangsmåden ASTM UOP961-12, hvilke overgangsmetaller hører til en hvilken som helst af kolonnerne 3 til 12 i det periodiske system.

10. Fremgangsmåde til fremstilling af en katalysatorsammensætning ifølge et hvilket som helst af kravene 1 til 9, kendetegnet ved, at trinnet c) med dampning af det krystallinske aluminosilikat udføres:

- ved en temperatur på mindst 200 °C, fortrinsvis mindst 250 °C; og/eller
- ved en temperatur på højst 350 °C; og/eller
- ved et fra 2 til 20 bar, mere fortrinsvis fra 2 til 15 bar; og/eller
- ved et delvist tryk af H_2O fra 3 til 10 bar.

11. Fremgangsmåde til dehydrering af en monoalkohol, eller af en blanding af mindst to monoalkoholer med mindst 2 carbonatomer og højst 7 carbonatomer, til olefiner med det samme antal carbonatomer, hvilken fremgangsmåde er kendetegnet ved, at den omfatter følgende trin:

i. tilvejebringelse af katalysatorsammensætning omfattende et modificeret krystallinsk aluminosilikat, hvor katalysatorsammensætningen fremstilles ifølge et hvilket som helst af kravene 1 til 10;

ii. tilvejebringelse af en tilførsel (A) omfattende monoalkoholerne, eventuelt vand, eventuelt en inert komponent;

iii. kontakt af tilførslen (A) med katalysatorsammensætningen under betingelser, der er effektive til at dehydrere mindst en del af monoalkoholen;

iv. udvinding af et spildevand (B) og fjernelse af vand, den eventuelle inerte komponent og eventuelle uomdannede alkoholer for at opnå olefinerne med det samme antal carbonatomer som monoalkoholen.

12. Fremgangsmåde til dehydrering af en monoalkohol, eller af en blanding af mindst to monoalkoholer med mindst 2 carbonatomer og højst 7 carbonatomer, til olefiner med det samme antal carbonatomer, hvilken fremgangsmåde udføres i en dehydreringsreaktor eller i en dehydrerings- og skeletisomeriseringsreaktor og er kendetegnet ved, at den omfatter følgende trin:

i. tilvejebringelse af en katalysatorsammensætning omfattende et krystallinsk aluminosilikat formet med, eller ekstruderet med, et bindemiddel, hvor katalysatorsammensætningen omfatter fra 5 til 95 vægt-% krystallinsk aluminosilikat baseret på den samlede vægt af katalysatorsammensætningen, og dampning af katalysatorsammensætningen in situ i dehydreringsreaktoren eller i dehydrerings- og skeletisomeriseringsreaktoren:

- ved en temperatur fra 100 °C til 380 °C;
- under en gasfaseatmosfære uden væske indeholdende fra 5 vægt-% til 100 vægt-% damp, idet resten er en eller flere gasser valgt blandt N_2, CO_2, Ar, He, CH_4, luft eller enhver blanding af deraf, idet luft fortrinsvis er valgt blandt luft og udtømt luft indeholdende under 10 vægt-% oxygen baseret på den samlede vægt af den udtømte luft, fortrinsvis under 5 vægt-%, mere fortrinsvis under 1 vægt-%;
- ved et tryk fra 2 til 200 bar;
- ved et delvist tryk af H_2O fra 2 til 200 bar, og
- hvilken damping udføres i mindst 30 minutter og op til 144 timer;

hvor det krystallinske aluminosilikat har et Si-/Al-rammemolforhold, der er større end 10;
hvor bindemidlet er valgt til at omfatte mindst 85 vægt-% sillka baseret på den samlede vægt af bindemidlet og mindre end 1000 vægt-ppm baseret på den samlede vægt af bindemidlet af aluminium, gallium, bor, jern og/eller krom, og
hvor trinnet med dampning af katalysatorsammensætningen omfattende et krystallinsk aluminosilikat resulterer i en katalysatorsammensætning omfattende et modificeret krystallinsk aluminosilikat;

ii. tilvejebringelse af en tilførsel (A) omfattende monoalkoholerne, eventuelt vand, eventuelt en inert komponent;

iii. kontakt af tilførslen (A) med katalysatorsammensætningen under betingelser, der er effektive til at dehydrere mindst en del af monoalkoholen;

iv. udvinding af et spildevand (B) og fjernelse af vand, den eventuelle inerte komponent og eventuelle uomdannede alkoholer for at opnå olefinerne med det samme antal carbonatomer som monoalkoholen.

13. Fremgangsmåde ifølge krav 11 eller 12, hvilken fremgangsmåde er kendetegnet ved, at betingelserne, der er effektive til dehydrering af monoalkoholen/-erne til olefiner med det samme antal carbonatomer, er en hvilken som helst kombination af:

- adiabatiske eller isotermiske driftsbetingelser eller en hvilken som helst mellemliggende betingelse indbefattende delvis varmekompensation eller mellemliggende genopvarmning
- en temperatur fra 200 °C til 500 °C, fortrinsvis 225 °C til 450 °C, mest fortrinsvis 250 °C til 400 °C; og/eller
- et tryk fra 0,5 til 15 absolut bar (50 kPa til 1,5 MPa), fortrinsvis 0,5 til 10 absolut bar (50 kPa til 1,0 MPa), mest fortrinsvis 1,2 til 9 absolut bar (0,12 MPa til 0,9 MPa); og/eller
- en WHSV fra 1 til 30 h^{-1}, fortrinsvis fra 2 til 21 h^{-1}, mere fortrinsvis fra 3 til 9 h^{-1}, hvor WHSV repræsenterer vægtstrømningshastigheden for monoalkoholen ved indgangen til reaktoren divideret med massen af katalysatoren i reaktoren; og/eller et delvist tryk af alkoholer i tilførslen (A) fra 0,1 til 15 absolut bar (0,01 MPa til 1,5 MPa), mere fortrinsvis fra 0,5 til 9,0 absolut bar (0,05 MPa til 0,9 MPa).

14. Fremgangsmåde til dehydrering af en monoalkohol, eller af en blanding af mindst to monoalkoholer, ifølge et hvilket som helst af kravene 11 til 13, kendetegnet ved, at:

- monoalkoholen/-erne har mindst 4 carbonatomer, og at dehydreringen af en monoalkohol fortrinsvis udføres sammen med en skeletisomerisering; og/eller
- monoalkoholen er isobutanol, og ved at isobutanol omdannes til n-butener og isobuten.

15. Fremgangsmåde til dehydrering af en monoalkohol, eller af en blanding af mindst to monoalkoholer, ifølge et hvilket som helst af kravene 11, 13 eller 14, kendetegnet ved, at katalysatorsammensætningen omfattende et krystallinsk aluminosilikat formet med, eller ekstruderet med, et bindemiddel er valgt til at have et modificeret krystallinsk aluminosilikat med en surhedsgrad mellem 350 og 500 µmol/g, fortrinsvis mellem 350 og

450 µmol/g, som målt ved temperaturprogrammeret desorption af ammoniak.