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(54) **Titre : UTILISATION D'UN CATALYSEUR COMPRENANT UNE ZEOLITHE MODIFIEE PAR DU PHOSPHORE DANS UN PROCEDE DE DESHYDRATATION D'ALCOOLS**
(54) **Title: USE OF A CATALYST COMPRISING A PHOSPHORUS MODIFIED ZEOLITE IN AN ALCOHOL DEHYDRATION PROCESS**

(57) **Abrégé/Abstract:**
The present invention relates, in a first embodiment, to the use of a catalyst to convert at least an alcohol into light olefins in a dehydration process to make an olefin having the same number of carbon atoms as the alcohol wherein said catalyst comprises a phosphorus modified zeolite and is made by a method comprising the following steps in this order, a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite, b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture, c) optionally making a ion-exchange, d) optionally steaming the shaped catalyst, optionally before step c), at least among said steaming of step d) and the steaming of step a) one is mandatory, e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus, said introduction being made by dry impregnation or chemical vapor deposition, f) optionally introducing a metal, optionally simultaneously with step e), g) optionally washing the catalyst, h) optionally calcinating the catalyst, i) steaming the catalyst, also referred to as the equilibration step. In a second embodiment phosphorus can be introduced by any means and at step i) the steaming severity (X) is at least about 2. In said second embodiment the catalyst is advantageously steamed at a temperature above 625°C, preferably in the range 700 to 800°C. The metal of step f) is advantageously Calcium.

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(54) Title: USE OF A CATALYST COMPRISING A PHOSPHORUS MODIFIED ZEOLITE IN AN ALCOHOL DEHYDRATION PROCESS

(57) Abstract: The present invention relates, in a first embodiment, to the use of a catalyst to convert at least an alcohol into light olefins in a dehydration process to make an olefin having the same number of carbon atoms as the alcohol wherein said catalyst comprises a phosphorus modified zeolite and is made by a method comprising the following steps in this order, a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite, b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture, c) optionally making a ion-exchange, d) optionally steaming the shaped catalyst, optionally before step c), at least among said steaming of step d) and the steaming of step a) one is mandatory, e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus, said introduction being made by dry impregnation or chemical vapor deposition, f) optionally introducing a metal, optionally simultaneously with step e), g) optionally washing the catalyst, h) optionally calcinating the catalyst, i) steaming the catalyst, also referred to as the equilibration step. In a second embodiment phosphorus can be introduced by any means and at step i) the steaming severity (X) is at least about 2. In said second embodiment the catalyst is advantageously steamed at a temperature above 625°C, preferably in the range 700 to 800°C. The metal of step f) is advantageously Calcium.

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USE OF A CATALYST COMPRISING A PHOSPHORUS MODIFIED ZEOLITE IN AN ALCOHOL DEHYDRATION PROCESS

[Field of the invention]

The present invention relates to a method for making a catalyst comprising a phosphorus modified zeolite to be used to convert an alcohol into light olefins in a dehydration process to convert at least an alcohol into the corresponding olefin wherein said catalyst comprises a phosphorus modified zeolite. Olefins are traditionally produced from petroleum feedstocks by catalytic or steam cracking processes. These cracking processes, especially steam cracking, produce light olefin(s), such as ethylene and/or propylene, from a variety of hydrocarbon feedstock. Ethylene and propylene are important commodity petrochemicals useful in a variety of processes for making plastics and other chemical compounds.

The limited supply and increasing cost of crude oil has prompted the search for alternative processes for producing hydrocarbon products.

Olefins can be produced by dehydration of the corresponding alcohol. Ethanol, as well as higher alcohols such as propanol, butanol can be obtained by fermentation of carbohydrates. Made up of organic matter from living organisms, biomass is the world's leading renewable energy source. Recently, new routes to produce ethanol and higher alcohols from syngas have been described.

[Background of the invention]

An efficient catalyst is a key in industrialization of dehydration of alcohols. One of the early catalysts employed for the dehydration of ethanol was alumina. This catalyst is relatively cheap but needs low space velocity, high reaction temperature and makes a lot of ethane, which needs to be separated. Zeolites, particularly phosphated zeolites, solves a problem with catalyst activity and provide with directly polymer grade or close to polymer grade ethylene fraction. Catalysts comprising a phosphorus modified zeolite (the phosphorus modified zeolite is also referred as P-zeolite) are known. The following prior arts have described various methods to make said catalysts.

US 2006 106270 relates to the use of a dual-function catalyst system in the hydrocarbon synthesis reaction zone of an oxygenate to propylene (OTP) process that operates at relatively high temperatures preferably with a steam diluent and uses moving bed reactor technology. The dual-functional catalyst system comprises a molecular sieve having dual-function capability dispersed in a phosphorus-modified alumina matrix containing labile phosphorus and/or aluminum anions. It is explained that the hydrothermal stabilization effect that is observed when this phosphorus-modifed alumima matrix is utilized is caused by migration or dispersion of phosphorus and/or aluminum anions from this matrix into the bound molecular sieve. These anions are then available to repair, anneal and/or stabilize the framework of the molecular sieve against the well-known dealumination mechanism of molecular sieve framework destruction or modification that is induced by exposure to steam at temperatures corresponding to those used in the OTP reaction zone and in the regeneration zone.

US 5,231,064 is directed to a fluid catalyst comprising clay and a zeolite, at least one of which has been treated with a phosphorus containing compound, for example ammonium dihydrogen phosphate or phosphoric acid, and which is spray dried at a low pH, preferably lower than about 3. Said catalysts are deemed to advantageously exhibit reduced attrition.

EP 511013 A2 provides an improved process for the production of C2-C5 olefins from higher olefinic or paraffinic or mixed olefin and paraffin feedstock’s. In accordance with this prior art, the hydrocarbon feed materials are contacted with a particular ZSM-5 catalyst at elevated temperatures, high space velocity and low hydrocarbon partial pressure to produce lower olefins. The catalysts is treated with steam prior to use in the hydrocarbon conversion. The active catalyst component is phosphorus-containing ZSM-5 having a surface Si/Al ratio in the range 20-60. Preferably, the phosphorus is added to the formed ZSM-5 as by impregnating the ZSM-5 with a phosphorus compound in accordance with the procedures described, for example, in U.S. Patent 3,972,832. Less preferably, the phosphorus compound can be added to the multicomponent mixture from which the catalyst is formed. The phosphorus compound is added in amount sufficient to provide a final ZSM-5 composition having 0. 1-10 wt.% phosphorus, preferably 1-3 wt.%.

The phosphorus-containing ZSM-5 is preferably combined with known binders or matrices such as silica, kaolin, calcium bentonite, alumina, silica aluminate and the like. The ZSM-5 generally comprises 1-50 wt.% of the catalyst composition, preferably 5-30 wt.% and most preferably 10-25 wt.%. This prior art doesn't concern the dehydration of alcohols to make an olefin having the same number of carbon atoms as the alcohol.

EP 568913 A2 describes a method for preparing a ZSM-5 based catalyst adapted to be used in the catalytic conversion of methanol or dimethyl ether to light olefins, wherein it comprises the following consecutive steps:

- mixing a zeolite ZSM-5 based catalyst with silica sol and ammonium nitrate solution,
- kneading, moulding, drying and calcining the mixture,
- exchanging the modified zeolite with a solution of HCl at 70-90°C,
- drying and calcining the H-modified zeolite,
- impregnating the H-modified zeolite with phosphoric acid under reduced pressure,
- drying and calcining the P-modified zeolite,
- impregnating the P-modified zeolite with a solution of rare earth elements under reduced pressure,
- drying and calcining the P-rare earths-modified zeolite,

- hydrothermally treating the P-rare earths-modified zeolite at 500-600°C with water vapour, and
- calcining the modified zeolite.

WO 03 020667 relates to a process of making olefin, particularly ethylene and propylene, from an oxygenate feed, comprising contacting an oxygenate feed with at least two different zeolite catalysts to form an olefin composition, wherein a first of the zeolite catalysts contains a ZSM-5 molecular sieve and a second of the zeolite catalysts contains a zeolite molecular sieve selected from the group consisting of ZSM-22, ZSM-23, ZSM-35, ZSM-48, and mixtures thereof. The ZSM-5 can be unmodified, phosphorus modified, steam modified having a micropore volume reduced to not less than 50% of that of the unsteamed ZSM-5, or various mixtures thereof. According to one embodiment, the zeolite is modified with a phosphorus containing compound to control reduction in pore volume. Alternatively, the zeolite is steamed, and the phosphorus compound is added prior to or after steaming. The amount of phosphorus, as measured on an elemental basis, is from 0.05 wt.% to 20 wt. %, and preferably is from 1 wt.% to 10 wt.%, based on the weight of the zeolite molecular sieve. Preferably, the atomic ratio of phosphorus to framework aluminum (i.e. in the zeolite framework) is not greater than 4:1 and more preferably from 2:1 to 4:1. Incorporation of a phosphorus modifier into the catalyst of the invention is accomplished, according to one embodiment, by contacting the zeolite molecular sieve either alone or the zeolite in combination with a binder with a solution of an appropriate phosphorus compound. The solid zeolite or zeolite catalyst is separated from the phosphorus solution, dried and calcined. In some cases, the added phosphorus is converted to its oxide form under such conditions. Contact with the phosphorus-containing compound is generally conducted at a temperature from 25°C to 125°C for a time from 15 minutes to 20 hours. The concentration of the phosphorus in the zeolite may be from 0.01 wt.% to 30 wt.%. This prior art discloses a non-formulated P-ZSM-5.

WO 2009 022990 A1 describes a catalyst composition for dehydration of an alcohol to prepare an alkene. The catalyst composition comprises a catalyst and a modifying agent which is phosphoric acid, sulfuric acid or tungsten trioxide, or a derivative thereof. There is no binder.

EP 2348004 A1relates to the dehydration of ethanol to make ethylene. The catalyst is made by the following process : A ZSM-5 is steamed, P is introduced by contacting the steamed zeolite with an H3PO4 solution under reflux conditions, the P modified zeolite is extruded with a binder, calcium is introduced and the resulting catalyst is steamed two hours at 600°C. This prior art discloses a formulated P-ZSM-5, where at least a part of phosphorous was introduced into zeolite before formulation step.

WO 2009-098262 A1relates to the dehydration of ethanol to make ethylene. The catalyst is made by the following process : A ZSM-5 is steamed, P is introduced by contacting the steamed zeolite with an H3PO4 solution under reflux conditions, the P modified zeolite is extruded with a binder, there is no final steaming. There is no introduction of calcium.

EP 2082802 A1relates to various petrochemical processes, the dehydration of alcohols to make an olefin having the same number of carbon atoms as the alcohol is not cited. Among the cited processes are the cracking of olefins and the conversion of oxygenates, e.g. methanol to make a mixture of ethylene, propylene, butenes and various hydrocarbons. The catalyst is made by the following process : A ZSM-5 is steamed, the steamed zeolite is extruded with a binder, P is introduced by contacting the steamed zeolite with an H3PO4 solution under reflux conditions, calcium is introduced in form of metal silicate and the resulting catalyst is steamed two hours at 600°C.

US 4,356,338 relates to the aromatization of hydrocarbon , the dehydration of alcohols to make an olefin having the same number of carbon atoms as the alcohol is not cited. The zeolite (ZSM-5) may be combined with a binder and is treated by a P containing component or steam or both steam and P containing component. The said catalyst has a reduced coking. There is no introduction of metals such as Ca in the catalyst.

A common way to produce a formulated P-zeolite containing catalyst consists in the impregnation of the already pre-formulated zeolite (e.g. the zeolite+ a binder) with P-compounds or phosphorus addition to the reaction medium followed by drying/calcination. This solution is appropriate for high temperature processes like FCC (fluid catalytic cracking), MTO (methanol to olefins conversion) etc. In this case the catalyst is self-equilibrating during regeneration processes occurring at high temperature in presence of steam. On the contrary, in case of alcohols dehydration, low reaction temperature doesn't offer the same opportunity. Moreover, the metals, refractory oxides and binder components may also adsorb the phosphorus interfering and even competing with zeolite. This prevents a proper zeolite phosphatation and requires an excess of phosphorus leading to a partial plugging of microporosity. The presence of the traces of alkali metals adsorbing preferentially the phosphorus could even more perturb the zeolite phosphatation. This often leads to non-selective catalysts due to a poor reproducibility.

The present invention provides a solution to selectively introduction of phosphorus into formulated catalyst (the catalyst + the binder) levelling off the side effects of the binder presence. Thus, the invention discloses that a preparation of a selective catalyst for alcohols dehydration requires a treatment of shaped zeolite advantageously substantially free of alkali metal with phosphorus followed by steaming of the modified solid. The said steam treatment facilitates interaction of zeolite with phosphorus in presence of binder, improve conversion of non-phosphated framework Al^{IV} sites into low acid alumina phase and level off the acidity of P-species adsorbed on a binder and stabilizing phosphorus on the catalyst. This method insures a reproducibility of the preparation and a good catalyst performance.

[Brief description of the invention]

The present invention relates, in a first embodiment, to the use of a catalyst to convert at least an alcohol into light olefins in a dehydration process to make an olefin having the same number of carbon atoms as the alcohol wherein said catalyst comprises a phosphorus modified zeolite and is made by a method comprising the following steps in this order,

a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite,

b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture,

c) optionally making a ion-exchange,

d) optionally steaming the shaped catalyst, optionally before step c), at least among said steaming of step d) and the steaming of step a) one is mandatory,

e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus, said introduction being made by dry impregnation or chemical vapor deposition,

f) optionally introducing a metal, optionally simultaneously with step e),

g) optionally washing the catalyst,

h) optionally calcinating the catalyst,

i) steaming the catalyst, also referred to as the equilibration step.

The present invention relates, in a second embodiment, to the use of a catalyst to convert at least an alcohol into light olefins in a dehydration process to make an olefin having the same number of carbon atoms as the alcohol wherein said catalyst comprises a phosphorus modified zeolite and is made by a method comprising the following steps in this order,

a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite,

b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture,

c) optionally making a ion-exchange,

d) optionally steaming the shaped catalyst, optionally before step c), at least among said steaming of step d) and the steaming of step a) one is mandatory,

e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus,

f) optionally introducing a metal, optionally simultaneously with step e),

g) optionally washing the catalyst,

h) optionally calcinating the catalyst,

i) steaming the catalyst, also referred to as the equilibration step, at a steaming severity (X) of at least about 2.

The above-described “steaming severity (X)” is an important, measurable and critical definition of treatment conditions for the steps d) which are useful in the instant invention.

“About” means that it could be slightly under 2. As explained hereunder the severity describes conditions of steaming to achieve a dealumination.

The matter is that the results of the steaming is a function of the nature of catalyst (type of zeolite, type of binder, Si/Al ratio, crystal size, crystallinity, structure defects, the presence of occluded contaminants etc) as well as of conditions of the treatment used. It is clear that the minimum severity is not an absolute value, considering the above parameters it can vary from a catalyst to another. The man skilled in the art can easily determine the minimun severity. To be sure he can, by way of example, extend the duration of treatment and/or increase the temperature. The critical parameters for the treatment include mainly steam partial pressure, temperature and duration of the treatment. If the objects of the treatment were similar nature the effect of the treatment is only a function of the “steaming severity”.

A steaming or a hydrothermal treatment of the zeolite above 500°C leads to a delumination of the framework. A degree of dealumination could be measured by ^{27}Al, ^{29}Si MAS NMR, by acidity measurement (like TPD NH_3) or by any other means, which are well known in the prior art. A rate of the dealumination is defined mainly by mentioned above parameters, namely, steam partial pressure, temperature and duration of the treatment.

Thus, the "steaming severity (X)" is defined as a ratio of the dealumination rates between an experimental condition vs a standard condition.

Steaming performed at 600°C, in 100% of steam at atmospheric pressure during 2h is selected as a standard condition for this invention.

The rate of dealumination (V) for the catalyst of invention is given by equation:

$V \div Const \times P(H_2O)^\wedge 1.5 \times t_{st} / EXP(-0.03 \times T_{st})$,

where $P(H_2O)$ – steam partial pressure (P/Patm); T_{st} – steaming temperature in °C; t_{st} – time in hours (duration) of treatment and ÷ means proportional.

X (The steaming severity) = $V_{\text{experimental condition}} / V_{\text{standard condition}}$

This equation is valid in a steaming interval from 500°C to 760°C.

So, the steaming severity value could be achieved even at lower temperature relative to the used in standard condition but for a higher time of duration.

The temperature 625°C provides roughly 2 times higher steam severity vs the standard condition at equal time steam partial pressure and duration of the treatment.

If the temperature of the equilibration step is above 760°C (out of the range), the duration of steaming is at least 0.1 h and the partial pressure of steam is at least 0.01 bar.

Advantageously in the second embodiment the temperature of the equilibration step is in the range 625 to 870°C.

In an embodiment the shaped zeolite (or molecular sieve) of step b) contains less than 1000 wppm of sodium.

In an embodiment the shaped zeolite (or molecular sieve) of step b) contains less that 1000 wppm of sodium, less that 1000 wppm of potassium and less that 1000 wppm of iron.

In an embodiment the shaped zeolite (or molecular sieve) of step b) contains less than 100 wppm of sodium

In an embodiment the shaped zeolite (or molecular sieve) of step b) contains less that 100 wppm of sodium, less that 100 wppm of potassium and less that 500 wppm of iron.

[Detailed description of the invention]

As regards the dehydration process to convert an alcohol into an olefin, this process has been described in a lot of patent applications. One can cite WO/2009/098262, WO/2009/098267, WO/2009/098268 and WO 2009/098269, the content of which is incorporated in the present application. The alcohol is any alcohol provided it can be dehydrated to the corresponding olefin. Advantageously the alcohol has two or more carbon atoms. The corresponding olefin is an olefin having the same number of carbons as the alcohol. By way of example mention may be made of alcohols having from 2 to 10 carbon atoms. Advantageously the invention is of interest for ethanol, propanol, butanol and phenylethanol.

As regards the zeolite of step a) containing at least one 10 members ring into the structure, one can cite the crystalline silicates. It is by way of example the MFI (ZSM-5, silicalite-1, boralite C, TS-1), MEL (ZSM-11, silicalite-2, boralite D, TS-2, SSZ-46), FER (Ferrierite, FU-9, ZSM-35), MTT (ZSM-23), MWW

(MCM-22, PSH-3, ITQ-1, MCM-49), TON (ZSM-22, Theta-1, NU-10), EUO (ZSM-50, EU-1), MFS (ZSM-57) and ZSM-48 family of microporous materials consisting of silicon, aluminium, oxygen and optionally boron.

Preferred zeolite structures are selected from the MFI, MTT, FER, MEL, TON, MWW, EUO, MFS.

In an embodiment, the zeolite is ZSM-5 with Si/Al atomic ratio ranging from 11 to 30, which has been made without direct addition of organic template.

In an embodiment, the zeolite is MFI zeolite with Si/Al atomic ratio ranging from 30 to 200.

The three-letter designations "MFI" and "MEL" each representing a particular crystalline silicate structure type as established by the Structure Commission of the International Zeolite Association. Examples of a crystalline silicate of the MFI type are the synthetic zeolite ZSM-5 and silicalite and other MFI type crystalline silicates known in the art. Examples of a crystalline silicate of the MEL family are the zeolite ZSM-11 and other MEL type crystalline silicates known in the art. Other examples are Boralite D and silicalite-2 as described by the International Zeolite Association (Atlas of zeolite structure types, 1987, Butterworths). The preferred crystalline silicates have pores or channels defined by ten oxygen rings.

Crystalline silicates are microporous crystalline inorganic polymers based on a framework of XO_4 tetrahedra linked to each other by sharing of oxygen ions, where X may be trivalent (*e.g.* Al,B,...) or tetravalent (*e.g.* Ge, Si,...). The crystal structure of a crystalline silicate is defined by the specific order in which a network of tetrahedral units are linked together. The size of the crystalline silicate pore openings is determined by the number of tetrahedral units, or, alternatively, oxygen atoms, required to form the pores and the nature of the cations that are present in the pores. They possess a unique combination of the following properties: high internal surface area; uniform pores with one or more discrete sizes; ion exchangeability; good thermal stability; and ability to adsorb organic compounds. Since the pores of these crystalline silicates are similar in size to many organic molecules of practical interest, they control the ingress and egress of reactants and products, resulting in particular selectivity in catalytic reactions. Crystalline silicates with the MFI structure possess a bidirectional intersecting pore system with the following pore diameters: a straight channel along [010]:0.53-0.56 nm and a sinusoidal channel along [100]:0.51-0.55 nm. Crystalline silicates with the MEL structure possess a bidirectional intersecting straight pore system with straight channels along [100] having pore diameters of 0.53-0.54 nm.

In an embodiment, the zeolite is pretreated by steam. The pretreatment is performed in the range 420 to 870°C, more preferably in the range 480 to 800°C. The water partial pressure may range from 13 to 100 kPa. The steam atmosphere preferably contains from 5 to 100 vol % steam with from 0 to 95 vol % of a gas, preferably nitrogen or air. The steam treatment is preferably carried out for a period of from 0,01 to 200 hours, more preferably from 0,05 to 50 hours,still more preferably for at least 0.1 hour and in a preferred way from 0,1 to 50 hours and in a more preferred way from 0.5 to 50 hours and still more preferred 1 to 50 hours.

The steam treatment tends to reduce the amount of tetrahedral aluminium in the crystalline silicate framework by forming alumina. Preferably, the amount of residual tetrahedral Al in the zeolite is between 60 to 95%. This value can be estimated by ^{27}Al MAS NMR or TPD NH3. Optionally said alumina can be removed by leaching with an acid.

In an embodiment, the ZSM-5 with Si/Al atomic ratio ranging from 11 to 30, which has been made without direct addition of organic template, is pretreated by steam.

Additionally, if during the preparation of the zeolite alkaline or alkaline earth metals have been used, the molecular sieve might be subjected to an ion-exchange step. Conventionally, ion-exchange is done in aqueous solutions using ammonium salts or inorganic acids.

In an embodiment, the zeolite is subjected to dealumination such as about 10% by weight of the aluminium is removed. Such dealumination can be done by any conventional techniques known per se but is advantageously made by a steaming optionally followed by a leaching. The crystalline silicate having a ratio Si/Al of at least about 30 to 200 can be synthetized as such or it can be prepared by dealumination of a crystalline silicate with lower initial Si/Al ratio.

As regards step b), and the binder, it is selected so as to be resistant to the temperature and other conditions employed in the processes using the catalyst. The binder can be an inorganic material selected from silica, metal silicates, zirconia, borates, alumina, silica-aluminas, phosphates, for example amorphous aluminophosphates, calcium phosphates, clays, metal oxides such as $Zr0_2$ and/or metals, or gels including mixtures of silica and metal oxides.

In an embodiment, the binder is substantially neutral (inert) and it is selected from inorganic material selected from silica, non-acid alumina, amorphous aluminophosphates, metalphosphates, clays or a mixture of thereof. The neutral nature of the binder allow limiting secondary reactions leading to formation of heavy oxygenates and hydrocarbons, etane, acetaldehyde etc.

A particularly preferred binder for the catalyst of the present invention comprises silica. The relative proportions of the finely divided crystalline silicate material and the inorganic oxide of the binder can vary widely.

Non-limiting examples of silicon sources include silicates, precipitated silicas, for example, Zeosil range available from Rhodia, fumed silicas, for example, Aerosil-200 available from Degussa Inc., New York, N.Y., silicon compounds such as tetraalkyl orthosilicates, for example, tetramethyl orthosilicate (TMOS) and tetraethylorthosilicate (TEOS), colloidal silicas or aqueous suspensions thereof, for example Ludox-HS-40 sol available from E.I. du Pont de Nemours, Wilmington, Del., silicic acid, alkali-metal silicate, or any combination thereof.

Other suitable forms of amorphous silica include silica powders, such as Ultrasil VN3SP (commercially available from Degussa).

Other non-limiting examples of a suitable solid silica source are special granulated hydrophilic fumed silicas, mesoporous silica grade EXP & high surface area precipitated silica SIPERNAT from Evonik, HiSil 233 EP (available from PPG Industries) and Tokusil (available from Tokuyama Asia Pacific).

In addition, suitable amorphous silica sources include silica sols, which are stable colloidal dispersions of amorphous silica particles in an aqueous or organic liquid medium, preferably water.

Non-limiting examples of commercially available silica sols include those sold under the tradenames Nyacol (available from Nyacol Nano Technologies, Inc. or PQ Corp.), Nalco (available from Nalco Chemical Company), Ultra-Sol (available from RESI Inc), Ludox (available from W.R. Grace Davison), NexSil (available from NNTI).

Many silica sols are prepared from sodium silicate and inevitably contain sodium. It is, however, found that the presence of sodium ions can cause sintering of the silica body at high temperature and/or affect catalytic performance. Therefore, if silica sols containing sodium are used, a step of ion exchange may be required in order to reduce or remove sodium. To avoid carrying out ion exchange steps, it is convenient to use silica sols that contain very little or, ideally, no detectable traces of sodium and have a pH value of less than 7. Most preferably, the silica sol used in the process is slightly acidic with or without polymeric stabilizers. Non limiting examples of silica sols that contain no detectable traces of sodium include Bindzil 2034DI, Levasil 200, Nalco 1034A, Ultra-Sol 7H or NexSil 20A.

In some case, silica dispersion prepared with alkylammonium might be useful. Non-limiting examples of commercially low sodium silica sols stabilized by ammonia or alkylammonium cations include LUDOX TMA (available from W.R. Grace Davison) or VP WR 8520 from Evonik.

The silica sols with higher SiO2 content than 30% and even up to 50wt%, for example W1250, W1836, WK341, WK7330 from Evonik are particularly preferred.

The preferred source of silicon is a silica sol or a combination of silica sol with precipitated or fumed silica.

Types of silica sols used to form a bound catalyst for use in alcohol dehydration process are commercially available as aquasols or organosols containing dispersed colloidal silica particles. For example, sodium silicate can be used as a silica sol. Otherwise, a silica gel, fumed or pyrogenic silica may also be used to provide a silica binder in the molecular sieve catalyst. Silicic acid is another possible source of silica. Advantageously, the binder contains low amount of sodium below 1000 ppm.

Clays are known to be essentially inert under a wide range of reaction conditions. Suitable clays include commercially available products such as kaolin, kaolinite, montmorillonite, attapulgite, saponite, and bentonite. These clays can be used as mined in their natural state, or they may also be employed in highly active forms, typically activated by an acid treatment procedure. Commercial suppliers of these clays include Thiele Kaolin Company, American Colloidal Co., and others.

Clays contribute to strength as a binder enhancing the attrition resistance properties of the catalyst particles, and clays in combination with binders contribute to the hardness of the particles. Clays also start as small particles and have a higher density, such that when combined with the molecular sieve and binder provide for denser particles, imparting the desirable characteristic of higher density.

Clays are used in this process to form a hardened product include, but are not limited to, kaolin, kaolinite, montmorillonite, saponite, bentonite, and halloysite.

In an embodiment, the binder material is often, to some extent, porous in nature and may be effective to promote the desired conversion of ethanol to ethylene. The binder might be a single amorphous entity, or a blend of two or more individual amorphous compounds.

In a related embodiment, the catalyst (zeolite +binder) has a volume of the pore between 30 Å and 1000 Å of at least 0.25 cc/g, advantageously between 0.25 and 1 cc/g preferably at least 0.26 cc/g, the most preferable between 0.27-0.92 cc/g. “cc” means cm3.

In an embodiment, the binder material possesses acid properties and may also promote conversion of the ethanol.

In referring to these types of binders that may be used, it should be noted that the term silica-alumina does not mean a physical mixture of silica and alumina but means an acidic and amorphous material that has been cogelled or coprecipitated. This term is well known in the art and is described, for example, in US-A-3,909,450 BI; US-A-3,274, 124 B1 and US-A-4,988,659 B I. In this respect, it is possible to form other cogelled or coprecipitated amorphous materials that will also be effective as either binder or filler materials. These include silica-zirconias, silica-thorias, silica-berylias, silica-titanias, silica-alumina-thofias, silica-alumina-zirconias, alurninophosphates, mixtures of these, and the like.

In another embodiment, catalyst contains alumina materials such as aluminum oxyhydroxide, γ-alumina, boehmite, diaspore, and transitional aluminas such as α-alumina, β-alumina, γ-alumina, δ-alumina, ε-alumina, κ-alumina, and ρalumina, aluminum trihydroxide, such as gibbsite, bayerite, nordstrandite, doyelite, and mixtures thereof.

It is desirable to provide a catalyst having a good crush strength. This is because in commercial use, it is desirable to prevent the catalyst from breaking down into powder-like materials. Such oxide binders have been employed normally only for the purpose of improving the crush strength of the catalyst.

The catalyst composition may be prepared, as indicated above, by any of the methods described in the art. Advantageously, however, the catalyst particles are combined with the binder material initially by dry-mixing, then in a liquid, preferably water, preferably with a plasticizer, to yield a paste.

As plasticizer (shaping additive), there may be mentioned one that will be decomposed during any subsequent heat treatment, e.g., calcination. Suitable materials for this purpose include, for example, alkylated cellulose derivatives, hydroxyethylcellulose (HEC), tylose, ammonium alginate, polyvinyl pyrrolidone, glycerol, and polyethylene glycol.

In addition to enhancing the catalyst strength properties, the binder material allows the molecular sieve crystallite powder to be bound into larger particle sizes suitable for commercial catalytic processes. The formulation of the mixture b) may be formed into a wide variety of shapes including extrudates, spheres, pills, and the like.

The uniformly mixed paste may subsequently be shaped, for example by spray drying to yield microspheres, pelletizing or, preferably, by extrusion.

The paste is then extruded, for example in a piston extruder, into strings, for example cylindrical, dried, again calcined, and chopped into pieces of a desired length.

As regards the proportions of the zeolite, the one or more binders and shaping additives, advantageously the proportion of the zeolite is from 5 to 95w% of the catalyst. The catalyst comprises the zeolite and at least a component selected among one or more binders and shaping additives. The amount of zeolite which is contained in the catalyst ranges more advantageously from 15 to 90 weight percent of the total catalyst, preferably 20 to 85 weight percent of the catalyst.

Once the molecular sieve catalyst composition is shaped, and in a substantially dry or dried state, a heat treatment, for example calcination, is advantageously performed to harden and/or activate the composition. Therefore the heat treatment is preferably carried out at a temperature of at least 400°C, for a period of from 1 to 48 hours. Calcination may be carried out, for example, in a rotary calciner, fluid bed calciner, or a batch oven.

As regards the Ion-exchange of step c), purpose is to get advantageously a formulated zeolitic molecular sieve with an inert binder, before subjecting in a contact with a phosphatation agent, having less than 1000 wppm of alkali & alkali-earth metals, Na, K, Fe as well as less than 200 ppm of red-ox & noble elements such as Zn, Cr, Rh, Mn, Ni, V, Mo, Co, Cu, Cd, Pt, Pd, Ir, Ru, Re. This may be achieved by an optional back ion-exchange step known per se.

In an embodiment, the catalyst comprises a molecular sieve has been treated to reduce alkali metal content to less than 100 ppm before or after the steaming step d).

Although in principle mixing with the binder and ion exchange may be carried out in any order, advantageously ion exchange is performed after shaping but before phosphorus introduction.

Advantageously, the ion exchange step is performed on shaped calcined catalyst before or after the steaming step d).

As regards the steaming of step d), it is also known as the pre-steaming by reference to the final steaming of step i). The treatment is performed in the range 420 to 870°C, more preferably in the range 480 to 800°C. The water partial pressure may range from 13 to 100 kPa. The steam atmosphere preferably contains from 5 to 100 vol % steam with from 0 to 95 vol % of a gas, preferably nitrogen or air. The steam treatment is preferably carried out for a period of from 0,01 to 200 hours, more preferably from 0,05 to 50 hours, still more preferably for at least 0.1 hour and in a preferred way from 0,1 to 50 hours and in a more preferred way from 0.5 to 50 hours and still more preferred 1 to 50 hours.

The steam treatment tends to reduce the amount of tetrahedral aluminium in the crystalline silicate framework by forming alumina. Preferably, the amount of residual tetrahedral Al in the zeolite is between 60 to 95%. This value can be estimated by ^{27}Al MAS NMR or TPD NH_3.

As regards the introduction of P of step e), said introduction of phosphorus can be performed under reduced or atmospheric pressure at temperature from 10 to 400°C. A non-limiting source of phosphorus can be provided in aqueous or non-aqueous medium.

In an embodiment, the non-aqueous medium is selected from the group containing ethanol, methanol or other alcohols.

The preferred techniques are impregnation and chemical vapour deposition. Said techniques are mandatory in the first embodiment of the invention.

These techniques imply a minimum waste to treat and allow maintaining substantially all phosphorus on the catalyst.

In an embodiment, the catalyst precursor is treated by a source of phosphorus injected into a steam flow. In this case, the phosphatation is performed under mild steaming condition with a steam flow containing phosphorus at 100-400°C.

In an embodiment, the phosphorus is introduced by a treatment of the catalyst precursor (zeolite + binder) in a solution contaning a source of phosphorus at temperature 25-100°C for 0.1-96h followed by filtering or evaporation.

In an embodiment amount of said acid solution containing P is advantageously between 2 and 10 liters per kg of zeolite plus binder. A typical period is around 0.5 to 24 hours. Advantageously the aqueous acid solution containing the source of P has a pH of 3, advantageously 2, or lower. Advantageously said aqueous acid solution is phosphorus acids, a mixture of phosphorus acids and organic or inorganic acid or mixtures of salts of phosphorus acids and organic or inorganic acids. The phosphorus acids or the corresponding salts can be of the phosphate ($[PO_4]^{3-}$, being tribasic), phosphite ($[HPO_3]^{2-}$, being dibasic), or hypophosphite ($[H_2PO_2]^{1-}$, being monobasic), type. Of the phosphate type also di or polyphosphates ($[P_nO_{3n+1}]^{(n+2)-}$) can be used. The contact of the zeolite+binder with the P containing component can be made under reflux conditions.

In a preferred embodiment the incipient wetness impregnation techniques is used. In this the phosphorus is introduced via impregnation using a limited amount of liquid water which is subjected to a contact with catalyst. This method is also known as the dry impregnation.

Incipient wetness (IW) or incipient wetness impregnation (IWI) is a commonly used technique for the synthesis of heterogeneous catalysts. Typically, the precursor (phosphorus-containing compounds) is dissolved in an aqueous or organic solution. The volume of solution, which is used for dissolution of the precursor, is substantially the same as the pore volume of catalyst precursor containing both binder and zeolite . Then the precursor-containing solution is added to a catalyst precursor.Capillary action draws the solution into the pores.

The catalyst can then be dried and calcined to drive off the volatile components within the solution, depositing the phosphorus on the catalyst surface.
The sample before impregnation can be dried or calcined. The impregnation could be performed at room or elevated temperature.

The adsorption capacity is typically measured by impregnating the dried extruded zeolite with water until the zeolite was completely wet. Weighing the zeolite before and after impregnation gives the absorption capacity:

$$Absorption\ capacity(\%) = \frac{weight\ after\ impregantion - dry\ weight}{dry\ weight} * 100$$

In an embodiment, H3PO4 solution is used for impregnation.

Advantageously, a mixture of H3PO4 with their ammonium salts providing a pH of the aqueous solution higher than 2.0 is used for impregnation

In an embodiment, the sources of phosphorus are substantially metal free components, for example H3PO4, ammonium phosphates or organic P-compounds. "substantially metal free" means a metal proportion with has no adverse effect on the P introduction. By way of example this proportion can be below 1000 wppm.

The amount of phosphorus on the catalyst can be from 0.5 to 30 wt%, but preferably from 0.5 to 9 w%.

In an embodiment, the phosphatation step is performed before or simultaneously with introduction of metal.

As regards step f), the introduction of metal, it can be one or more metals. Advantageously said metals are selected among alkaline earth or rare earth metals. The alkaline earth or rare earth metal M is preferably selected from one or more of: Mg, Ca, Sr, Ba, La, Ce. More preferably, M is an alkaline earth metal. Most preferably, M is Ca. Particularly in the case of P-modification via steaming and leaching, M can be a rare earth metal such as La and Ce. Advantageously the metal is introduced in a soluble form.

The M-containing component is preferably in the form of an organic compound, a salt, hydroxide or oxide. The compound is preferably in a solubilized form when bringing it into contact with the molecular sieve. Alternatively, the solution of the M-containing compound can be formed after bringing the molecular sieve in contact with said compound.

Possible M-containing compounds include compounds such as sulphate, formate, nitrate, acetate, halides, oxyhalides, oxalate, borates, carbonate, hydroxide, oxide and mixtures thereof. One can cite calcium carbonate.

Those M-containing compounds, which are poorly water-soluble, can be dissolved to form a well-solubilized solution by heating and/or by modifying the pH of the solution by addition of phosphoric, acetic or nitric acid or corresponding ammonium salts of said acids.

As regards step g), a washing step can be envisaged. In accordance with the present invention, the catalyst is treated with water for a period of time from 0.1 to 48 hours, preferably for a period of time from about 0.5 to 36 hours and most preferably from about 1 to 24 hours. The water was at a temperature between about 20°C and 180°C, preferably between about 20°C and 100°C and most preferably between about 25°C and 60°C. By way of example the water can be at 30°C. Following the water treatment, the catalyst may be dried at about >60° C. Optionally, the water can contain at least one dissolved solid selected from the group consisting of ammonium chloride, ammonium phosphate, ammonium sulfate, ammonium acetate, ammonium carbonate, ammonium nitrate and mixtures thereof.

As regards step h), said calcination can be made in air or an inert gas, typically at a temperature of from 350 to 900°C for a period of from 1 to 48 hours. Optionally the air or an inert gas may contain steam in concentration from 10 to 90 vol%.

As regards step i), in the first embodiment of the invention it can be performed in the range 420 to 870°C, preferably in the range 480 to 870°C , preferably from 625 to 870°C and more preferably from 700 to 800°C, still more preferably in the range 720 to 800°C. Alternatively it can be performed in the range 420 to 600°C, preferably 420 to 580°C.

In the second embodiment of the invention it is performed by steaming at steaming severity above about 2 or alternatively at temperature above 625°C, preferably from 625 to 870°C and more preferably from 700 to 800°C still more preferably in the range 720 to 800°C. The water partial pressure may range from 13 to 100 kPa. The steam atmosphere preferably contains from 5 to 100 vol % steam with from 0 to 95 vol % of a gas, preferably nitrogen or air. The steam treatment is preferably carried out for a period of from 0,01 to 200 hours, preferably from 0,05 to 50 hours, more preferably for at least 0.1 hour and in a preferred way from 0,1 to 50 hoursand in a more preferred way from 0.5 to 50 hours and still more preferred 1 to 50 hours.

One skilled in the art will also appreciate that the olefins made by the dehydration process of the present invention can be, by way of example, polymerized. When the olefin is ethylene it can be, by way of example,

polymerized to form polyethylenes,

dimerized to butene and then isomerised to isobutene, said isobutene reacting with ethanol to produce ETBE, dimerized to butane followed by reacting with ethylene via methatesis to produce propylene;

converted to propylene over metal, acid or bifunctional catalyst,used for alkylation of benzene to form ethyl -benzene,

dimerised to 1-butene, trimerised to 1-hexene or tetramerised to 1-octene, said alpha-olefins comonomers are further reacted with ethylene to produce polyethylene

dimerised to 1-butene, said 1-butene is isomerised to 2-butene and said 2-butene is further converted with ethylene by metathesis reaction into propylene and said propylene can be polymerised to polypropylene,

converted to ethylene oxide and glycol or

converted to vinyl chloride.

The present invention relates also to said polyethylenes, polypropylene, propylene, butene, hexane, octene, isobutene, ETBE, vinyl chloride, ethylene oxide and glycol.

[Examples]

EXAMPLE 1

A sample of zeolite ZSM-5 (Si/Al=12) in NH4-form (contained 250 ppm of Na & synthesized without template) was blended with a silica binder in a ratio 80:20 followed by addition of extrusion additives and shaping. A final Na content in the catalyst was 320 ppm.

The extruded sample was dried for 2h at 140°C, calcined for 2h at 600°C followed by steaming at 550°C for 6h in 100% steam.

Steamed solid was incipient wetness impregnated with an aqueous solution of phosphoric acid to introduce about 3wt% of phosphorus to the catalyst. The impregnated solid was dried for 16h at 110°C.

Then, the phosphated sample was incipient wetness impregnated with a solution of calcium nitrate obtained by dissolution of calcium carbonate to introduce about 1wt% of calcium to the solid. The impregnated solid was dried for 16h at 110°C.

Resulted catalyst containing 2.8wt% of phosphorus and 0.8 % of calcium was steamed at 600°C for 2h in 100% of steam (steaming severity 1). The sample is hereinafter identified as **sample A.**

Resulted catalyst containing about 2.8wt% of phosphorus and 0.8 % of calcium was steamed at 750°C for 1h in 100% of steam (steaming severity 45). The sample is hereinafter identified as **sample B.** Total pore volume measured by mercury intrusion porosimetry is 0.36 cm3/g.

Catalyst tests were performed on 1 ml of catalyst grains (35-45 meshes) loaded in a tubular reactor with internal diameter 11mm. A mixture 25wt%EthOH/75wt% H_2O was subjected to a contact with catalyst described in the example I in a fixed bed reactor at 380°C, WHSV = 7h^{-1} P=2 bara. The results are given in table 1 hereunder. The values are the weight percents on carbon basis.

Example 2

A sample of zeolite ZSM-5 (Si/Al=12) in NH4-form (containing 250 ppm of Na & synthesized without template) was blended with a silica binder in a ratio 80:20 followed by addition of extrusion additives and shaping. A final Na content in the catalyst was 320 ppm.

The extruded sample was dried for 16h at 110°C, calcined for 10h at 600°C followed by steaming at 550°C for 6h in 100% steam.

Steamed shaped zeolite was then contacted with an aqueous solution of H_3PO_4 (85%wt) under conditions of incipent wetness. Then 1 g of $CaCO_3$ was introduced.

After stirring during 30min, the system is cooled down at room temperature and the excess of solution is removed by filtration without washing. The recovered solid is dried at 110°C for 16h followed by steaming at 600°C for 2h in 100% of steam (steaming severity 1).

Resulted catalyst contained about 1.7wt% of phosphorus and 0.4wt% of calcium. The sample is hereinafter identified as <u>**sample C**</u>

The performances of the catalyst were then evaluated under the same operating conditions as described above, using 1 ml of catalyst (35-45 mesh) loaded in a tubular reactor with internal diameter 11mm. A mixture of 25wt%EtOH/75wt% H_2O has been processed on catalyst C, in a fixed bed reactor at 380°C, WHSV = 7h^{-1} P=2 bara. The results are given in table 1. The values are the weight percents on carbon basis.

EXAMPLE 3

A sample of zeolite ZSM-5 (Si/Al=12) in NH4-form (containing 250 ppm of Na & synthesized without template) was blended with a silica binder in a ratio 80:20 followed by addition of extrusion additives and shaping. A final Na content in the catalyst was 320 ppm.

The extruded sample was dried for 16h at 110°C, calcined for 10h at 600°C followed by steaming at 550°C for 6h in 100% steam.

12g of steamed solid was incipient wetness impregnated with an aqueous solution containing 1.54g of NH4H2PO4. The impregnated solid was dried for 16h at 110°C.

Then, the phosphated sample was incipient wetness impregnated with a solution of calcium nitrate obtained by dissolution of 0.3g calcium carbonate in nitric acid. The impregnated solid was dried for 16h at 110oC followed by steaming at 600°C for 2h in 100% of steam (steaming severity 1).

Resulted catalyst contained about 2.54wt% of phosphorus and 0.82wt% of calcium. The sample is hereinafter identified as **sample D.**

The performances of the catalyst were then evaluated under the same operating conditions as described above, using 1 ml of catalyst (35-45 mesh) loaded in a tubular reactor with internal diameter 11mm. A mixture of 25wt%EtOH/75wt% H_2O has been processed on catalyst D, in a fixed bed reactor at 380°C, WHSV = $7h^{-1}$ P=2 bara. The results are given in table 1. The values are the weight percents on carbon basis.

Table 1

Sample	A	B	C	D
P (bara)	2	2	2	2
T (°C)	380	380	380	380
WHSV (H-1)	7	7	7	7
EtOH conversion (% wt CH2)	99.9	99.8	99.9	99.9
DEE	0.0	0.0	0.0	0.0
Acetaldyde	0.31	0.17	0.17	0.13
EtOH	0.10	0.20	0.05	0.05
Yield on C-basis (%wt CH2)				
CH4	0.00	0.00	0.00	0.00
C2	0.13	0.06	0.11	0.12
C2=	97.9	99.0	97.3	97.4
C3=	0.56	0.07	0.7	0.8
C4+ olef	0.86	0.48	1.6	1.4
Unknown	0.10	0.06	0.07	0.08
Selectivity on C-basis (%wt CH2)				
C2=	98.0	99.20	97.4	97.4
C2's cut purity (%)	99.87	99.94	99.88	99.87

CLAIMS

1 Use of a catalyst to convert at least an alcohol into light olefins in a dehydration process to make an olefin having the same number of carbon atoms as the alcohol wherein said catalyst comprises a phosphorus modified zeolite and is made by a method comprising the following steps in this order,

a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite,

b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture,

c) optionally making a ion-exchange,

d) optionally steaming the shaped catalyst, optionally before step c), at least among said steaming of step d) and the steaming of step a) one is mandatory,

e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus, said introduction being made by dry impregnation or chemical vapor deposition,

f) optionally introducing a metal, optionally simultaneously with step e),

g) optionally washing the catalyst,

h) optionally calcinating the catalyst,

i) steaming the catalyst, also referred to as the equilibration step.

2 Use according to claim 1 wherein the phosphorus introduction of step e) is made by incipient wetness (IW) or incipient wetness impregnation (IWI).

3 Use according to claim 1 or 2 wherein the steaming of step i) is performed in the range 420 to 870°C.

4 Use according to claim 3 wherein the steaming of step i) is performed in the range 480 to 870°C.

5 Use according to claim 4 wherein the steaming of step i) is performed in the range 625 to 870°C.

6 Use according to claim 5 wherein the steaming of step i) is performed in the range 700 to 800°C.

7 Use according to claim 6 wherein the steaming of step i) is performed in the range 720 to 800°C.

8 Use according to claim 3 wherein the steaming of step i) is performed in the range 420 to 600°C.

9 Use according to claim 8 wherein the steaming of step i) is performed in the range 420 to 580°C.

10 Use of a catalyst to convert at least an alcohol into light olefins in a dehydration process to make an olefin having the same number of carbon atoms as the alcohol wherein said catalyst comprises a phosphorus modified zeolite and is made by a method comprising the following steps in this order,

a) providing a zeolite comprising at least one ten members ring in the structure, optionally steaming said zeolite,

b) mixing said zeolite of step a) with at least a component selected among one or more binders and shaping additives, then shaping said mixture,

c) optionally making a ion-exchange,

d) optionally steaming the shaped catalyst, optionally before step c), at least among said steaming of step d) and the steaming of step a) one is mandatory,

e) introducing phosphorus on the catalyst to introduce at least 0.1 wt% of phosphorus,

f) optionally introducing a metal, optionally simultaneously with step e),

g) optionally washing the catalyst,

h) optionally calcinating the catalyst,

i) steaming the catalyst, also referred to as the equilibration step, at a steaming severity (X) of at least about 2.

11 Use according to claim 10 wherein the steaming of step i) is performed in the range 625 to 870°C.

12 Use according to claim 11 wherein the steaming of step i) is performed in the range 700 to 800°C.

13 Use according to claim 12 wherein the steaming of step i) is performed in the range 720 to 800°C.

14 Use according to any one of the preceding claims wherein the shaped zeolite (or molecular sieve) of step b) contains less than 100 wppm of sodium.

15 Use according to claim 14 wherein the shaped zeolite (or molecular sieve) of step b) contains less than 100 wppm of sodium, less than 100 wppm of potassium and less than 500 wppm of iron.

16 Use according to any one of the preceding claims wherein the alcohol is selected among ethanol, propanol, butanol and phenylethanol.

17 Use according to any one of the preceding claims wherein the zeolite is selected from the MFI, MTT, FER, MEL, TON, MWW, EUO, MFS.

18 Use according to claim 17 wherein the zeolite is ZSM-5 with Si/Al atomic ratio ranging from 11 to 30, which has been made without direct addition of organic template.

19 Use according to claim 17 wherein the zeolite is MFI with Si/Al atomic ratio ranging from 30 to 200.

20 Use according to any one of the preceding claims wherein at step e) the amount of phosphorus on the catalyst is from 0.5 to 30 wt%.

21 Use according to claim 20 wherein the amount of phosphorus on the catalyst is from 0.5 to 9 w%.

22 Use according to any one of the preceding claims wherein at step f) the metal is an alkaline earth or rare earth metal M preferably selected from one or more of: Mg, Ca, Sr, Ba, La, Ce.

23 Use according to any one of the preceding claims wherein the catalyst, zeolite+binder, has a volume of the pores between 30 Å and 1000 Å of at least 0.25 cc/g.