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(54) **Title:** PROCESS FOR THE OXYGEN FREE CONVERSION OF METHANE TO ETHYLENE ON ZEOLITE CATALYSTS

(57) **Abstract:** The present invention relates to a process for the oxygen free conversion of methane to ethylene on zeolite catalysts and catalysts comprising a small-pore zeolite, a metal and a further component.

Process for the oxygen free conversion of methane to ethylene on zeolite catalysts

Description

- 5 The present invention relates to a process for the oxygen free conversion of methane to ethylene on zeolite catalysts and catalysts comprising a small-pore zeolite, a metal and a further component.

10 Methane, as the key component of natural gas, landfill gas and a by-product from oil refining and chemical, can be utilized as clean fossil energy or as hydrocarbon source for platform molecules in the chemical industry. In 2009, the known reserves were estimated with 180 trillion cubic meters, which is comparable of that to known crude oil reserves. Especially the decreasing methane price in the US has stimulated research efforts in the last years, dealing with oxidative coupling, oxyhalogenation, aromatization and selective oxidation to methanol. However, the
15 high stability of the C-H bonds remains a major issue to provide economically feasible processes, which can compete with state of the art technology based on crude oil.

In order to convert CH₄ into other economically valuable products a number of reactions are known. One is the reaction of methane to benzene (MTB), see e.g. WO 2009/124870 and WO
20 2009/141366. The use of zeolites for MTB is known. Exemplarily, J. Am. Chem. Soc. 130 (2008) 3722 is cited.

Another possible reaction to integrate CH₄ in the value chains of chemical industries is the conversion of methane to ethylene (MTE). Currently, the oxidative coupling of methane (OCM) is
25 the state of the art technology in this area. It involves the reaction of CH₄ and O₂ over a heterogeneous catalyst at temperatures >650°C to form C₂H₆ and C₂H₄ with H₂O, CO₂ and H₂ as by-products. In recent literature reports, various mixed metal oxide species such as La/CaO, Mn/Na₂WO₄/SiO₂ or Li/MgO are discussed.

30 Scientific articles describing the OCM include Catalysis Today 171 (2011) 15-23; Journal of Natural Gas Chemistry 19 (2010) 25-30; Fuel Processing Technology 90(2009) 403-410; and Chemical Engineering Journal 116 (2006) 187-195.

A direct conversion of methane to ethene over Mo/SAPO-34 catalysts has been published in
35 Chinese Journal of Catalysis (Cuihua Xuebao) 16 (1995) 3-4. However, the activity of the catalysts and, thus, the yields of ethene are extremely low.

In spite of the work existing on OCM, this technology has not yet been commercialized because there are several disadvantages connected to this process. One disadvantage is that since C₂
40 hydrocarbons are much more reactive than methane, high selectivity in the process can be obtained only at low methane conversion. Another disadvantage is that as the reaction is conducted at high temperatures, a catalyst with high thermal and hydrothermal stability is required.

The term "thermal stability" describes that no or only few degradation of a zeolite takes place under exposition to high temperatures.

5 The term "hydrothermal stability" describes that no or only few degradation of a zeolite takes place under exposition to high temperatures in combination with the presence of water.

10 A further disadvantage is that using a low O_2/CH_4 molar ratio in the feed, the selectivity to C_2 hydrocarbons is high, but CH_4 conversion is rather low. An additional disadvantage is that due to the low concentration of ethylene in the exit stream the cost of its separation is high, thereby rendering its separation uneconomical.

15 It was the problem of the present invention to provide a process that does not exhibit the disadvantages presented above or only to a minor extent when compared to a process of the state of the art.

The problem has been solved by providing a process comprising the step of converting methane to ethene under non-oxidative conditions in the presence of a catalyst comprising
(a) a small-pore zeolite;
(b) a metal
20 whereas the metal (b) is loaded onto the small-pore zeolite (a).

The conversion of methane to ethylene under non-oxidative conditions is depicted in Reaction 1:

25 Catalytic reaction: $2 CH_4 \rightarrow C_2H_4 + 2 H_2$ (Reaction 1)

30 According to the present invention, "nonoxidative" means, in relation to the MTE reaction, that the concentration of oxidizing agents such as oxygen or nitrogen oxides in the reactant stream E is below 5% by weight, preferably below 1% by weight, more preferably below 0.1% by weight. Most preferably, the mixture is free of oxygen. Likewise particularly preferred is a concentration of oxidizing agents in the mixture E which is equal to or less than the concentration of oxidizing agents in the source from which the methane originates.

35 In relation to the regeneration, which is described later, "nonoxidative" in the context of the present invention means that the coke deposits originating from the MTE on the catalyst, to regenerate the catalyst, are not converted to CO and/or CO_2 by means of oxidizing agents such as air or oxygen. In particular, the concentration of oxidizing agents in the mixture H for use for regeneration in step II is below 5% by weight, preferably below 1% by weight, more preferably below 0.1% by weight.

40 Since there is practically no H_2O formed during reaction, zeolite based catalysts are applicable at this high temperatures. They combine a high surface area with defined pore structures and well adjustable acidic centers, which can be used to improve the ethylene yield in the product

stream. To suppress the deactivation of the catalyst due to coke formation, zeolite based catalysts can be regenerated with H₂ formed in Reaction 1 to recover CH₄, which can then be re-used in the educt stream during catalytic reaction.

5 Regeneration of the catalyst: C (coke) + 2 H₂ → CH₄ (Reaction 2)

By means of this approach unwanted oxidation of hydrocarbons, which is one reason for the low efficiency of OCM based processes, can be excluded during the whole process.

10 The term "zeolite" shall have the following meaning within the frame of the present invention: a zeolite comprising, preferred consisting essentially of, both tetravalent and trivalent structural components Y and X as YO₂ and X₂O₃, respectively, wherein Y is a tetravalent element, and X is a trivalent element; and wherein the Y : X molar ratios of the zeolite is respectively comprised in the range of from 1 to 50, preferably of from 1.5 to 35, more preferably of from 2 to 25, more
15 preferably of from 2.5 to 15, more preferably of from 3 to 10, more preferably of from 3.5 to 7, more preferably of from 4 to 6, and even more preferably in the range of from 4 to 5.

In particular, the zeolite does not comprise pentavalent structural components Z as Z₂O₅ wherein Z is a pentavalent element.

20 Within the meaning of the present invention, YO₂ and optionally X₂O₃ comprised in the zeolite framework structure of the zeolite are contained therein as structure building elements, as opposed to non-framework elements which can be present in the pores and cavities formed by the framework structure and typical for zeolites in general.

25 According to the present invention, there is no particular restriction as to the number and/or types of zeolites, provided that they have a small-ring framework structure and comprise YO₂ and X₂O₃. Thus, by way of example, a zeolite may comprise a chemical composition which is selected from the group consisting of [Al-Si-O]-, [B-Si-O]-, [Ga-Si-O]-, [Ti-Si-O]-, Al-rich and pure
30 silica.

Furthermore, according to the present invention, Y comprised in a zeolite stands for any conceivable tetravalent element, wherein Y is one or more tetravalent elements. Preferred tetravalent elements according to the present invention include Si, Sn, Ti, Zr, and Ge, and combinations thereof. More preferably, Y stands for Si, Ti, or Zr, or any combination of said trivalent elements, even more preferably for Si and/or Sn. According to the present invention, it is particularly preferred that Y stands for Si.

40 According to the present invention, the framework of a zeolite comprises X₂O₃, wherein X stands for any conceivable trivalent element, X being one or more trivalent elements. Preferred trivalent elements according to the present invention include Al, B, In, and Ga, and combinations thereof. More preferably, Y stands for Al, B, or In, or any combination of said trivalent ele-

ments, even more preferably for Al and/or B. According to the present invention, it is particularly preferred that X stands for Al.

5 There is no particular restriction according to the present invention as to the combinations of YO_2 and X_2O_3 which are comprised in a zeolite. Thus, in principle, any conceivable combination of one or more tetravalent elements Y in YO_2 may be comprised in one or more of the zeolites in combination with one or more trivalent elements X in X_2O_3 , wherein the aforementioned elements Y and X respectively refer to constitutive elements of the small-pore framework structure. According to particularly preferred embodiments, however, the one or more tetravalent elements Y comprise Si, and the one or more trivalent elements X comprise Al, wherein even more
10 preferably the one or more of the one or more zeolites comprise SiO_2 and Al_2O_3 .

As concerns the proportions of YO_2 to X_2O_3 which may be comprised in a zeolite, in terms of the corresponding Y : X molar ratios, a zeolite generally displays molar ratios ranging anywhere
15 from 1 to 50. Preferably, the Y : X molar ratio of the tetravalent element Y to the trivalent element X ranges from 1.5 to 35, more preferably of from 2 to 25, more preferably of from 2.5 to 15, more preferably of from 3 to 10, more preferably of from 3.5 to 7, and even more preferably of from 4 to 6. According to particularly preferred embodiments of the present invention, the Y : X molar ratio ranges from 4 to 5. Thus, according to particularly preferred embodiments of
20 the present invention wherein a zeolite comprise SiO_2 and Al_2O_3 , it is yet further preferred that the Si : Al molar ratio displayed by the framework structure is comprised in the range of from 1 to 50, preferably of from 1.5 to 35, more preferably of from 2 to 25, more preferably of from 2.5 to 15, more preferably of from 3 to 10, more preferably of from 3.5 to 7, more preferably of from 4 to 6, and even more preferably in the range of from 4 to 5.

25 Small-pore zeolites

Zeolites are divided into categories depending on the largest pore opening in their structures.

Small pore: the largest pore opening is an 8-ring pore.

Medium pore: the largest pore opening is a 10-ring pore.

30 Large pore: the largest pore opening is a 12-ring pore or a larger pore.

A zeolite (a) according to the present invention is a small-pore zeolite. In one embodiment the small-pore molecular zeolite (a) is selected from the Framework Type Codes consisting of:
35 ACO, AEI, AEN, AFN, AFT, AFX, ANA, APC, APD, ATT, CDO, CHA, DDR, DFT, EAB, EDI, EPI, ERI, GIS, GOO, IHW, ITE, ITW, LEV, KFI, MER, MON, NSI, OWE, PAU, PHI, RHO, RTH, SAT, SAV, SFW, SIV, SVV, THO, TSC, UEI, UFI, VNI, YUG, and ZON.

In a preferred embodiment, the small-pore zeolite (a) is selected from the structural group consisting of LEV, CHA, CDO and mixtures thereof.

40 In a further preferred embodiment, the small-pore zeolite (a) is selected from the group consisting of RUB-37, RUB-50, LEV and mixtures thereof.

Table 1:

a) small-pore materials

Material	RUB-37	RUB-50	LEV	SAPO-34	CHA
	zeolite	zeolite	zeolite	zeolite-analogous	zeolite
Framework Type (+)	CDO	LEV	LEV	CHA	CHA
Max. diameter of a sphere that can be included [Å] (+)	5.8	7.1	7.1	7.37	7.37
Max. diameter of a sphere that can diffuse along a/b/c [Å] (+)	3.44 / 1.52 / 3.35	3.53 / 3.53 / 2.5	3.53 / 3.53 / 2.5	3.72 / 3.72 / 3.72	3.72 / 3.72 / 3.72
Ring sizes (# T-atoms) (+)	8 5	8 6 4	8 6 4	8 6 4	8 6 4
Building blocks (+)	fer	D6R	D6R	D6R cha	D6R cha

(+) according to the IZA database

5 b) medium- pore materials and large-pore materials

Material	BETA	ZSM-5
	zeolite	zeolite
Framework Type (+)	*BEA	MFI
Max. diameter of a sphere that can be included [Å] (+)	6.68	6.36
Max. diameter of a sphere that can diffuse along a/b/c (+)	5.95 / 5.95 / 5.95	4.7 / 4.46 / 4.46
Ring sizes (# T-atoms) (+)	12 6 5 4	10 6 5 4
Building blocks (+)	Mor bea mtw	Mor cas mel mfi

(+) according to the IZA database

10 According to the invention, at least one small-pore zeolite (a) is loaded with at least one metal (b). It is preferred that the metal (b) is selected from the group consisting of Mo, Fe, Co, Ni, Cu, Ag, Mg, W, Re, Ga, Ru, Rh, Pd, Ir, Pt and mixtures thereof, preferred Mo.

According to the invention, the loading of the at least one metal is performed by wet chemical or dry chemical means.

15 In wet chemical methods, the metals are applied in the form of aqueous, organic or organic-aqueous solutions of their salts or complexes by impregnating the support with the corresponding solution. The solvent used may also be supercritical CO₂. The impregnation can be effected

by the incipient wetness method, in which the porous volume of the support is filled by about the same volume of impregnation solution and - if appropriate after maturation - the support is dried. It is also possible to work with an excess of solution, in which case the volume of this solution is greater than the porous volume of the support. In this case, the support is mixed with the im-
5 pregnation solution and stirred for a sufficiently long period. In addition, it is possible to spray the support with a solution of the appropriate metal compound. Other preparation methods known to those skilled in the art are also possible, such as precipitation of the metal compounds onto the support, spray application of a solution comprising metal compound, sol impregnation, etc. After the application of the at least one metal to the support, the catalyst is dried at from
10 about 80 to 130°C under reduced pressure or under air, typically for from 4 to 20 hours.

According to the invention, the at least one metal can also be applied by dry chemical methods, for example by depositing the metal carbonyls which are gaseous at higher temperatures, such as $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$ and $\text{Re}_2(\text{CO})_{10}$, on the support from the gas phase. The deposition of the
15 metal carbonyl compound is performed after the calcination of the support.

The metal can be applied by wet chemical means together in one solution, or in different solu-
20 tions in succession with drying steps between the individual applications. The metal can also be applied in mixed form, i.e. one portion by wet chemical means and another portion by dry chem- ical means. Between the applications of the metal compounds, calcination can be effected if required according to the above description.

Preferred is a process wherein the amount of metal (b) is higher than 4 wt%, preferred 5 wt% or more, more preferred 6 wt% or more, based on the total weight of the catalyst.

25

Further component (c)

In a preferred embodiment of the inventive process the catalyst further comprises

- (c) a further component selected from the group consisting of
30 (c1) at least one further small-pore zeolite different from (a);
 (c2) at least one small-pore zeolite analogous material;
 (c3) at least one further metal different from (b); and
 mixtures thereof,

35

whereas the metal (b) and -if applicable- the at least one further metal (c3) is/are loaded onto

- the small-pore zeolite (a) and/or
- -if applicable- the at least one further small-pore zeolite (c1) and/or
- -if applicable- the at least one small-pore zeolite analogous material (c2).

40

In a more preferred embodiment of the inventive process the catalyst comprises

- a small-pore zeolite (a) and at least one small-pore zeolite (c1); and
- at least one metal (b) which is loaded onto at least one of the small-pore zeolites (a) and (c1).

In another more preferred embodiment of the inventive process the catalyst comprises

- a small-pore zeolite (a);
- at least one small-pore zeolite analogous material (c2);
- at least one metal (b) which is loaded onto a small-pore zeolite (a) and/or at least one small-pore zeolite analogous material (c2).

5

In a preferred embodiment of the process, the small-pore zeolite (a) is selected from the structural group consisting of LEV, CHA, CDO and mixtures thereof.

10 In a further preferred embodiment of the process, the small-pore zeolite (a) is selected from the group consisting of RUB-37, RUB-50, LEV and mixtures thereof.

In a further preferred embodiment of the process, the metal (b) is selected from the group consisting of Mo, Fe, Co, Ni, Cu, Ag, Mg, W, Re, Ga, Ru, Rh, Pd, Ir, Pt and mixtures thereof, preferred Mo.

15

In a further preferred embodiment of the process, the amount of metal (b) is higher than 4 wt%, preferred 5 wt% or more, more preferred 6 wt% or more, based on the total weight of the catalyst.

20

In a more preferred process the catalyst comprises at least two different metals (b) and (c3) which are selected from the group consisting of Mo, Fe, Co, Ni, Cu, Ag, Mg, W, Re, Ga, Ru, Rh, Pd, Ir, Pt and mixtures thereof, preferred Fe, Co, Ni, Cu and mixtures thereof, more preferred Mo-Fe, Mo-Co and Mo-Ni.

25

According to the invention, the catalyst may comprise a metal (b) in conjunction with at least one metal (c3). In this case, the at least one metal (c3) is present in the catalyst, according to the invention, in a concentration of at least 0.1% by weight, preferably at least 0.2% by weight, most preferably at least 0.5% by weight, based on the total weight of the catalyst.

30

In principle, there is no general restriction as to how the zeolite is obtained, provided that they respectively have small-pore framework structure comprising YO_2 and X_2O_3 and that they display Y : X molar ratios comprised within the ranges and preferred ranges outlined in the foregoing. According to preferred embodiments, the zeolite is provided from synthesis as opposed to being obtained from natural sources, wherein it is further preferred that the zeolite is obtainable from an organotemplate-free synthetic process. According to particularly preferred embodiments of the present invention, the zeolite is obtained from an organotemplate-free synthetic process.

35

40 Therefore, according to preferred embodiments, the zeolite is obtainable, and preferably obtained, from an organotemplate-free synthetic process.

As regards the preferred embodiments wherein the zeolite is obtainable, and preferably obtained, from an organotemplate-free synthetic process, there is no particular restriction as to the synthetic procedure which may be used to this effect, provided that it does not employ an organotemplate as structure directing agent.

5

According to particularly preferred embodiments of the present invention, the zeolite is obtainable, and preferably obtained, according to a synthetic process for the organotemplate-free synthesis of a zeolite having a small-pore framework structure, wherein said synthetic process comprises the steps of

- 10 (1) preparing a mixture comprising seed crystals and one or more sources for YO_2 ; and
(2) crystallizing the mixture;

wherein when the small-pore framework preferably comprises X_2O_3 , the mixture according to step (1) further comprises one or more sources for X_2O_3 .

15 According to said preferred synthesis for providing the zeolite, at no point does the mixture provided in step (1) and crystallized in step (2) contain more than an impurity of an organic structure directing agent specifically used in the synthesis of the one or more zeolites having a small-pore framework structure, in particular specific tetraacylammonium salts and/or related organotemplates such as tetraethylammonium and/or dibenzylmethylammonium salts, and
20 dibenzyl-1,4-diazabicyclo[2,2,2]octane. Such an impurity can, for example, be caused by organic structure directing agents still present in seed crystals used in the preferred synthesis. Organotemplates contained in seed crystal material may not, however, participate in the crystallization process since they are trapped within the seed crystal framework and therefore may not act structure directing agents within the meaning of the present invention.

25

According to the present invention, a zeolite having a small-pore framework structure is crystallized in step (2) of the preferred synthetic method. For this purpose, YO_2 can be provided in step (1) in any conceivable form, provided that a zeolite having a small-pore framework structure comprising YO_2 can be crystallized in step (2). Preferably, YO_2 is provided as such and/or as a
30 compound which comprises YO_2 as a chemical moiety and/or as a compound which (partly or entirely) is chemically transformed to YO_2 during the inventive process. In preferred embodiments of the present invention, wherein Y stands for Si or for a combination of Si with one or more further tetravalent elements, the source for SiO_2 provided in step (1) can be any conceivable source. There can therefore be used, for example, all types of silica and silicates, preferably
35 fumed silica, silica hydrosols, reactive amorphous solid silicas, silica gel, silicic acid, water glass, sodium metasilicate hydrate, sesquisilicate or disilicate, colloidal silica, pyrogenic silica, silicic acid esters, or tetraalkoxysilanes, or mixtures of at least two of these compounds.

According to preferred embodiments of the preferred synthetic method, wherein the mixture
40 according to step (1) comprises one or more sources for SiO_2 , said source preferably comprises one or more compounds selected from the group consisting of silica and silicates, preferably alkali metal silicates. Among the preferred alkali metal silicates, the one or more sources preferably comprise water glass, more preferably sodium and/or potassium silicate, and more pref-

erably sodium silicate. In particularly preferred embodiments of the present invention, the source for SiO_2 is sodium silicate. Furthermore, in further preferred embodiments comprising silica, fumed silica is particularly preferred.

- 5 According to preferred embodiments of the present invention, wherein the zeolite having a small-pore framework structure comprise X_2O_3 , one or more sources for X_2O_3 are provided in step (1) of the preferred synthetic method. In general, X_2O_3 can be provided in any conceivable form, provided that a zeolite having a small-pore framework structure comprising X_2O_3 can be crystallized in step (2). Preferably, X_2O_3 is provided as such and/or as a compound which comprises X_2O_3 as a chemical moiety and/or as a compound which (partly or entirely) is chemically transformed to X_2O_3 during the inventive process.

15 According to preferred embodiments of the preferred synthetic method, wherein X stands for Al or for a combination of Al with one or more further trivalent elements, the source for Al_2O_3 provided in step (1) can be any conceivable source. There can be used for example any type of alumina and aluminates, aluminum salts such as, for example, alkali metal aluminates, aluminum alcoholates, such as, for example, aluminum triisopropylate, or hydrated alumina such as, for example, alumina trihydrate, or mixtures thereof. Preferably, the source for Al_2O_3 comprises one or more compounds selected from the group consisting of alumina and aluminates, preferably aluminates, more preferably alkali metal aluminates. Among the preferred alkali metal aluminates, the one or more sources preferably comprises sodium and/or potassium aluminate, more preferably sodium aluminate. In particularly preferred embodiments of the preferred synthetic method, the source for Al_2O_3 is sodium aluminate.

- 25 In cases wherein the mixture of step (1) further comprises one or more sources for X_2O_3 including one or more boron compounds, for example free boric acid and/or borates and/or boric esters, such as, for example, triethyl borate or trimethyl borate, can be used as starting materials.

30 According to particularly preferred embodiments of the preferred synthetic method, the mixture according to step (1) comprises one or more silicates as a source for YO_2 and one or more aluminates as a source for X_2O_3 , more preferably one or more alkali metal silicates and/or one or more alkali metal aluminates, and even more preferably one or more water glass compounds and/or one or more alkali metal aluminates, wherein the alkali metal of said preferred embodiments preferably comprises sodium and/or potassium, more preferably sodium, and wherein the alkali metal even more preferably is sodium.

40 According to further embodiments of the preferred synthetic method which are particularly preferred, the mixture according to step (1) comprises silica and one or more silicates as a source for YO_2 and one or more aluminates as a source for X_2O_3 , more preferably fumed silica and one or more alkali metal silicates and/or one or more alkali metal aluminates, and even more preferably silica and one or more water glass compounds and/or one or more alkali metal aluminates, wherein the alkali metal of said preferred embodiments preferably comprises sodium and/or

potassium, more preferably sodium, and wherein the alkali metal even more preferably is sodium.

5 In preferred embodiments of the preferred synthetic method wherein the mixture according to step (1) comprises one or more sources for X_2O_3 , the $YO_2 : X_2O_3$ molar ratio of the mixture can have any conceivable value, provided that a zeolite having a small-pore framework structure comprising both YO_2 and X_2O_3 is crystallized in step (2). Generally, the molar ratio ranges from 1 to 100, preferably from 5 to 75, more preferably from 10 to 50, more preferably from 15 to 40, more preferably from 18 to 35, and particularly preferably from 20 to 33.

10 In embodiments of the preferred synthetic method which are further preferred, the zeolite obtained and/or obtainable and/or the inventive material as such according to the preferred synthetic method comprises one or more alkali metals M, preferably sodium and/or potassium, and more preferably sodium. The alkali metal can be added at any conceivable stage of the preferred synthetic method, wherein preferably it is also added in step (1). More preferably, the entire quantity of the alkali metal comprised in the zeolite having a small-pore framework structure is added in step (1) of the preferred synthetic method. In particularly preferred embodiments of the preferred synthetic method, the alkali metal is partly or entirely contained in the one or more sources for YO_2 and/or X_2O_3 provided in step (1), wherein preferably, the alkali metal is entirely contained in the one or more sources for YO_2 and/or X_2O_3 , and more preferably in both the one or more sources for YO_2 and/or X_2O_3 .

15 In general, the alkali metal M can be contained in the mixture according to step (1) of the preferred synthetic method in any conceivable amount, provided that a zeolite having a small-pore framework structure is crystallized in step (2). Preferably, the M : YO_2 molar ratio in the mixture according to step (1) ranges from 0.1 to 2, more preferably from 0.2 to 1.2, more preferably from 0.3 to 1, more preferably from 0.4 to 0.85, more preferably from 0.5 to 0.75, and more preferably from 0.55 to 0.7. According to particularly preferred embodiments of the preferred synthetic method, the M : YO_2 molar ratio in the mixture according to step (1) ranges from 0.61 to 0.65.

20 According to preferred embodiments of the preferred synthetic method, the mixture according to step (1) comprises one or more sources for X_2O_3 and one or more alkali metals M. In general, any conceivable amounts of these components can be contained in the mixture provided that a zeolite having a small-pore framework structure is crystallized in step (2). Preferably, the $YO_2 : X_2O_3 : M$ molar ratios in the mixture according to step (1) range from (1 - 100) : 1 : (2 - 90), more preferably from (5 - 75) : 1 : (4 - 60), more preferably from (10 - 50) : 1 : (6 - 40), more preferably from (15 - 40) : 1 : (8 - 30), more preferably from (18 - 35) : 1 : (10 - 25), and even more preferably from (20 - 33) : 1 : (12 - 22).

30 According to further preferred embodiments of the preferred synthetic method, seed crystals are provided in step (1), wherein said seed crystals comprise a zeolite having a small-pore framework structure. In general, said seed crystals can comprise any zeolite having a small-pore framework structure, provided that a zeolite having a small-pore framework structure is crystal-

lized in step (2). Preferably, the zeolite having a small-pore framework structure comprised in the seed crystals is a zeolite which is obtainable and preferably obtained according to the preferred synthetic method. More preferably, the zeolite having a small-pore framework structure comprised in the seed crystals is the same as the zeolite having a small-pore framework structure which is then crystallized in step (2). Particularly preferred are seed crystals comprising zeolite Beta, more preferably zeolite Beta which is obtainable or has preferably been obtained according to the preferred synthetic method. In particularly preferred embodiments, the seed crystals are zeolite Beta crystals, preferably zeolite Beta crystals which are obtainable or have preferably been obtained according to the preferred synthetic method.

According to the preferred synthetic method, any suitable amount of seed crystals can be provided in the mixture according to step (1), provided that a zeolite having a small-pore framework structure is crystallized in step (2). In general, the amount of seed crystals contained in the mixture according to step (1) ranges from 0.1 to 50 wt.-% based on 100 wt.-% of YO_2 in the one or more sources for YO_2 , preferably from 0.5 to 35 wt.-%, more preferably from 1 to 20 wt.-%, more preferably from 1.5 to 10 wt.-%, more preferably from 2 to 5 wt.-%, and even more preferably from 2.5 to 3.5 wt.-%.

In step (1) according to the preferred synthetic method, the mixture can be prepared by any conceivable means, wherein mixing by agitation is preferred, preferably by means of stirring.

In preferred embodiments of the preferred synthetic method, the mixture according to step (1) further comprises a solvent. Any conceivable solvent can be used in any conceivable amount, provided that a zeolite having a small-pore framework structure can be crystallized in step (2) of the preferred synthetic method. Preferably, the solvent comprises water, wherein the $H_2O : YO_2$ molar ratio of the mixture ranges from 1 to 100, preferably from 5 to 70, more preferably from 10 to 50, more preferably from 12 to 35, more preferably from 15 to 25, more preferably from 16 to 20, and particularly preferably from 17 to 18. In particularly preferred embodiments, the solvent provided in step (1) is distilled water.

In general, the single components for providing the mixture of step (1) of the preferred synthetic method can be added in any order, provided that a zeolite having a small-pore framework structure is crystallized from the mixture in step (2) of the preferred synthetic method. This may, for example, involve the addition of the optional solvent and the one or more sources for X_2O_3 followed by the addition of the one or more sources for YO_2 , wherein the seed crystals are only added to the mixture afterwards. Alternatively, the addition of the optional solvent and the one or more sources for X_2O_3 may be first followed by the addition of the seed crystals, wherein the one or more sources for YO_2 is only added thereafter.

In general, step (2) according to the preferred synthetic method can be conducted in any conceivable manner, provided that a zeolite having a small-pore framework structure is crystallized from the mixture according to step (1). The mixture can be crystallized in any type of vessel,

wherein a means of agitation is optionally employed, said agitation being preferably achieved by rotation of the vessel and/or stirring, and more preferably by stirring the mixture.

5 According to the preferred synthetic method, the mixture is preferably heated during at least a portion of the crystallization process in step (2). In general, the mixture can be heated to any conceivable temperature of crystallization, provided that a zeolite having a small-pore frame-
work structure is crystallized from the mixture. Preferably, the mixture is heated to a tempera-
10 ture of crystallization ranging from 80 to 200°C, more preferably from 90 to 175°C, more prefer-
ably from 95 to 150°C, more preferably from 100 to 140°C, more preferably from 110 to 130°C,
and even more preferably from 115 to 125°C.

The preferred heating in step (2) of the preferred synthetic method can be conducted in any
conceivable manner suitable for the crystallization of a zeolite having a small-pore framework
structure. In general, heating may be conducted at one temperature of crystallization or vary
15 between different temperatures. Preferably, a heat ramp is used for reaching the temperature of
crystallization, wherein, by way of example, the heating rate may range from 10 to 100°C/h,
more preferably from 15 to 70°C/h, more preferably from 20 to 50°C/h, more preferably from 25
to 40°C/h, and even more preferably from 30 to 35°C/h.

20 In preferred embodiments of the preferred synthetic method, the mixture according to step (1) is
subjected in step (2) to a pressure which is elevated with regard to normal pressure. The term
"normal pressure" as used in the context of the present invention relates to a pressure of
101,325 Pa in the ideal case. However, this pressure may vary within boundaries known to the
person skilled in the art. By way of example, this pressure can be in the range of from 95,000 to
25 106,000 or of from 96,000 to 105,000 or of from 97,000 to 104,000 or of from 98,000 to 103,000
or of from 99,000 to 102,000 Pa.

In preferred embodiments of the preferred synthetic method wherein a solvent is present in the
mixture according to step (1), it is furthermore preferred that heating in step (2) is conducted
30 under solvothermal conditions, meaning that the mixture is crystallized under autogenous pres-
sure of the solvent which is used, for example by conducting heating in an autoclave or other
crystallization vessel suited for generating solvothermal conditions. In particularly preferred em-
bodiments wherein the solvent comprises or consists of water, preferably of distilled water,
heating in step (2) is accordingly preferably conducted under hydrothermal conditions.

35 The apparatus which can be used in the preferred synthetic method for crystallization is not par-
ticularly restricted, provided that the desired parameters for the crystallization process can be
realized, in particular with respect to the preferred embodiments requiring particular crystalliza-
tion conditions. In the preferred embodiments conducted under solvothermal conditions, any
40 type of autoclave or digestion vessel can be used, wherein a Teflon-lined apparatus is pre-
ferred.

In general, the duration of the crystallization process in step (2) of the preferred synthetic method is not particularly limited. In preferred embodiments involving heating of the mixture according to step (1), said crystallization process is conducted for a period ranging from 10 to 200 h, more preferably from 30 to 150 h, more preferably from 100 to 140 h, and even more preferably from 110 to 130 h.

According to preferred embodiments of the preferred synthetic method, wherein the mixture is heated in step (2), said heating may be conducted during the entire crystallization process or during only one or more portions thereof, provided that a zeolite having the small-pore framework structure is crystallized. Preferably, heating is conducted during the entire duration of crystallization.

In general, the process of the preferred synthetic method can optionally comprise further steps for the work-up and/or further physical and/or chemical transformation of the zeolite having a small-pore framework structure crystallized in step (2) from the mixture provided in step (1). The crystallized material can for example be subject to any sequence of isolation and/or washing procedures, wherein the zeolite obtained from crystallization in step (2) is preferably subject to one or more isolation and one or more washing procedures.

Isolation of the crystallized product can be achieved by any conceivable means. Preferably, isolation of the crystallized product can be achieved by means of filtration, ultrafiltration, diafiltration, centrifugation and/or decantation methods, wherein filtration methods can involve suction and/or pressure filtration steps.

With respect to one or more optional washing procedures, any conceivable solvent can be used. Washing agents which may be used are, for example, water, alcohols, such as methanol, ethanol or propanol, or mixtures of two or more thereof. Examples of mixtures are mixtures of two or more alcohols, such as methanol and ethanol or methanol and propanol or ethanol and propanol or methanol and ethanol and propanol, or mixtures of water and one or more alcohols, such as water and methanol or water and ethanol or water and propanol or water and methanol and ethanol or water and methanol and propanol or water and ethanol and propanol or water and methanol and ethanol and propanol. Water or a mixture of water and one or more alcohols, preferably water and ethanol, is preferred, distilled water being very particularly preferred as the only washing agent.

Preferably, the separated zeolite is washed until the pH of the washing agent, preferably the washwater, is in the range of from 6 to 8, preferably from 6.5 to 7.5, as determined via a standard glass electrode.

Furthermore, the preferred synthetic method can optionally comprise one or more drying steps. In general, any conceivable means of drying can be used. Drying procedures preferably include heating and/or applying vacuum to the zeolite having a small-pore framework structure. In en-

visaged embodiments of the preferred synthetic method, one or more drying steps may involve spray drying, preferably spray granulation of the zeolite.

5 In embodiments which comprise one or more drying steps, the drying temperatures are preferably in the range of from 25°C to 150°C, more preferably of from 60 to 140°C, more preferably of from 70 to 130°C and even more preferably in the range of from 75 to 125°C. The durations of drying are preferably in the range of from 2 to 60 h, more preferably in the range of 6 to 48 hours, and even more preferably of from 12 to 24 h.

10 According to the preferred synthetic method, the zeolite crystallized in step (2) can optionally be subject to one or more ion-exchange procedures. In general, any conceivable ion-exchange procedure with all possible ionic elements and/or molecules can be conducted on the zeolite. Preferably, as ionic elements one or more cation and/or cationic elements are employed which preferably comprise one or more cations and/or cationic elements selected from the group consisting of H⁺, NH₄⁺, lithium, potassium, calcium, magnesium, barium, transition metals, and
15 combinations thereof, more preferably from the group consisting of H⁺, NH₄⁺, lithium, potassium, calcium, magnesium, barium, lanthanum, cerium, nickel, platinum, palladium, and combinations thereof, wherein even more preferably the one or more cation and/or cationic elements comprise H⁺ and/or NH₄⁺, preferably NH₄⁺.

20 In general, the optional washing and/or isolation and/or ion-exchange procedures comprised in the preferred synthetic method can be conducted in any conceivably order and repeated as often as desired.

25 Therefore, according to further preferred embodiments, the preferred synthetic method optionally comprises one or more of the following steps of

(3) isolating the zeolite having a small-pore framework structure, preferably by filtration, and/or

(4) washing the zeolite having a small-pore framework structure,

30 and/or

(5) drying the zeolite having a small-pore framework structure, and/or

(6) subjecting the zeolite having a small-pore framework structure to an ion-exchange procedure,

35 wherein the steps (3) and/or (4) and/or (5) and/or (6) can be conducted in any order, and wherein one or more of said steps is preferably repeated at least once.

Preferably, the preferred synthetic method comprises one or more steps of isolating the zeolite crystallized according to step (2), more preferably by filtration thereof. According to the preferred synthetic method it is further preferred that after the one or more steps of isolating, the
40 zeolite is subject to one or more steps of drying, wherein more preferably the zeolite is subject to one or more steps of washing prior to the one or more drying steps. In a particularly preferred

embodiment, the zeolite crystallized according to step (2) is subject to one or more steps of isolating, followed by one or more steps of washing, followed by one or more steps of drying.

5 According to a further embodiment of the preferred synthetic method, the zeolite crystallized in step (2) is directly subject to one or more steps of drying, preferably to spray drying and or spray granulation, without isolating, washing, or drying of the zeolite beforehand. Directly subjecting the mixture obtained from step (2) of the preferred synthetic method to a spray drying or spray granulation stage has the advantage that isolation and drying is performed in a single stage.

10 According to a further embodiment of the preferred synthetic method, the zeolite obtained from crystallization in step (2) is subject to one or more isolating steps prior to being subject to one or more ion-exchange procedures, preferably to one or more isolating steps followed by one or more washing steps, and more preferably to one or more isolating steps followed by one or more washing steps followed by one or more drying steps.

20 The preferred synthetic method preferably does not comprise a calcination step generally involving the heating of the zeolite crystallized according to step (2) above a temperature of 500°C. More preferably, the preferred synthetic method for the production of a zeolite having a small-pore framework structure which does not comprise a calcination step refers to synthetic methods, wherein the zeolite crystallized according to step (2) is not subject to a temperature exceeding 450°C, more preferably 350°C, more preferably 300°C, more preferably 250°C, more preferably 200°C, more preferably 150°C, and even more preferably 100°C.

25 Thus, according to the present invention, the one or more zeolites provided in step (i) of the inventive process are preferably obtainable, and even more preferably obtained according to one or more of the aforementioned preferred and particularly preferred synthetic methods.

30 According to the present invention, the zeolite preferably does not contain more than an impurity of an organic structure directing agent typically used in the synthesis of zeolites having a small-pore framework structure, in particular specific tetraacylammonium salts and/or related organotemplates such as tetraethylammonium and/or dibenzylmethylammonium salts, and dibenzyl-1,4-diazabicyclo[2,2,2]octane. Such an impurity can, for example, be caused by organic structure directing agents still present in seed crystals used in the preferred synthetic process.

35 Furthermore, it is preferred according to the present invention that the zeolite is non-calcined, meaning that they have not been subject to a calcination step. Within the meaning of the present invention, a calcination step generally designates a process involving the heating of the one or more zeolites above a temperature of 500°C. More preferably, however, a non-calcined zeolite according to the present invention designates a material not having been subject to a temperature exceeding 450°C, more preferably 350°C, more preferably 300°C, more preferably 250°C, more preferably 200°C, and even more preferably not exceeding 150°C. In general, a

calcination step may designate any step which may be employed in the synthesis of the zeolite used in the inventive process. According to the present invention, however, a calcination step preferably only refers to a step conducted after completion of the crystallization of the zeolite from one or more precursor compounds which do not have the wanted framework structure, with the exception of any seeding crystals which may be employed therein. According to a yet further preferred embodiment of the present invention, a calcination step only refers to a step which is normally or suitably performed after completed crystallization of the zeolite for the removal of organotemplates from the framework structure.

10 Thus, according to preferred embodiments of the present invention, the zeolite is non-calcined.

According to the present invention, there is no particular restriction as to the crystalline structure of the zeolite, provided that these display a small-pore framework structure, and, in particular, that the zeolite affords an X-ray diffraction pattern comprising the reflections typical of respective framework structure.

According to the present invention, there is no particular restriction as to the surface area of the zeolite provided that the zeolite is suitable for catalyzing the inventive process. Thus, with respect to the BET surface area of the one or more zeolites determined according to DIN 66135, by way of example these may from 200 to 700 m²/g, wherein preferably the BET surface area is comprised in the range of from 400 to 650 m²/g, more preferably of from 475 to 575 m²/g, and even more preferably of from 500 to 550 m²/g. According to particularly preferred embodiments, the BET surface area determined according to DIN 66135 ranges from 510 to 530 m²/g.

25 According to the present invention it is preferred that prior to step (ii) at least a portion of the one or more alkali metals M preferably comprised in the one or more zeolites provided in step (i) is exchanged with H⁺ and/or NH₄⁺. According to particularly preferred embodiments, at least a portion of the one or more alkali metals M are exchanged with NH₄⁺.

30 Thus, according to particularly preferred embodiments, prior to the procedure in step (ii) at least a portion of the alkali metal atoms M contained in the one or more zeolites provided in step (i) is exchanged with H⁺ and/or NH₄⁺, preferably with NH₄⁺.

With respect to the exchange of the one or more alkali metals M in the preferred one or more zeolites provided in step (i), there is no particular restriction as to the method according to which the substitution or exchange is achieved, provided that the zeolites which are obtained prior to step (ii) are suited for the subsequent procedure for removing at least a portion of X in step (ii) of the inventive process. According to particularly preferred embodiments, the substitution or exchange is achieved by ion-exchange. According to the present invention, the term "ion-exchange" generally refers to non-framework ionic elements and/or molecules contained in the one or more zeolites.

As regards the preferred ion-exchange procedure conducted prior to step (ii) for substituting at least a portion of the alkali metal atoms M, said procedure may in principle be conducted in any suitable fashion using any suitable conditions for achieving the aforementioned substitution of alkali metal atoms M. According to particularly preferred embodiments, the procedure is conducted in a suitable solvent and preferably in aqueous solution. Furthermore, in embodiments employing a solvent which is preferably water, it is further preferred to conduct the ion-exchange procedure at a neutral or acidic pH, and preferably at an acidic pH. Thus, by way of example, the pH employed in said preferred embodiments may range anywhere from 0 to 7, wherein more preferably the pH is comprised in the range of from 1 to 6, more preferably of from 1 to 4, more preferably of from 1.5 to 3.5, and even more preferably of from 2 to 3.5. According to particularly preferred embodiments, the pH is comprised in the range of from 2.5 to 3.5.

Thus, according to particularly preferred embodiments, the ion-exchange process conducted prior to step (ii) is performed at a pH in the range of from 0 to 7, preferably of from 1 to 6, more preferably of from 1 to 4, more preferably of from 1.5 to 3.5, more preferably of from 2 to 3.5, and even more preferably of from 2.5 to 3.5.

According to the present invention, the procedure conducted in step (ii) of the inventive process leads to the removal of at least a portion of the trivalent element X from the small-pore framework structure of the one or more zeolites. In this respect, there is no particular restriction as to the process and conditions which may be used in step (ii) provided that at least a portion of the element X originally present in the small-pore framework as a constituting element thereof is removed. Within the meaning of the present invention, the term "removing" with respect to the removal of at least a portion of the framework element X indicates that said procedure leads to the alteration of the framework such that said portion of X which has been removed is not present in the one or more zeolites provided in step (i) and/or is not contained therein as a framework element. Within the meaning of the present invention, the term "framework element" or "framework ion" defines a constituting element or ion of the small-pore framework structure, and in particular with respect to its coordination in the framework structure. In this respect, a framework element X preferably refers to X which is comprised in the framework structure in a tetrahedral coordination.

The term "non-framework element" or "non-framework" ion, on the other hand, refers to any element or ion contained in the zeolite having a small-pore framework structure which is not a constituting the framework structure, meaning that it is for example contained in the micropores of the structure and/or that it only serves to compensate the structural framework, for example as counter ion or the like. Furthermore, said terms also refer to originally constituting elements or ions of the small-pore framework structure which have been altered from their original coordination state. In particular, a non-framework element X refers to X originally contained in the framework structure as a constituting element, and in particular as tetrahedrally coordinated X in the small-pore framework, and which has been subsequently removed from the framework structure for example by a change in its original coordination state and/or by being contained in

the micropores of the zeolite as opposed to the framework thereof. Thus, according to a preferred definition of the present invention, a non-framework element or ion X refers to X which was originally tetrahedrally coordinated in the small-pore framework structure, and which subsequently displays a different coordination state and preferably a higher coordination state. In particular, it is particularly preferred according to the present invention that a non-framework element X refers to originally tetrahedrally coordinated X which after having been subject to step (ii) is contained in the zeolite in a pentahedral and/or octahedral coordination, and preferably in an octahedral coordination state.

10 According to a preferred embodiment of the inventive process, at least a portion of X is removed from the small-pore framework structure by steam treatment of the one or more zeolites provided in step (i). In this respect, there are no particular limitations according to the present invention as to the procedure and conditions which may be employed in said preferred procedure used in step (ii), provided that at least a portion of X is removed from the small-pore framework structure.

Thus, according to preferred embodiments of the present invention, the procedure in step (ii) for removing at least a portion of X from the small-pore framework structure comprises one or more steam-treatment steps (S).

20 In principle, any conceivable temperature may be employed in the preferred steam-treatment step (S), provided that at least a portion of X is removed from the small-pore framework structure. Thus, by way of example, the one or more steam-treatment steps may be conducted at any temperature comprised in the range of from 200 to 1,000°C, wherein preferably the steam temperature is comprised in the range of from 300 to 900°C, more preferably of from 400 to 800°C, and even more preferably of from 500 to 700°C. According to particularly preferred embodiments, the one or more of the one or more steam-treatment steps (S) is conducted at a temperature comprised in the range of from 550 to 650°C.

30 Furthermore, according to the present invention, there is no particular restriction as to the duration of the one or more steam-treatment steps (S) preferably employed in step (ii) of the inventive process, provided that at least a portion of X is removed from the small-pore framework structure. In this respect, a duration of the steam treatment step ranging anywhere from 0.1 to 48 h may be mentioned by way of example, wherein preferably the duration is comprised in a range of anywhere from 0.2 to 24 h, more preferably of from 0.3 to 12 h, more preferably from 0.35 to 6 h, more preferably of from 0.4 to 4 h, and even more preferably of from 0.45 to 2 h. According to the present invention it is however particularly preferred that the preferred steam treatment step (S) is conducted for a period ranging from 0.5 to 1.5 h.

40 According to the preferred embodiments of the present invention wherein step (ii) of the inventive process includes one or more steam-treatment step (S), either pure steam may be used or one or more further gases may be additionally present in the steam. In embodiments wherein the steam includes further gases, there is in principle no particular restriction neither to the type

nor to the amount of the one or more further gases which may be used, provided that at least a portion of X may be removed from the small-pore framework structure using said steam containing gas. According to the present invention it is however preferred that one or more additional gases to steam be used which do not chemically react with the one or more zeolites. Thus, according to particularly preferred embodiments, one or more inert gases and preferably nitrogen is used as a further gas in addition to steam in the one or more steam-treatment steps (S).

In preferred embodiments of the present invention wherein the steam used in the preferred steam-treatment step (S) comprises one or more further gases, preferably one or more further inert gases and more preferably nitrogen, the content of steam in the resulting gas mixture may, by way of example, range anywhere from 5 to 75 vol.-%, wherein preferably the steam content is comprised in the range of from 10 to 50 vol.-%, and even more preferably of from 15 to 25 vol.-%.

Thus, according to particularly preferred embodiments of the present invention, the the one or more steam-treatment steps (S) employed in step (ii) are conducted using a steam concentration of from 5 to 75 vol.-%, preferably of from 10 to 50 vol.-%, and more preferably of from 15 to 25 vol.-%, wherein the remaining volume is preferably an inert gas, more preferably nitrogen.

According to the inventive process it is further preferred that one or more steam-treatment steps (S) employed in step (ii) are followed by one or more acid-treatment steps (A). As concerns the types of acids, the procedure, and the conditions which may be employed in said particularly preferred embodiments of the inventive process, no particular limitation applies provided that said one or more acid-treatment steps do not interfere with the removal of at least a portion of X from the small-pore framework structure in step (ii). Furthermore the procedure is chosen such that the small-pore framework structure of the treated zeolite is retained as least in part, wherein it is preferred that the small-pore framework structure is not deteriorated or partly destroyed during the acid-treatment step compared the its condition prior thereto.

Therefore, according to particularly preferred embodiments of the present invention it is further preferred that the procedure in step (ii) further comprises subjecting the one or more zeolites obtained from the one or more steam-treatment steps (S) to one or more acid-treatment steps (A).

Regarding the particularly preferred additional acid-treatment step (A), the procedure may be conducted under any suitable conditions leading to the contacting of the steam-treated zeolite with one or more acids or acidic compounds, wherein the procedure is preferably conducted in a suitable solvent and preferably in aqueous solution. As concerns the preferred procedures conducted with the aid of a solvent and in particular in aqueous solution, there is no particular restriction as to the pH of the solution, provided that it is acidic. Thus, by way of example, the one or more particularly preferred acid-treatment steps may be conducted at a pH of 4 or less, wherein a pH of 3.5 or less is preferred. According to particularly preferred embodiments, the pH is comprised in the range of from -1.5 to 3, more preferably of from -1 to 2.5, more prefera-

bly of from -0.5 to 2, and even more preferably of from -0.5 to 1, wherein it is yet further preferred according to said embodiments that the pH is comprised in the range of from -0.5 to 0.5.

5 Thus, it is further preferred according to said particularly preferred embodiment of the inventive process that the one or more acid-treatment steps (A) involve contacting the one or more zeolites with an acidic solution having a pH of 4 or less, preferably of 3.5 or less, wherein preferably the pH is in the range of from -1.5 to 3, more preferably of from -1 to 2.5, more preferably of from -0.5 to 2, more preferably of from -0.5 to 1, and even more preferably of from -0.5 to 0.5.

10 As concerns the conditions used for the particularly preferred additional acid-treatment step (A), there is again no particular limitation in this respect. Accordingly, the procedure may be conducted at ambient temperature or, preferably, under heating. Regarding particularly preferred embodiments wherein the acid-treatment step (A) is conducted at temperatures which are elevated with respect to ambient conditions, it is further preferred that the acid-treatment is conducted at a temperature comprised in the range of from 50 to 100°C, wherein more preferably the temperature employed for the acid-treatment step is comprised in the range of from 60 to 95°C, more preferably of from 70 to 90°C, and even more preferably of from 75 to 85 °C.

20 Furthermore, there is also no particular limitation according to the particularly preferred acid-treatment step (A) as concerns the duration thereof, provided that the small-pore framework structure of the treated zeolite is retained as least in part, and that the small-pore framework structure is preferably not deteriorated or partly destroyed due to the particular duration of the acid-treatment step compared the zeolite's condition prior thereto. According to the present invention it is however preferred that the duration of the acid-treatment step (A) is comprised in the range of from 0.25 to 5 h, and more preferably of from 0.5 to 4.5 h, more preferably of from 1 to 4 h, more preferably of from 1 to 3.5 h, wherein even more preferably the duration of the acid-treatment step (A) is comprised in the range of from 1.5 to 3.5 h.

30 Therefore, according to the particularly preferred embodiments of the inventive process involving one or more additional acid-treatment steps (A), said one or more acid-treatment steps (A) involve contacting the one or more zeolites with an acidic solution at a temperature of from 50 to 100°C, preferably of from 60 to 95°C, more preferably of from 70 to 90°C, and even more preferably of from 75 to 85 °C. Furthermore, according to said particularly preferred embodiments it is further preferred that the one or more acid-treatment steps (A) involve contacting the one or more zeolites with an acidic solution for a period of from 0.25 to 5 h, preferably of from 0.5 to 4.5 h, more preferably of from 1 to 4 h, more preferably of from 1 to 3.5 h, and even more preferably of from 1.5 to 3.5 h.

40 According to alternatively preferred embodiments of the inventive process, the procedure in step (ii) for removing at least a portion of X from the small-pore framework structure comprises one or more calcination steps (C).

As for the aforementioned preferred steam-treatment and particularly preferred additional acid-treatment procedures, there is also no particular limitation with respect to the procedure and conditions which may be employed in the alternatively preferred calcination step for the removal of X from the small-pore framework structure, provided that that the small-pore framework structure of the calcinated zeolite is retained as least in part, wherein it is preferred that the small-pore framework structure is not deteriorated or partly destroyed during the preferred calcination step compared the its condition prior thereto. Thus, as regards the temperature which may be employed for the calcination procedure, temperatures comprised in the range of from 450 to 800°C may be mentioned by way of example, wherein preferably the calcination temperature is comprised in the range of from 550 to 750°C, and more preferably of from 600 to 720°C. According to particularly preferred embodiments, calcination temperatures are employed which are comprised in the range of from 620 to 700°C. Furthermore, concerning the duration of calcination, there is again no particular limitation in this respect, wherein it is preferred that the duration be comprised in the range of from 0.5 to 10 h, more preferably of from 1 to 6 h, and even more preferably of from 1.5 to 3 h.

Thus, according to alternatively preferred embodiments of the present invention, the one or more calcination steps (C) are conducted at a temperature of from 450 to 800°C, preferably of from 550 to 750°C, more preferably of from 600 to 720°C, and even more preferably of from 620 to 700°C. Furthermore and preferably in addition thereto, the one or more calcination steps (C) are conducted for a period ranging from 0.5 to 10 h, preferably of from 1 to 6 h, and even more preferably of from 1.5 to 3 h.

According to the inventive process, the step (ii) of subjecting the one or more zeolites provided in step (i) to a procedure for removing at least a portion of X may be repeated. In this respect, there is no particular limitation as to the number of repetitions, provided that the zeolite is retained as least in part, and preferably that the small-pore framework structure is not deteriorated or partly destroyed as a result of excessive repetition of step (ii). Thus, by way of example, step (ii) of the inventive process may be repeated anywhere from once to 5 times, wherein preferably step (ii) is repeated 1 to 5 times, more preferably 1 to 3 times, and even more preferably once or twice. According to particularly preferred embodiments of the inventive process, step (ii) is repeated twice.

Furthermore, according to the particularly preferred embodiments involving the repetition of step (ii) it is yet further preferred that said repetition comprises the repetition of one or more of the one or more calcination steps (C). In this respect, there is no particular preference as to the specific type of the one or more calcination steps (C) according to the preferred embodiments of the inventive process as outlined above which may be repeated, wherein it is particularly preferred that in those embodiments involving the repetition of the one or more calcination steps in step (ii), the calcination steps according to the particularly preferred embodiments of the present invention as outlined in the foregoing are repeated therein.

Therefore, according to preferred embodiments of the inventive process, step (ii) is repeated one or more times, preferably 1 to 5 times, more preferably 1 to 3 times, more preferably 1 or 2 times, and even more preferably 2 times, wherein it is particularly preferred that the repetition of step (ii) comprises the repetition of one or more of the one or more calcination steps (C) according to preferred embodiments and in particular according to particularly preferred embodiments as outlined in the foregoing.

Furthermore, according to the particularly preferred embodiments involving the repetition of step (ii) involving one or more calcination steps (C), it is particularly preferred according to said embodiments that prior to at least one of said repetitions, and preferably prior to each of said repetitions, the one or more zeolites are subject at least one ion-exchange procedure. In particular, it is especially preferred according to said embodiments that at least part of the non-framework element X which has been removed from the small-pore framework in step (ii) is first removed from the zeolite prior to a repetition of the one or more calcination steps (C) in a further step (ii). According to said particularly preferred embodiments, there is no particular restriction as to the specific type of ion-exchange procedure which is employed prior to the repetition of step (ii), provided that at least a portion and preferably all of the non-framework X which has been removed from the small-pore framework structure in the initial and/or preceding step (ii) may be exchanged with one or more cations and/or cationic elements, wherein the non-framework X preferably comprises octahedrally coordinated non-framework X. According to said particularly preferred embodiments it is further preferred that the non-framework X comprised in the one or more zeolites obtained from an initial and/or preceding step (ii) is exchanged with H⁺ and/or NH₄⁺, and more preferably with NH₄⁺ prior to the repetition of step (ii), and in particular to the one or more calcination steps (C).

Thus, according to particularly preferred embodiments of the inventive process, at least part of the non-framework ions respectively present in the one or more zeolites are exchanged with one or more cations and/or cationic elements prior to repeating step (ii), wherein the one or more cation and/or cationic elements preferably comprise H⁺ and/or NH₄⁺, wherein even more preferably at least part of the non-framework ions are exchange with NH₄⁺. In particular, according to yet preferred embodiments of said particularly preferred embodiments, the non-framework ions comprise X, preferably X which has been removed from the small-pore framework structure in a previous step (ii).

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Form

According to the present invention the zeolite may in principle be used in any suitable form, provided that it is capable of catalyzing the reaction. Thus, the zeolite can be employed as such, such as by way of example in the form of a powder, a spray powder or a spray granulate.

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When the inventive process is employed on an industrial scale, it is however preferable not to employ the zeolite as powder or sprayed material but rather in the form of a molding.

Therefore, according to preferred embodiments of the inventive process, the zeolite is provided in the form of a molding.

In general, the powder or sprayed material can be shaped to form a molding without any other compounds, such as for example by suitable compacting, to obtain moldings of a desired geometry, such as in the form of tablets, cylinders, and/or spheres. The molding may however comprise all conceivable further compounds in addition to the zeolite, provided that it is ensured that the resulting molding is capable of catalyzing the inventive process. According to said preferred embodiments, it is further preferred that at least one suitable binder material is used in the production of the molding. In the context of this preferred embodiment, more preferably a mixture of the zeolite and the one or more binders is prepared. Suitable binders are in general all compounds which impart adhesion and/or cohesion between the one or more zeolites which are to be bound, in particular beyond the physisorption which may be present without a binder. Examples of such binders are metal oxides, such as SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 or MgO , or clays or mixtures of two or more of these compounds. As Al_2O_3 binders, clay minerals and naturally occurring or synthetic aluminas, for example alpha-, beta-, gamma-, delta-, eta-, kappa-, chi- or theta-alumina and the inorganic or organometallic precursor compounds thereof, such as gibbsite, bayerite, boehmite, pseudoboehmite or trialkoxyaluminates, such as aluminum triisopropylate are preferred in particular. Further preferred binders are amphiphilic compounds having a polar and a nonpolar moiety, and graphite. Further binders are, for example, clays, such as montmorillonites, kaolins, bentonites, halloysites, dickites, nacrites or anaxites.

According to the present invention, the binders can be used as such for the production of a molding. In the context of the present invention, it is however also possible to use compounds from which the binder is formed in at least one further step in the production of the moldings. Examples of such binder precursors are tetraalkoxysilanes, tetraalkoxytitanates, tetraalkoxyzirconates or a mixture of two or more different tetraalkoxysilanes or a mixture of two or more different tetraalkoxytitanates or a mixture of two or more different tetraalkoxyzirconates or a mixture of at least one tetraalkoxysilane and at least one tetraalkoxytitanate or of at least one tetraalkoxysilane and at least one tetraalkoxyzirconate or of at least one tetraalkoxytitanate and at least one tetraalkoxyzirconate or a mixture of at least one tetraalkoxysilane and at least one tetraalkoxytitanate and at least one tetraalkoxyzirconate. In the context of the present invention, binders which either completely or partly consist of SiO_2 or are a precursor of SiO_2 , from which SiO_2 is formed in at least one further step in the production of the moldings are to be mentioned. In this context, both colloidal silica and "wet process" silica as well as "dry process" silica can be used. These are very particularly preferably amorphous silica, the size of the silica particles being, for example, in the range of from 5 to 100 nm and the surface of the silica particles being in the range of from 50 to 500 m^2/g . Colloidal silica, preferably in the form of an alkaline and/or ammoniacal solution, more preferably in the form of an ammoniacal solution, is, for example, commercially available as, inter alia, Ludox®, Syton®, Nalco® or Snowtex®. "Wet process" silica is, for example, commercially available, inter alia, as Hi-Sil®, Ultrasil®, Vulcasil®, Santocel®, Valron-Estersil®, Tokusil® or Nipsil®. "Dry process" silica is, for example, commercially available, inter alia, as Aerosil®, Reolosil®, Cab-O-Sil®, Fransil® or ArcSilica®. The binders are pref-

erably used in an amount which leads to the finally resulting moldings whose binder content is up to 80 % by weight, more preferably in the range of from 5 to 80 % by weight, more preferably in the range of from 10 to 70 % by weight, more preferably in the range of from 10 to 60 % by weight, more preferably in the range of from 15 to 50 % by weight, more preferably in the range of from 15 to 45 % by weight, particularly preferably in the range of from 15 to 40 % by weight, based in each case on the total weight of the finally resulting molding.

In principle, the molding comprising the zeolite may be obtained according to any suitable procedure, provided that the molding may catalyze the inventive process. According to preferred embodiments of the present invention, the molding is obtainable and preferably obtained according to a process for the production of a molding comprising the steps of

- (I) preparing of a mixture containing zeolite, and optionally at least one binder;
- (II) optionally kneading of the mixture;
- (III) molding of the kneaded mixture to give at least one molding;
- (IV) optionally drying of the at least one molding; and/or
- (V) optionally calcining of the at least one dried molding.

The term "finally resulting molding" as used in the context of the present invention relates to a molding as obtainable and preferably obtained from the optional drying and/or calcining steps (IV) and/or (V), particularly preferably as obtainable and preferably obtained from step (IV).

Therefore, the mixture of binder or precursor of a binder and the zeolite can be mixed with at least one further compound for further processing and for the formation of a plastic material. Here, inter alia, pore formers may preferably be mentioned. In the process of the present invention, all compounds which, with regard to the finished molding, provide a certain pore size and/or a certain pore size distribution and/or certain pore volumes can be used as pore formers. Preferably used pore formers in the process of the present invention are polymers which are dispersible, suspendable or emulsifiable in water or in aqueous solvent mixtures. Preferred polymers here are polymeric vinyl compounds, for example polyacetylene oxides, such as polyethylene oxides, polystyrene, polyacrylates, polymethacrylates, polyolefins, polyamides and polyesters, carbohydrates, such as cellulose or cellulose derivatives, for example methylcellulose, or sugars or natural fibers. Further suitable pore formers are, for example, pulp or graphite. If pore formers are used in the preparation of the mixture according to (I), the pore former content, preferably the polymer content of the mixture according to (I) is preferably in the range of from 5 to 90 % by weight, preferably in the range of from 15 to 75 % by weight, and particularly preferably in the range of from 25 to 55 % by weight, based in each case on the amount of the one or more zeolites in the mixture according to (I). If desired for the pore size distribution to be achieved, a mixture of two or more pore formers may also be used. In a preferred embodiment of the process of the present invention, the pore formers are removed in a step (V) by calcination to give the porous molding. According to the present invention, however, it is particularly preferred that the molding obtained in step (III) is subsequently not subject to a calcination step. With respect to the calcination of the molding preferably used in the inventive process, the term "calcination" refers to a calcination step as defined in the foregoing with respect to the one or

more zeolites. Therefore, according to particularly preferred embodiments of the present invention wherein the molding obtained in step (III) is subsequently not subject to a calcination step, it is accordingly preferred according to said embodiments either not to employ a pore former or, alternatively, to use one or more pore formers which may be suitably removed either by a heating step which is not a calcination step within the meaning of the present invention and/or which may be removed by other means than by suitable heating of the preferred molding containing one or more pore formers.

In the context of a likewise preferred embodiment of the present invention, at least one pasting agent is added in the preparation of the mixture according to (I). Pasting agents which may be used are all compounds suitable for this purpose. These are preferably organic, in particular hydrophilic polymers, for example cellulose, cellulose derivatives, such as methylcellulose, starch, such as potato starch, wallpaper paste, polyacrylates, polymethacrylates, polyvinyl alcohol, polyvinylpyrrolidone, polyisobutene or polytetrahydrofuran. Accordingly, particular compounds which also act as pore formers can be used as pasting agents. In a particularly preferred embodiment of the process of the present invention as described below, these pasting agents are removed in a step (V) by calcination to give the porous molding. According to the present invention, however, it is particularly preferred that the molding obtained in step (III) is subsequently not subject to a calcination step. Therefore, according to particularly preferred embodiments of the present invention wherein the molding obtained in step (III) is subsequently not subject to a calcination step, it is accordingly preferred according to said embodiments either not to employ a pasting agent or, alternatively, to use one or more pasting agents which may be suitably removed either by a heating step which is not a calcination step within the meaning of the present invention and/or which may be removed by other means than by suitable heating of the preferred molding containing one or more pasting agents.

According to a further embodiment of the present invention, at least one acidic additive may be added during the preparation of the mixture according to (I). In this respect organic acidic compounds are preferred which can be removed in an optional calcination step (V). Carboxylic acids, for example formic acid, oxalic acid and/or citric acid, are particularly preferred. It is also possible to use two or more of these acidic compounds. As for the aforementioned pore formers and pasting agents, however, it is preferred to use one or more acidic additives and preferably one or more organic acidic compounds which may be removed either by a heating step which is not a calcination step within the meaning of the present invention and/or which may be removed by other means than by suitable heating of the preferred molding containing one or more acidic additives, preferably one or more organic acidic compounds.

The order of addition of the components of the mixture according to (I) which contains the zeolite is not critical. In particular it is both possible first to add the at least one binder, then the at least one pore former and the at least one acidic compound and finally the at least one pasting agent and to interchange the sequence with regard to the at least one binder, the at least one pore former, the at least one acidic compound and the at least one pasting agent.

After the addition of the binder to the zeolite to which, if appropriate, at least one of the compounds described above have already been added, the mixture according to (I) is normally homogenized for from 10 to 180 minutes. Inter alia, kneaders, edge mills or extruders are particularly preferably used for the homogenization. The mixture is preferably kneaded. On the industrial scale, treatment in an edge mill is preferably employed for the homogenization. The homogenization is carried out as a rule at temperatures in the range of from about 10 °C to the boiling point of the pasting agent and normal pressure or slightly superatmospheric pressure. Thereafter, if appropriate, at least one of the compounds described above can be added. The mixture thus obtained is homogenized, preferably kneaded, until an extrudable plastic material has formed.

According to the preferred process of the present invention for the production of a molding, the homogenized mixture is subsequently molded. In the context of the present invention, those processes in which the molding is effected by extrusion in conventional extruders, for example to give extrudates having a diameter of preferably from 1 to 10 mm, particularly preferably from 2 to 5 mm, are preferred for the shaping processes. Such extrusion apparatuses are described, for example, in Ullmann's Enzyklopädie der Technischen Chemie, 4th Edition, Vol. 2, page 295 et seq., 1972. In addition to the use of a screw-type extruder, a plunger-type extruder is also preferably used for the molding. In principle, however, all known and/or suitable kneading and molding apparatuses and processes may be used for the shaping. Examples of these are inter alia: briquetting, i.e. mechanical compression with or without addition of additional binder material; pelleting, i.e. compacting by circular and/or rotational movements; sintering, i.e. the material to be molded is subjected to a thermal treatment. The shape of the moldings produced according to the invention can be chosen as desired. In particular, inter alia spheres, oval shapes, cylinders or tablets are possible.

In the context of the present invention, step (III) is preferably followed by at least one drying step. In principle, any suitable drying step may be used, provided that a dry molding is provided. According to the present invention it is however preferred that the drying step does not involve temperatures used in a calcination step within the meaning of the present invention.

In the context of the present invention, an optional drying step (IV) is optionally followed by at least one calcination step (V). According to certain embodiments, a calcination step (V) is directly carried out after the molding step (III). According to the present invention it is however preferred that the preferred molding containing the acylation catalyst comprising the one or more zeolites having the small-pore framework structure is not subject to a calcination step (V) subsequently to the optional drying step (IV), wherein according to said particularly preferred embodiments not involving a calcination step (V) it is preferred that the production process comprises one or more drying steps (IV) subsequently to the molding step (III).

According to embodiments wherein the preferred molding is obtainable and preferably obtained according to the aforementioned preferred method for the production of a molding which comprises one or more calcination steps (V), the calcination may be generally carried out at any

temperature as defined within the meaning of the present invention, wherein it is preferably carried out at temperatures in the range of from 300 to 700 °C, and more preferably from 400 to 600 °C. According to said embodiments, the calcination can be effected under any suitable gas atmosphere, air and/or lean air being preferred. Furthermore, the calcination is preferably carried out in a muffle furnace, a rotary kiln and/or a belt calcination oven. It is possible for the temperatures during a calcination step to remain constant or to be changed continuously or discontinuously. If calcination is effected twice or more often, the calcination temperatures can be different or identical in the individual steps.

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- Before and/or after the optional drying step (IV) and/or before and/or after the optional calcination step (V), the at least one molding can, if appropriate, be treated with a concentrated or dilute Broenstedt acid or a mixture of two or more Broenstedt acids. Suitable acids are, for example, hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid or carboxylic acids, dicarboxylic acids or oligo- or polycarboxylic acids, such as nitrilotriacetic acid, sulfosalicylic acid or ethylenediaminetetraacetic acid. If appropriate, this at least one treatment with at least one Broenstedt acid is followed by at least one drying step (IV) and/or at least one calcination step (V).

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According to a further embodiment of the process of the present invention, the moldings preferably provided in step (a) and used in step (b) can, for better hardening, be subject to a water steam treatment, after which preferably drying is effected at least once again and/or calcination is effected at least once again. For example, after at least one drying step and at least one subsequent calcination step, the calcined molding is subjected to the steam treatment and is then dried at least once again and/or calcined at least once again.

25 Zeolite analogous material

The term "zeolite analogous material" shall have the following meaning within the frame of the present invention: a material exhibiting a zeolite structure and comprising tetravalent, trivalent and pentavalent structural components Y, X and Z as YO_2 , X_2O_3 , and Z_2O_5 respectively, wherein Y is a tetravalent element, X is a trivalent element and Z is a pentavalent element. Y and X

30 have the same meaning as described for zeolites. Preferred Z is phosphor.

Exemplarily, zeolite analogous materials comprise materials that are known as SAPO. A particular preferred zeolite analogous material is SAPO-34.

Zeolite / zeolite analogous material

35 A small-pore zeolite (a) and the at least one small-pore zeolite analogous material (c2) can be used as physical mixtures comprising particles which either comprise the small-pore zeolite or the small-pore analogous material.

They can also be used as mixtures comprising particles which comprise both the zeolite and the zeolite-analogous material.

40 A preferred material is a material,

wherein the core-portion comprises one or more zeolites selected from the group consisting of (Ni(deta)₂)-UT-6, Chabazite, |Li-Na| [Al-Si-O]-CHA, DAF-5, Dehyd. Na-Chabazite, K-Chabazite (Iran), LZ-218, Linde D, Linde R, MeAPSO-47, Phi, SAPO-34, SAPO-47, SSZ-13, SSZ-62, UiO-

- 21, Willhendersonite, ZK-14, ZYT-6, and combinations of two or more thereof, preferably from the group consisting of (Ni(deta)₂)-UT-6, Chabazite, [Li-Na] [Al-Si-O]-CHA, DAF-5, Dehyd. Na-Chabazite, K-Chabazite (Iran), LZ-218, Linde D, Linde R, Phi, SSZ-13, SSZ-62, UiO-21, Willhendersonite, ZK-14, ZYT-6, and combinations of two or more thereof, and wherein even more preferably the core-portion comprises Chabazite and/or SSZ-13, preferably Chabazite; and
- wherein the shell-portion comprises a material selected from the group consisting of [Al-As-O]-CHA, [Al-Co-P-O]-CHA, [Co-Al-P-O]-CHA, [Mg-Al-P-O]-CHA, [Zn-Al-P-O]-CHA, AIPO-34, CoAPO-44, CoAPO-47, GaPO-34, MeAPO-47, MeAPSO-47, SAPO-34, SAPO-47, ZYT-6, and combinations of two or more thereof, preferably from the group consisting of MeAPSO-47, SAPO-34, SAPO-47, ZYT-6, and combinations of two or more thereof, wherein even more preferably the shell-portion comprises SAPO-34.
- Such materials are described in WO 2013/038372.
- Preparation of the metal-loaded small-pore zeolite and/or metal-loaded small-pore zeolite analogous material
- In principle, there is no general restriction as to how the metal-loaded small-pore zeolite and/or the metal-loaded small-pore zeolite analogous material is obtained.
- In a preferred embodiment, the at least one metal is impregnated with a solution of a respective precursor.
- Preferred, the solution is an aqueous solution.
- Preferred, the precursor is a metal salt. In the case of Mo a preferred salt is (NH₄)₆Mo₇O₂₄·4H₂O. In the case of Fe a preferred salt is Fe(NO₃)₃·9H₂O. In the case of Co a preferred salt is Co(NO₃)₃·6H₂O.
- The concentration of the solution is from 0.1 wt% to 30 wt% (calculated as metal per solvent), preferred from 1 wt% to 20 wt%, more preferred 1.5 wt% to 15 wt%, even more preferred 2 wt% to 10 wt%. Particularly preferred is a concentration of 3 wt% to 8 wt%.
- The impregnated small-pore zeolite and/or small-pore zeolite material is then dried.
- Preferred, the drying is performed in two steps.
- Preferred, a first drying is performed at a temperature which is lower than the temperature in the second drying step, preferred the first drying is performed at room temperature, i.e. a temperature of 20°C.
- In a further preferred embodiment it is performed under reduced pressure, more preferred under vacuum.
- Preferred, a second drying is performed at an elevated temperature, which in particular is higher than the temperature in the first drying step. Preferred the temperature in the second drying step is from 50 to 200°C, preferred from 80 to 150°C, more preferred from 90 to 120 °C. Particularly preferred is a temperature in the second drying step of 100°C.
- In a further step the catalyst is calcined. Preferred the calcination is performed under air. The calcination temperature is from 300 to 1000°C, preferred from 400 to 800°C, more preferred from 450 to 600°C, even more preferred from 480 to 550°C. Most preferred the calcination temperature is 500°C.

According to the invention, the conversion methane to ethene is performed in the presence of a catalyst at temperatures of from 400 to 1000°C, preferably from 500 to 900°C, more preferably from 600 to 800°C, especially from 700 to 800°C, at a pressure of from 0.5 to 100 bar, preferably from 1 to 30 bar, more preferably from 1 to 10 bar, especially from 1 to 5 bar. According to the present invention, the reaction is performed at a GHSV (Gas Hourly Space Velocity) of from 100 to 10 000 h⁻¹, preferably from 200 to 3000 h⁻¹.

The conversion of methane to ethene and also the regeneration of the catalyst deactivated by coke deposits with hydrogen can in principle be carried out in all reactor types known from the prior art. A suitable reactor form is the fixed bed reactor, radial flow reactor, tubular reactor or tube bundle reactor. In these reactors, the catalyst is present as a fixed bed in one reaction tube or in a bundle of reaction tubes. The catalysts may likewise be used as a fluidized bed or moving bed in the corresponding reactor types suitable for this purpose, and the process according to the invention may be carried out with the catalysts present in such a form.

In a preferred embodiment of the invention, the process further comprises a regeneration step.

The regeneration step is performed at temperatures of from 600°C to 1000°C and more preferably from 700°C to 900°C, and pressures of from 1 bar to 30 bar, preferably from 1 bar to 15 bar and more preferably from 1 to 10 bar.

In a preferred embodiment of the invention, the regeneration step is in the presence of hydrogen.

In a preferred embodiment of the invention, in the regeneration step coke is reacted to volatile organic compounds, preferred methane.

In a preferred embodiment of the invention, the process comprising a regeneration step is performed in parallel reactors.

The step of converting methane to ethane is performed in at least one reactor and the regeneration step is performed simultaneously in at least one other reactor.

According to the invention, the catalyst used for the conversion of methane to ethene is regularly regenerated with the hydrogen present in a gas stream H. This converts at least a portion of the deposited coke to methane. This forms a methane-containing gas stream M which, as well as the methane formed, comprises unconverted hydrocarbon and substances already present in mixture H. According to the invention, at least a portion of the methane formed in the regeneration is fed to a reaction zone. After removal from the gas stream M, the methane can be fed to a reaction zone. Preferably at least 50% of the methane formed during the regeneration, more preferably at least 70%, especially at least 90% of the methane formed during the regeneration is fed to a reaction zone. Very particular preference is given to feeding all of the methane formed in the regeneration to a reaction zone.

In a preferred embodiment of the present invention, at least a portion of the methane-containing gas stream M formed in the regeneration is fed to a reaction zone. The gas stream M can be fed to a reaction zone without preceding removal of one or more constituents, but it is also possible for one or more constituents to be removed before the recycling of gas stream M. This allows the CH₄/H₂ ratio on entry to a reaction zone to be adjusted in a controlled manner. Before the recycling of at least a portion of gas stream M, preference is given to removing at least a portion of the unconverted hydrogen present therein.

The methane or the methane-containing gas stream M formed during the regeneration can be fed directly to a reaction zone or can be supplied to reactant stream E by addition of the methane or of the gas stream M.

Reaction zone and regeneration zone can be interconverted to one another by altering the gas streams. In a preferred embodiment of the present invention, a reaction zone is converted to a regeneration zone by reducing reactant stream E and supplying gas stream H. Reducing reactant stream E means that the reactant stream E makes up at most 10% by volume of the gases fed to the reaction zone, preferably at most 5% by volume and more preferably at most 1% by volume. Especially preferred is the complete closure of supply of reactant stream E.

In a preferred embodiment of the invention, a regeneration zone is converted to a reaction zone by reducing gas stream H and supplying reactant stream E. Reducing gas stream H means that gas stream H forms at most 10% by volume of the gases fed to a regeneration zone, preferably at most 5% by volume and more preferably at most 1% by volume, based on the total volume of the gas supply. More preferably, the supply of gas stream H is closed completely.

In a further embodiment, reactant stream E does not comprise any hydrogen; in that case, the supply of gas stream H, when a regeneration zone is converted to a reaction zone, can also be throttled only to such an extent that a content of hydrogen which has a positive effect on the coking is established in a reaction zone.

More preferably, the conversion of a reaction zone to a regeneration zone and the conversion of a regeneration zone to a reaction zone are carried out coupled to one another in alternation, such that a reaction zone is present at time intervals alternatingly as a reaction zone in which the conversion of methane to ethene (MTE) takes place and as a regeneration zone in which at least a portion of the coke deposited is converted to methane with the aid of hydrogen. In each case offset in time from this, the other reaction zone is present as a regeneration zone and as a reaction zone. According to the invention, one reaction zone is present as a reaction zone (NTE) for from 5 minutes to 5 hours and as a regeneration zone (regeneration) for from 5 minutes to 5 hours.

According to the invention, more than one reaction zone and more than one regeneration zone may be present; it is merely necessary in each case for at least one reaction zone and at least one regeneration zone to be present. It is also possible for reaction zones which are in the phase of conversion from a reaction zone to a regeneration zone to be present; in addition, it is

possible for reaction zones in which the catalyst is regenerated by other methods to be present, for example by means of oxygen or steam, in which case a re-carbidization step possibly becomes necessary. According to the invention, preferably only reaction zone and regeneration zones are present.

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To regenerate the catalyst from the MTE conversion deactivated by coke deposits, it is, in accordance with the invention, regularly regenerated with hydrogen in a regeneration zone. In one embodiment of the invention, for this purpose, the catalyst is transferred from a reaction zone to a regeneration zone and regenerated there with the aid of the hydrogen-comprising gas stream H. The regenerated catalyst is then recycled back into a reaction zone. In a further embodiment of the invention, a reaction zone, as described above, is converted to a regeneration zone by reducing the supply of reactant stream E and supplying gas stream H, the deactivated catalyst is regenerated and a regeneration zone is then converted back to a reaction zone as described above.

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Catalyst

It was a further object of the present invention to provide a catalyst comprising

- (a) a small-pore zeolite;
- (b) a metal; and
- 20 (c) a further component selected from the group consisting of
 - (c1) at least one further small-pore zeolite and/or
 - (c2) at least one small-pore zeolite analogous material and/or
 - (c3) at least one further metal different from (b)

25 whereas the metal (b) and –if applicable- the at least one further metal (c3) is/are loaded onto

- the small-pore zeolite (a) and/or
- -if applicable- the at least one further small-pore zeolite (c1) and/or
- -if applicable- the at least one small-pore zeolite analogous material (c2).

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Preferred, the inventive catalyst consists essentially of

- (a) a small-pore zeolite;
- (b) a metal; and
- 35 (c) a further component selected from the group consisting of
 - (c1) at least one further small-pore zeolite and/or
 - (c2) at least one small-pore zeolite analogous material and/or
 - (c3) at least one further metal different from (b)

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whereas the metal (b) and –if applicable- the at least one further metal (c3) is/are loaded onto

- the small-pore zeolite (a) and/or
- -if applicable- the at least one further small-pore zeolite (c1) and/or
- -if applicable- the at least one small-pore zeolite analogous material (c2).

More preferred, the inventive catalyst consists of

- (a) a small-pore zeolite;
- (b) a metal; and
- (c) a further component selected from the group consisting of
 - (c1) at least one further small-pore zeolite and/or
 - (c2) at least one small-pore zeolite analogous material and/or
 - (c3) at least one further metal different from (b)

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whereas the metal (b) and –if applicable- the at least one further metal (c3) is/are loaded onto

- the small-pore zeolite (a) and/or
- -if applicable- the at least one further small-pore zeolite (c1) and/or
- -if applicable- the at least one small-pore zeolite analogous material (c2).

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In one preferred embodiment the catalyst comprises

- a small-pore zeolite (a) and at least one small-pore zeolite (c1); and
- at least one metal (b) which is loaded onto at least one of the small-pore zeolites (a) and (c1).

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In another preferred embodiment the catalyst comprises

- a small-pore zeolite (a);
- at least one small-pore zeolite analogous material (c2);
- at least one metal (b) which is loaded onto a small-pore zeolite (a) and/or at least one small-pore zeolite analogous material (c2).

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In a preferred embodiment of the catalyst the small-pore zeolite (a) is selected from the structural group consisting of LEV, CHA, CDO and mixtures thereof.

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In a further preferred embodiment of the catalyst the small-pore zeolite (a) is selected from the group consisting of RUB-37, RUB-50, LEV and mixtures thereof.

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In a preferred embodiment of the catalyst the metal (b) is selected from the group consisting of Mo, Fe, Co, Ni, Cu, Ag, Mg, W, Re, Ga, Ru, Rh, Pd, Ir, Pt and mixtures thereof, preferred selected from the group consisting of Mo, Fe, Co, Ni, Cu and mixtures thereof, more preferred Mo.

In a more preferred embodiment of the catalyst the amount of metal (b) is higher than 4 wt%, preferred 5 wt% or more, more preferred 6 wt% or more, based on the total weight of the catalyst.

40

In a preferred embodiment of the catalyst metal (b) and an at least one further metal (c3) different from (b) are selected from the group consisting of Mo, Fe, Co, Ni, Cu, Ag, Mg, W, Re, Ga, Ru, Rh, Pd, Ir, Pt and mixtures thereof, preferred Fe, Co, Ni, Cu and mixtures thereof, more preferred Mo-Fe, Mo-Co and Mo-Ni.

The terms and definitions used in the description of the inventive process with respect to the catalyst, the small-pore zeolite (a), metal (b) and further component (c) shall have the same meaning when applied to the inventive catalyst.

- 5 The present invention is further illustrated by means of the following examples, figures and tables without limiting the invention to the information provided therein.

Figures

- 10 Figure 1 XRD Pattern of TF-RUB-50
- Figure 2 XRD Pattern of TF-BEA
- Figure 3 XRD Pattern of RUB-36
- 15 Figure 4 XRD Pattern of RUB-37
- Figure 5 XRD pattern of Mo/RUB-37, Mo/TF-RUB-50 and Mo/TF-BEA
- 20 Figure 6 ^{29}Si MAS NMR spectra of RUB-37, LEV and Beta
- Figure 7 ^{29}Si MAS NMR spectra of 6 wt.% Mo/RUB-37, Mo/LEV and Mo/Beta
- Figure 8 ^{27}Al MAS NMR spectra of RUB-37, LEV and Beta
- 25 Figure 9 ^{27}Al MAS NMR spectra of 6 wt.% Mo/RUB-37, Mo/LEV and Mo/Beta
- Figure 10 ^1H MAS NMR spectra of RUB-37, LEV and Beta
- 30 Figure 11 ^1H MAS NMR spectra of 6 wt.% Mo/RUB-37, Mo/LEV and Mo/Beta
- Figure 12 Reactor Concept
- Figure 13 Long term activity test: methane to ethylene reaction; Reaction with CH_4 / Re-
- 35 generation Cycle with H_2 : 10 min /30 min

Examples

- 40 Zeolite Preparation:
- Example 1: Preparation of template-free RUB-50 (TF-RUB-50)
- In the first step 1.42kg solid sodium hydroxide were dissolved in 32.71 l deionized water (DI H_2O). Afterwards 0.21kg sodium aluminate, 3.12kg fumed SiO_2 (Aerosil 200) and 2.38kg etha-

nol were added under stirring to the reaction mixture. After 5h, 0.155kg TF-RUB-50 seed crystals (prepared according to the description in Microporous and Mesoporous Materials 155 (2012), 1-7) were dispersed in the reaction mixture. The crystallization of TF-RUB-50 was done in a stirred steel autoclave at 120°C for 120h. After the reaction mixture was cooled down to room temperature, the obtained white solid was separated from the reaction mixture by filtration and subsequent washing with DI H₂O until a pH of 7 was reached in the washing fraction. Finally the solid was dried under N₂ at 120°C for 10h. To remove Na⁺ ions from the zeolite framework, 0.40kg Al-RUB-50 are dispersed in an ammonium nitrate solution (0.32kg NH₄NO₃ in 2.2 l DI H₂O) and stirred at 80°C for 2h. Afterwards, the solid is filtered and washed with H₂O to remove residual nitrate ions. The described ion exchange step is then repeated one more time. Finally, the obtained white solid is dried under air at 120°C for 10h.

The XRD pattern of TF-RUB-50 is depicted in Figure 1.

Elemental Analysis: C <0.5 g/100g, Al 8.2g/100g, Na 0.44g/100g, Si 33.5g/100g

N₂-Sorption at 77K: BET 476m²/g, Langmuir = 688m²/g

Example 2: Preparation of template-free Zeolite BEA (TF-BEA)

0.32 kg sodium aluminate 7.57kg DI H₂O and 0.06kg BEA seed crystals (CP814C derived from Zeolyst) are mixed under stirring at room temperature. Afterwards the reaction mixture is added into 8.06kg water glass (26.0wt-% SiO₂, 8.0%Na₂O in H₂O) under stirring at 200 rpm. The crystallization of TF-BEA was done in a steel autoclave at 120°C under stirring for 120h. After the reaction mixture was cooled down to room temperature, the obtained white solid was separated from the reaction mixture by filtration and subsequent washing with DI H₂O until a pH of 7 was reached in the washing fraction. Finally the solid was dried under N₂ at 120°C for 16h. For the removal of Na⁺ from the zeolite framework, 0.65kg TF-BEA are dispersed in an ammonium nitrate solution (0.65kg NH₄NO₃ in 5.8 l DI H₂O) in H₂O and stirring at 80°C for 2h. Afterwards, the solid is filtered and washed with H₂O to remove residual nitrate ions. Finally, the obtained white solid is dried under air at 120°C for 10h.

The XRD pattern of TF-BEA is depicted in Figure 2.

Elemental Analysis: C <0.5 g/100g, Al 6.8g/100g, Na 0.1g/100g, Si 31.0g/100g

N₂-Sorption at 77K: BET 530m²/g, Langmuir = 692m²/g

Example 3: Preparation of RUB-37

Step 1: Synthesis of RUB-36

0.04kg sodium aluminate are dissolved in 13.05kg of a 20.62wt-% solution of diethyl dimethyl ammonium hydroxide in DI H₂O. Then, 0.09kg sodium hydroxide were added under stirring to the reaction gel followed by the addition of fumed SiO₂ (Aerosil 200). Finally 0.08kg RUB-36 seed crystals (prepared according to the description in Chem. Mater. 2012, 24, 1536–1545) were dispersed in the reaction gel. At 105°C, 2.16kg H₂O were removed from the gel by distillation to adjust the concentration of diethyl dimethyl ammonium hydroxide. The crystallization of RUB-36 was done in a steel autoclave at 150°C under stirring for 192h. After the reaction mixture was cooled down to room temperature, the obtained white solid was separated from the reaction mixture by filtration and subsequent washing with DI H₂O until a pH of 7 was reached in the washing fraction. The solid was dried under air at 120°C for 16h.

The XRD pattern of RUB-36 is depicted in Figure 3.

Elemental Analysis: C <0.5 g/100g, Al 0.37g/100g, Na 0.36g/100g, Si 36.0g/100g

Step 2: Synthesis of RUB-37

- 5 RUB-36 is calcined at 600°C for 10h (heating rate 1 K/min) transforming to obtain RUB-37 through interlayer condensation. To remove Na⁺ from the zeolite framework, 0.21kg RUB-37 are dispersed in an ammonium nitrate solution (0.44kg dissolved in 3.9 l DI H₂O) and heated under stirring to 80°C for 2h. Afterwards, the solid is filtered and washed with H₂O to remove residual nitrate ions. The described ion exchange step is then repeated one more time. Finally, the ob-
- 10 tained white solid is dried under air at 120°C for 10h.

The XRD pattern of RUB-37 is depicted in Figure 4.

Elemental Analysis: Al 0.53g/100g, Si 35.0g/100g

BET 334m²/g

- 15 Example 4: Preparation of CHA + SAPO-34 (this example is identical with Example 1 of WO 2013/038372):

Step 1: Preparation of the Chabazite seed crystals

- 38.95 kg of a trimethyl-1-adamantylammonium hydroxide solution (TMAA, 13.4 wt.-% in water) were placed in an autoclave. Subsequently, 2.65 kg of a 50% sodium hydroxide solution were
- 20 added and the resulting mixture stirred until the solution was clear. 4.26 kg aluminum triisopropoxide (ATIP, Aldrich) were then added within 5-15 minutes, and stirring was continued for about 2 hours until the solids were reacted and the solution was a uniform suspension. Subsequently, 50 kg Ludox AS-40 were added while stirring to obtain a composition having molar ratios of 36 SiO₂ : 1.1 Al₂O₃ : 2.6 TMAA : 1.8 Na₂O : 377 H₂O.

- 25 The autoclave was then sealed and heated to a temperature of 170 °C and maintained at that temperature for 20 hours under stirring at 200 rpm. The pressure within the autoclave was 7.8 bar, and the pH was 13.4 at the beginning of the reaction. The autoclave was then cooled to 35 °C, thus obtaining a suspension having a pH of 11.9. Per 1 kg of reactor content 168 g of diluted acid were added. About 80% of the calculated total amount of premixed nitric acid (10 wt.-%
- 30 aqueous solution) was fed into the reactor under agitation. About 20% were slowly added in smaller portions until pH reached about 7-7.5. The resulting mixture was then filtrated with a filter press, and the filter cake was washed with deionized water to a conductivity of 200 microSiemens/cm. The wet product was heated to a temperature of 120 °C in air within 30 min and dried at that temperature for 4 hours. The dried product was then heated to a temperature
- 35 of 600 °C within 4 hours and calcined in air at 600 °C for 5 hours to afford zeolite crystals having a CHA framework as observed by XRD.

- For preparing the ammonium form of the calcined zeolite crystals an ammonium nitrate solution was prepared by mixing 55.6 g of 54 wt.-% ammonium nitrate with 530 g of deionized water at
- 40 80 °C. 300 g of the calcined zeolitic material was then added to this solution. The ion-exchange reaction between the Na/H-form of the zeolitic material and the ammonium ions was carried out by agitating the slurry at 60 °C for 1 hour. The pH was between 2.7 and 2.4 during the reaction.

The resulting mixture was then filtered, washed until the filtrate had a conductivity of < 200 microSiemens/cm, and the washed sample finally air dried.

The Si : Al molar ratio of the Chabazite seed crystals amounted to 16.7 as measured by inductively coupled plasma (ICP).

5

Step 2: Synthesis of a Chabazite/SAPO-34 core-shell zeolite

2.914 g of Boehmite (Al_2O_3 , 70 wt.%) were added into 14.696 g of H_2O . After stirring at room temperature for 1 h, 2.132 mL of H_3PO_4 were added. After stirring at room temperature for 1 h, 2.286 g of silica sol gel (31.5wt%) were added, followed by addition of 4.14 mL of DEA (diethylamine) used as the organotemplate. After stirring at room temperature for 12 h, 0.2 g of the Chabazite seed crystals was added into the gel. After stirring at room temperature for 15 min, the gel was placed into an autoclave for crystallization at 200 °C for 12 h. After having let the reaction mixture cool to room temperature, the crystallization product was filtered off from the mother liquor and dried.

15

Catalyst Preparation

The concentration of the respective metal solution is calculated as metal per solvent and indicated as wt. %.

20 Catalyst Preparation of supported Mo catalysts

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was used as Mo precursor to prepare supported Mo catalysts, such as Mo/RUB-37, Mo/TF-RUB-50 or Mo/TF-BEA. The respective zeolites were used in H-form.

Catalyst Preparation of Mo/RUB-37

25 6 wt-% Mo/RUB-37 was prepared as follows: 1.0g dried RUB-37 (H-form) was incipient impregnated by 1.2ml 4.6 wt.% Mo water solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, and firstly dried under vacuum at room temperature, then dried at 100°C in an oven for 12h in air. Finally, the catalyst was calcined under air at 500°C for 6h.

The other Mo catalysts have been prepared accordingly.

30

Catalyst Preparation of supported Mo-Fe catalysts

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was used as Mo precursor and $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was used as Fe precursor to prepare supported Mo-Fe catalysts such as Mo-Fe/RUB-37 or Mo-Fe/CHA+SAPO-34. The respective zeolites and/or zeolite-analogous materials were used in H-form.

35 Catalyst Preparation of Mo-Fe/CHA+SAPO-34

6 wt-% Mo-0.5wt% Fe/CHA+SAPO-34 was prepared as follows: 1.0g dried CHA/SAPO was incipient impregnated by 1.2ml 4.6 wt.% Mo water solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and 1 ml 3.6 wt% Fe water solution of $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, and firstly dried under vacuum at room temperature, then dried at 100°C in an oven for 12h in air. Finally, the catalyst was calcined under air at 40 500°C for 6h.

The other Mo-Fe catalysts have been prepared accordingly.

Catalyst Preparation of supported Mo-Ni catalysts

(NH₄)₆Mo₇O₂₄·4H₂O was used as Mo precursor and Ni(NO₃)₃·6H₂O was used as Fe precursor to prepare supported Mo-Ni catalysts such as Mo-Ni/RUB-37. The respective zeolites and/or zeolite-analogous materials were used in H-form.

5

Catalyst Preparation of Mo-Ni/RUB-37

6 wt-% Mo-0.5wt% Ni/RUB-37 was prepared as follows: 1.0g dried RUB-37 was incipient impregnated by 1.2ml 4.6 wt.% Mo water solution of (NH₄)₆Mo₇O₂₄·4H₂O and 1 ml 2.5 wt% Ni water solution of Ni(NO₃)₃·6H₂O, and firstly dried under vacuum at room temperature, then dried at 100°C in an oven for 12h in air. Finally, the catalyst was calcined under air at 500°C for 6h. The other Mo-Ni catalysts have been prepared accordingly.

10

Catalyst Preparation of supported Mo-Co catalysts

(NH₄)₆Mo₇O₂₄·4H₂O was used as Mo precursor and Co(NO₃)₃·6H₂O was used as Co precursor to prepare supported Mo-Co catalysts. The respective zeolites and/or zeolite-analogous materials were used in H-form.

15

Catalyst characterization

Table 2: Loadings of Mo/zeolite (based on the amount of zeolite)

Theoretical loadings of Catalysts	Loadings of Mo <ICP analysis>
6wt.% Mo/RUB-37	5.92wt-%
6wt.% Mo/RUB-50	5.90wt-%
6wt.% Mo/Beta	6.03wt-%

20

The XRD patterns of Mo/RUB-37, Mo/TF-RUB-50 and Mo/ TF-BEA are depicted in Figure 5.

The ²⁹SiMAS NMR spectra of RUB-37, LEV, Beta, Mo/RUB-37, Mo/LEV, and Mo/Beta are depicted in Figure 6 and Figure 7, respectively.

25

The ²⁷Al MAS NMR spectra of RUB-37, LEV, Beta (left) and 6 wt.% Mo/RUB-37, Mo/LEV, Mo/Beta (right) are depicted in Figure 8 and Figure 9, respectively.

The ¹H MAS NMR spectra of RUB-37, LEV, Beta (left) and 6 wt.% Mo/RUB-37, Mo/LEV, Mo/Beta (right) are depicted in Figure 10 and Figure 11, respectively.

30

Catalytic testing

The supported Mo catalyst was pelleted to 40-60 mesh at 2Mpa, and then loaded into single pass fix-bed catalytical evaluation device with a transparent and visible tube furnace. Subsequently, the catalysts were activated at 600 °C with CH₄ (30ml/min) for 30min, and further elevated with 10°C/min to ca 750°C, and then reaction gas was switched to the evaluation device. The catalytic reaction was conducted under 0.1Mpa CH₄/N₂=90/10 (N₂ as internal standard) with a gas space hour velocity 2400 h⁻¹. The reaction and regeneration process is a periodic CH₄/H₂

35

switching, e.g. after reaction gas (CH₄/N₂) was conducted into the device for 10min, regeneration gas (25ml/min, H₂) switched into the device for 30min.

Analysis

- 5 All gas lines after the reactor were kept at 120 °C. The effluents were analyzed by an online GC (Agilent 7890A), which was equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Four chromatography columns were installed, i.e. Porapak Q and 5 Å molecular sieves packed columns, and modified Al₂O₃ and FFAP capillary columns.

10 Table 3: Catalysis Results with one metal

Catalyst	Mo/ RUB-37	Mo/ TF-RUB- 50	Mo/ CHA + SAPO-34	Mo/ SAPO-34	Mo/ HZSM-5	Mo/ TF-BEA
inv = inventive; comp = comparative	inv	inv	inv	comp	comp	comp
CH ₄ conversion (%)	3.0	5.3	4.2	1.8	15	19.1
CO (%)	5.8	4.5	8.9	5.9	1.8	3.5
C ₂ H ₄ selectivity (%)	18	15.3	22.0	22.9	3.3	2.1
C ₂ H ₆ selectivity (%)	2.3	2.0	5.3	3.2	0.9	0.5
C ₃ ⁺ =, C ₃ ⁺ (%)	1.4	2.6	4.0	1.3	2.9	3.3
C ₆ H ₆ selectivity (%)	1.7	7.6	1.5	0.9	52.5	6.2
C ₁₀ H ₈ selectivity (%)	0.3	1.5	0.6	0.4	0.5	3.4
Coke (%)	67	65	60	65	37.1	80

Table 3a: Catalysis Results with two metals

Catalyst	Mo, Ni/ RUB-37	Mo, Fe / CHA + SAPO-34
inv = inventive; comp = comparative	inv	inv
CH ₄ conversion (%)	4.5	6.8

CO (%)	10	8.9
C ₂ H ₄ selectivity (%)	23	28.5
C ₂ H ₆ selectivity (%)	4.4	5.0
C ₃ ⁺ -,C ₃ ⁺ (%)	2.3	4.3
C ₆ H ₆ selectivity (%)	3.8	1.5
C ₁₀ H ₈ selectivity (%)	1.5	0.6
Coke (%)	55	51.5

Regeneration of the catalyst:

5 Table 4: Non-oxygen coupling of Methane to ethylene over Mo/RUB-37

Entry	Conv. (%)	Time on Stream ^a	Sel. (%)							
	Methane		CO	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ ⁺ -,C ₃ ⁺	C ₆ H ₆	C ₁₀ H ₈	Coke
1	4.2	10min	5.6	0.15	15	1.1	1.2	1.6	0.1	75
2	3.0	40min	5.8	0.5	18	2.3	1.4	1.7	0.3	67
3	2.8	80min	4.8	1.2	19	2.7	1.3	1.5	0.2	68
4	2.8	120min	3.3	0.7	20	2.4	1.6	1	0.1	70.6
5	2.6	160min	4.8	0.96	18	2.7	0.8	0.1	0.2	73.5

The interval of entry 1 and 2 is 30min, which is a regeneration process

Claims

1. A process comprising the step of converting methane to ethene under non-oxidative conditions in the presence of a catalyst comprising
- 5 (a) a small-pore zeolite;
(b) a metal
whereas the metal (b) is loaded onto the small-pore zeolite (a).
2. A process of claim 1 wherein the small-pore zeolite (a) is selected from the structural group consisting of LEV, CHA, CDO and mixtures thereof.
- 10 3. A process of claim 1 or 2 wherein the small-pore zeolite (a) is selected from the group consisting of RUB-37, RUB-50, LEV and mixtures thereof.
- 15 4. A process of any of claims 1 to 3 wherein the metal (b) is selected from the group consisting of Mo, Fe, Co, Ni, Cu, Ag, Mg, W, Re, Ga, Ru, Rh, Pd, Ir, Pt and mixtures thereof, preferred Mo.
- 20 5. A process of any of claims 1 to 4 wherein the amount of metal (b) is higher than 4 wt%, preferred 5 wt% or more, more preferred 6 wt% or more, based on the total weight of the catalyst.
- 25 6. A process of any of claims 1 to 5 wherein the catalyst further comprises (c) a further component selected from the group consisting of
(c1) at least one further small-pore zeolite different from (a);
(c2) at least one small-pore zeolite analogous material;
(c3) at least one further metal different from (b); and
mixtures thereof,
- 30 whereas the metal (b) and –if applicable- the at least one further metal (c3) is/are loaded onto
- the small-pore zeolite (a) and/or
- -if applicable- the at least one further small-pore zeolite (c1) and/or
- -if applicable- the at least one small-pore zeolite analogous material (c2).
- 35
7. A process of claim 6 wherein the catalyst comprises
- a small-pore zeolite (a) and at least one small-pore zeolite (c1); and
- at least one metal (b) which is loaded onto at least one of the small-pore zeolites (a) and (c1).
- 40
8. A process of claim 6 wherein the catalyst comprises
- a small-pore zeolite (a);

- at least one small-pore zeolite analogous material (c2);
- at least one metal (b) which is loaded onto a small-pore zeolite (a) and/or at least one small-pore zeolite analogous material (c2).

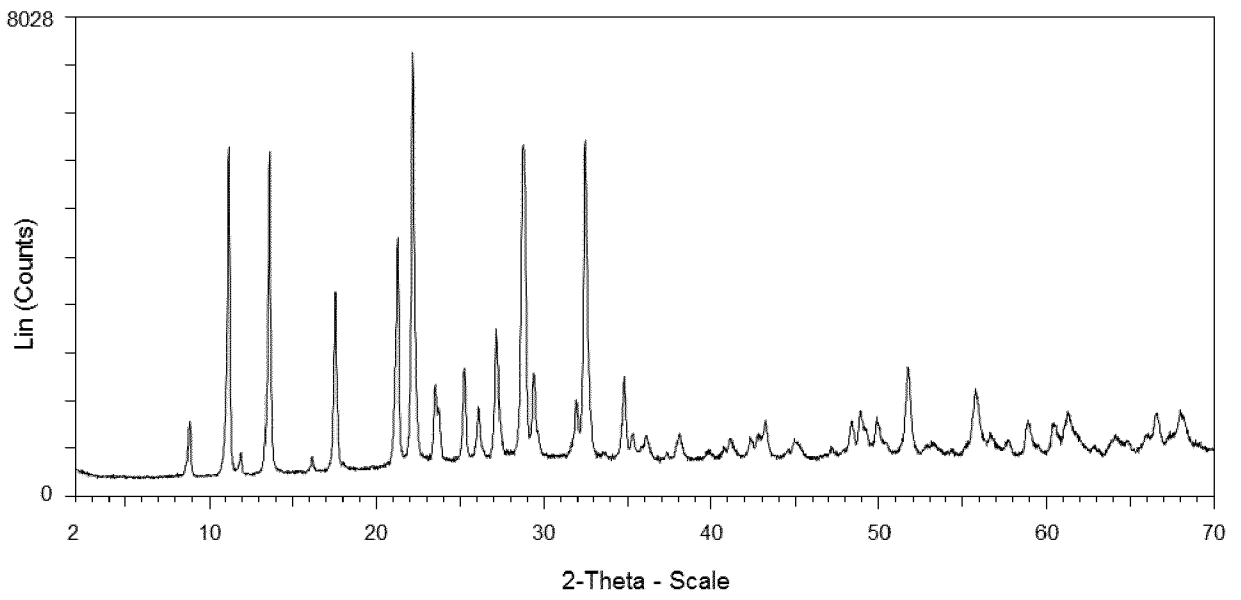
- 5 9. A process of any of claims 6 to 8 wherein the small-pore zeolite (a) is selected from the structural group consisting of LEV, CHA, CDO and mixtures thereof.
10. A process of any of claims 6 to 9 wherein the small-pore zeolite (a) is selected from the group consisting of RUB-37, RUB-50, LEV and mixtures thereof.
- 10 11. A process of any of claims 6 to 10 wherein the metal (b) is selected from the group consisting of Mo, Fe, Co, Ni, Cu, Ag, Mg, W, Re, Ga, Ru, Rh, Pd, Ir, Pt and mixtures thereof, preferred selected from the group consisting of Mo, Fe, Co, Ni, Cu and mixtures thereof, more preferred Mo.
- 15 12. A process of any of claims 6 to 11 wherein the amount of the metal (b) is higher than 4 wt%, preferred 5 wt% or more, more preferred 6 wt% or more, based on the total weight of the catalyst.
- 20 13. A process of any of claims 6 to 12 wherein the catalyst comprises at least two different metals (b) and (c3) which are selected from the group consisting of Mo, Fe, Co, Ni, Cu, Ag, Mg, W, Re, Ga, Ru, Rh, Pd, Ir, Pt and mixtures thereof, preferred Fe, Co, Ni, Cu and mixtures thereof, more preferred Mo-Fe, Mo-Co and Mo-Ni.
- 25 14. A process of any of claims 1 to 13 further comprising a regeneration step.
15. A process of claim 14 in the presence of hydrogen.
16. A process of claim 14 or 15 wherein coke is reacted to volatile organic compounds, preferred methane.
- 30 17. A process of any of claims 14 to 16 which is performed in parallel reactors.
18. A process of claim 17 wherein the step of converting methane to ethane is performed in at least one reactor and the regeneration step is performed simultaneously in at least one other reactor.
- 35 19. Catalyst comprising
- 40 (a) a small-pore zeolite;
- (b) a metal; and
- (c) a further component selected from the group consisting of
- (c1) at least one further small-pore zeolite and/or
 - (c2) at least one small-pore zeolite analogous material and/or

(c3) at least one further metal different from (b)

whereas the metal (b) and –if applicable- the at least one further metal (c3) is/are loaded onto

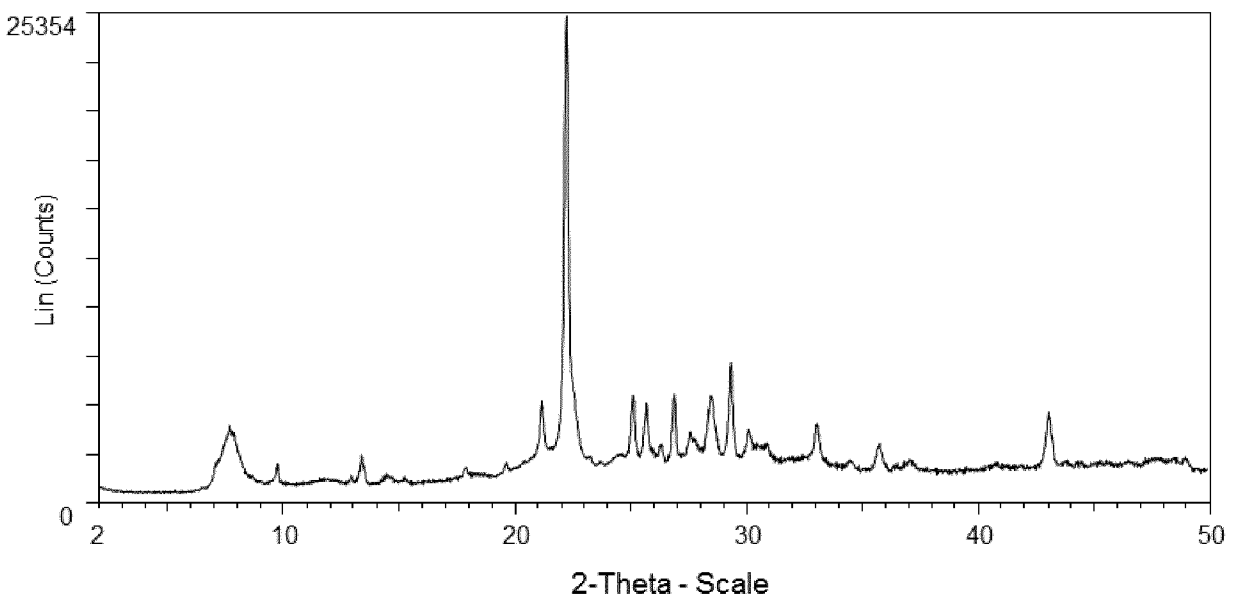
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- the small-pore zeolite (a) and/or
- -if applicable- the at least one further small-pore zeolite (c1) and/or
- -if applicable- the at least one small-pore zeolite analogous material (c2).
20. Catalyst according to claim 19 comprising
10
- a small-pore zeolite (a) and at least one small-pore zeolite (c1); and
- at least one metal (b) which is loaded onto at least one of the small-pore zeolites (a) and (c1).
21. Catalyst according to claim 19 comprising
15
- a small-pore zeolite (a);
- at least one small-pore zeolite analogous material (c2);
- at least one metal (b) which is loaded onto a small-pore zeolite (a) and/or at least one small-pore zeolite analogous material (c2).
- 20 22. Catalyst according to any of claims 19 to 21 wherein at least one small-pore zeolite (a) is selected from the structural group consisting of LEV, CHA , CDO and mixtures thereof.
23. Catalyst according to any of claims 19 to 22 wherein the small-pore zeolite (a) is
25 selected from the group consisting of RUB-37, RUB-50, LEV and mixtures thereof.
24. Catalyst according to any of claims 19 to 23 wherein the metal (b) is selected from
the group consisting of Mo, Fe, Co, Ni, Cu, Ag, Mg, W, Re, Ga, Ru, Rh, Pd, Ir, Pt
and mixtures thereof, preferred selected from the group consisting of Mo, Fe, Co, Ni,
30 Cu and mixtures thereof, more preferred Mo.
25. Catalyst according to any of claims 19 to 24 wherein the amount of the metal (b) is
higher than 4 wt%, preferred 5 wt% or more, more preferred 6 wt% or more, based
on the total weight of the catalyst.
35
26. Catalyst according to any of claims 19 to 25 comprising a metal (b) and an at least
one further metal (c3) different from (b) which are selected from the group consisting
of Mo, Fe, Co, Ni, Cu, Ag, Mg, W, Re, Ga, Ru, Rh, Pd, Ir, Pt and mixtures thereof,
preferred Fe, Co, Ni, Cu and mixtures thereof, more preferred Mo-Fe, Mo-Co and
40 Mo-Ni.

Figure 1



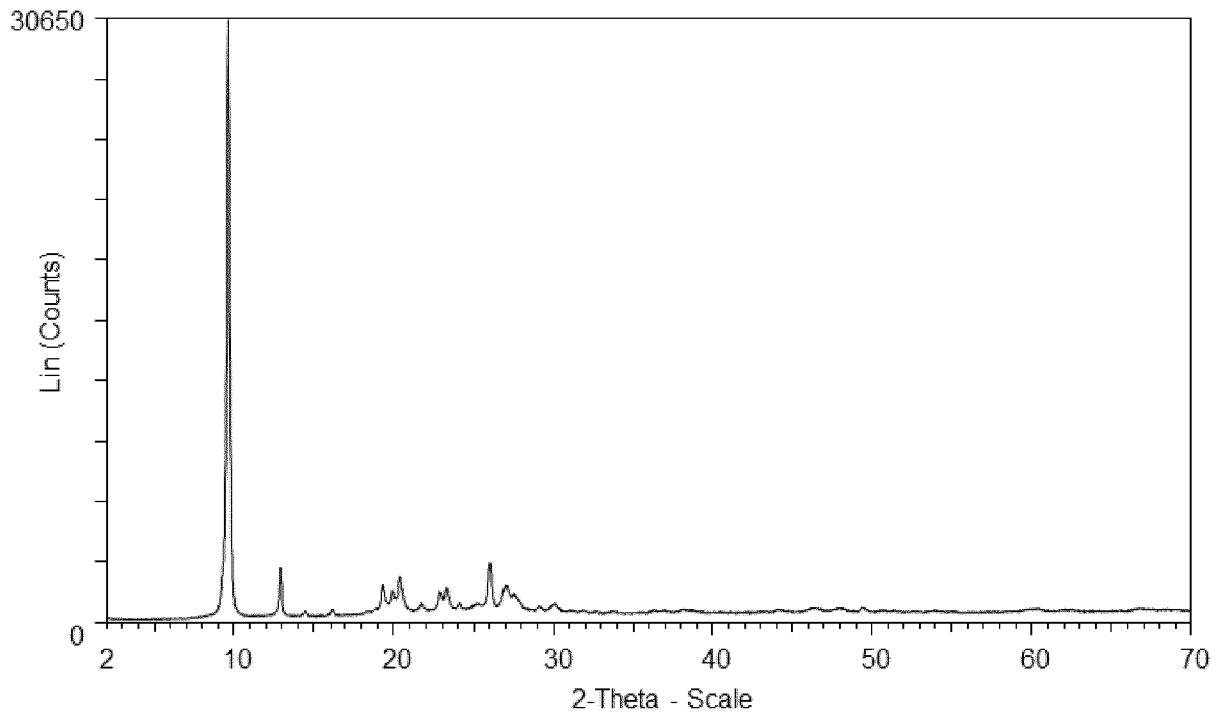
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Figure 2



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Figure 3



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Figure 4

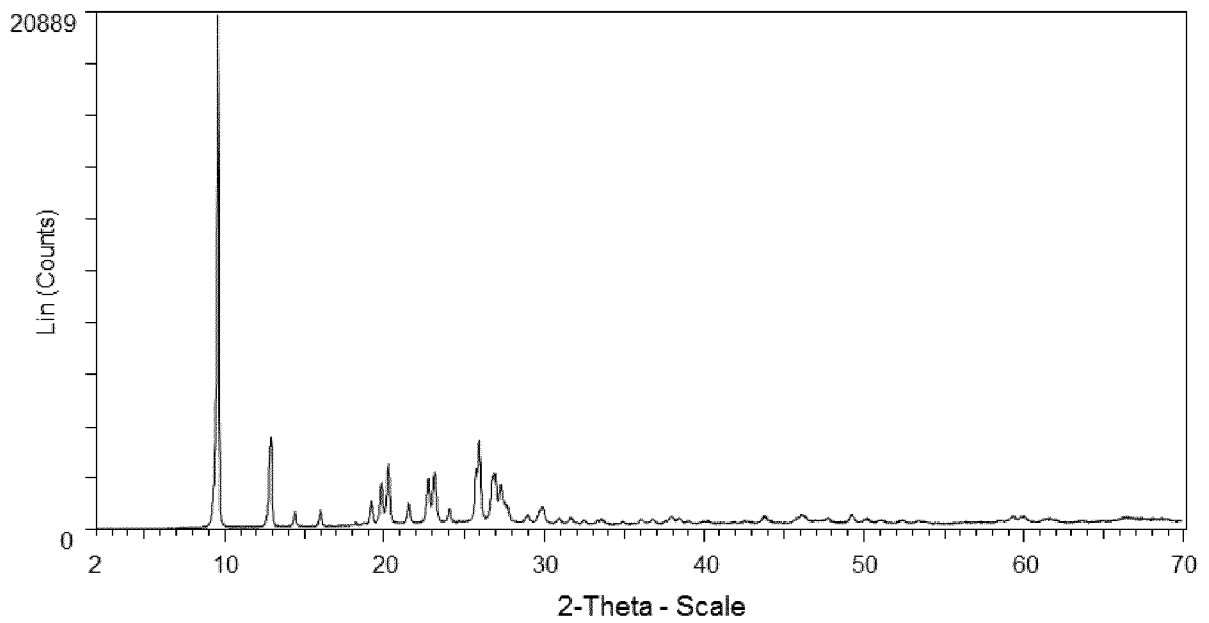
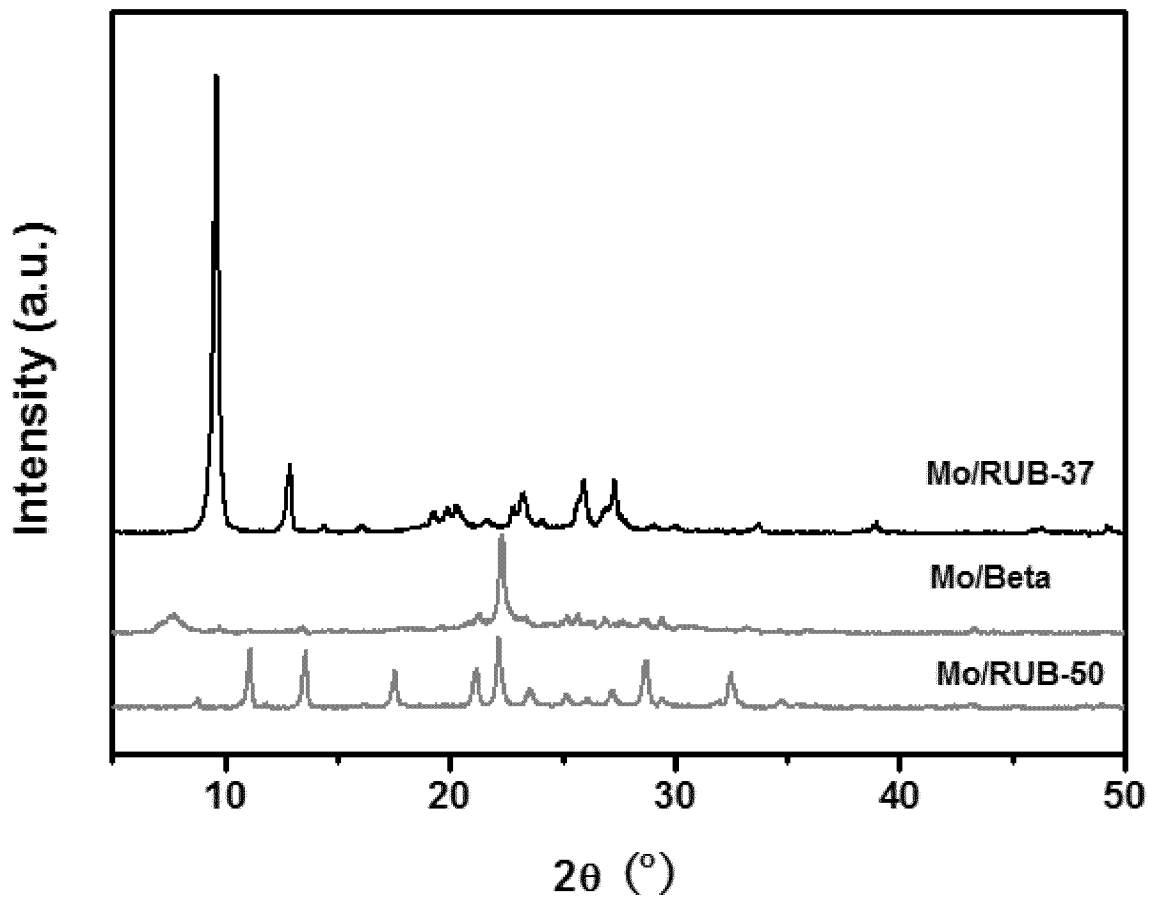
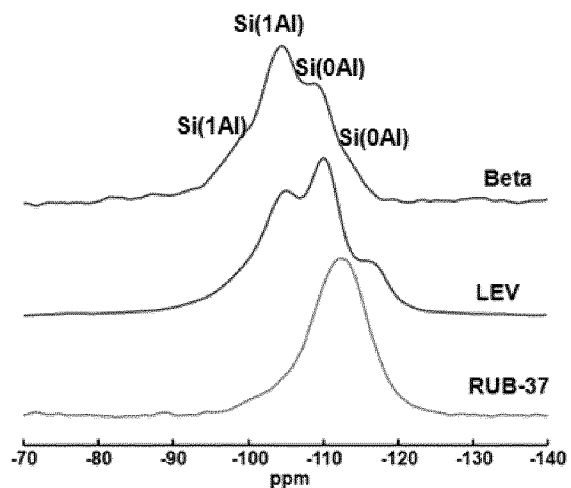


Figure 5



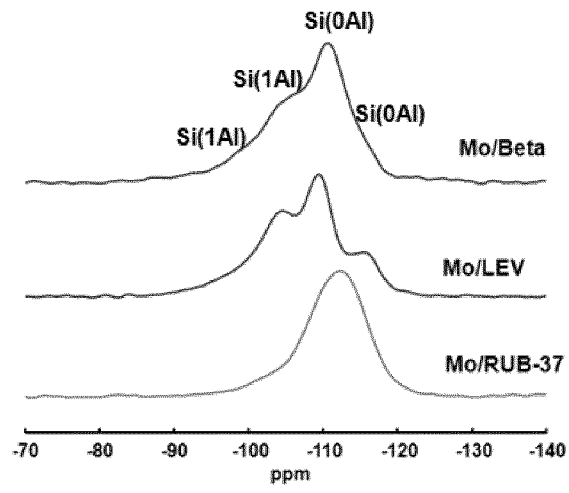
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Figure 6

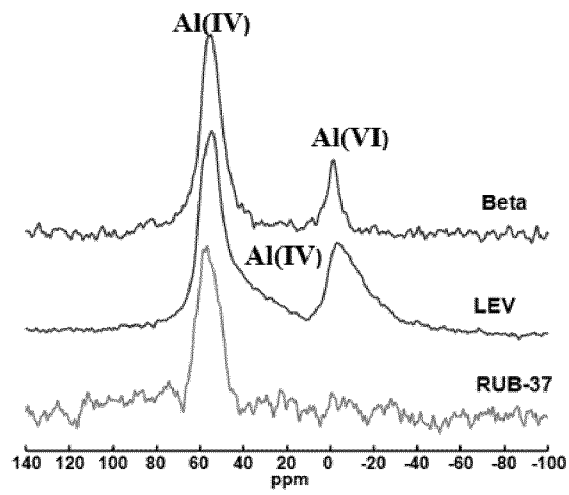


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Figure 7



5 Figure 8



10 Figure 9

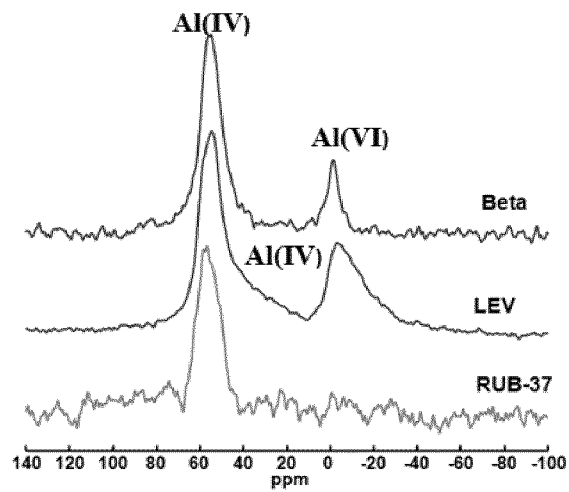
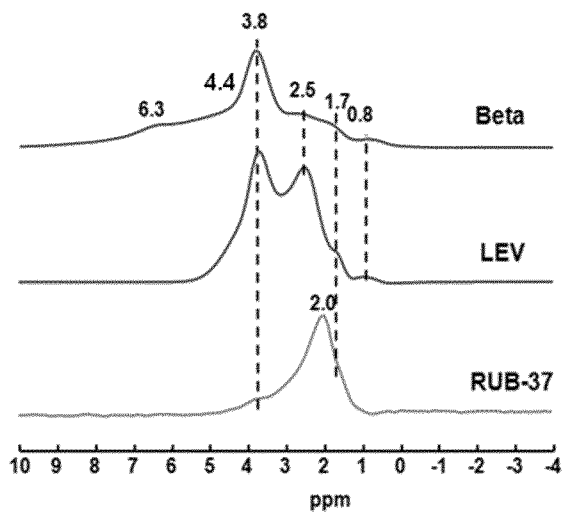


Figure 10



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Figure 11

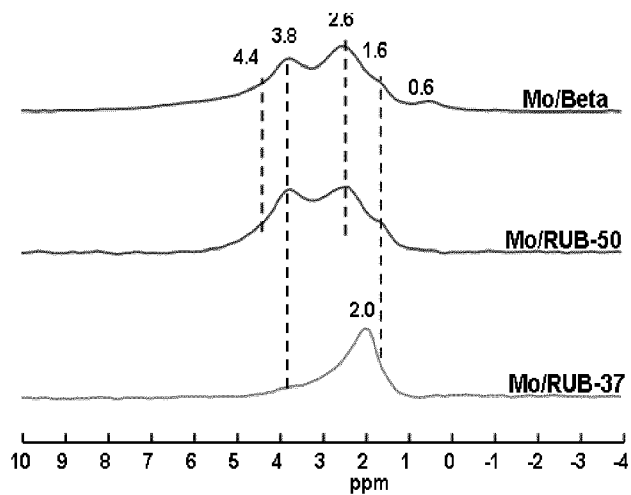
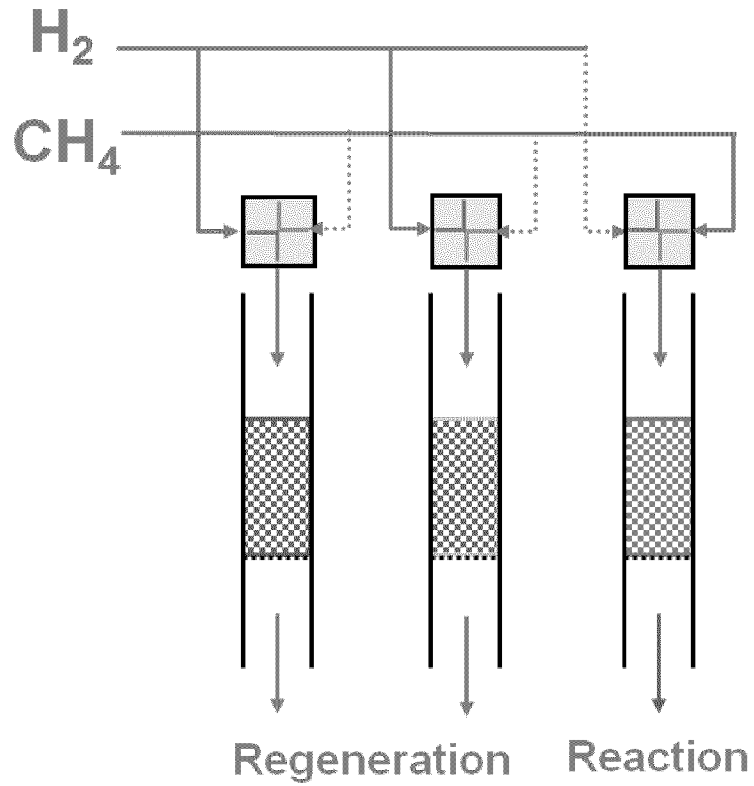
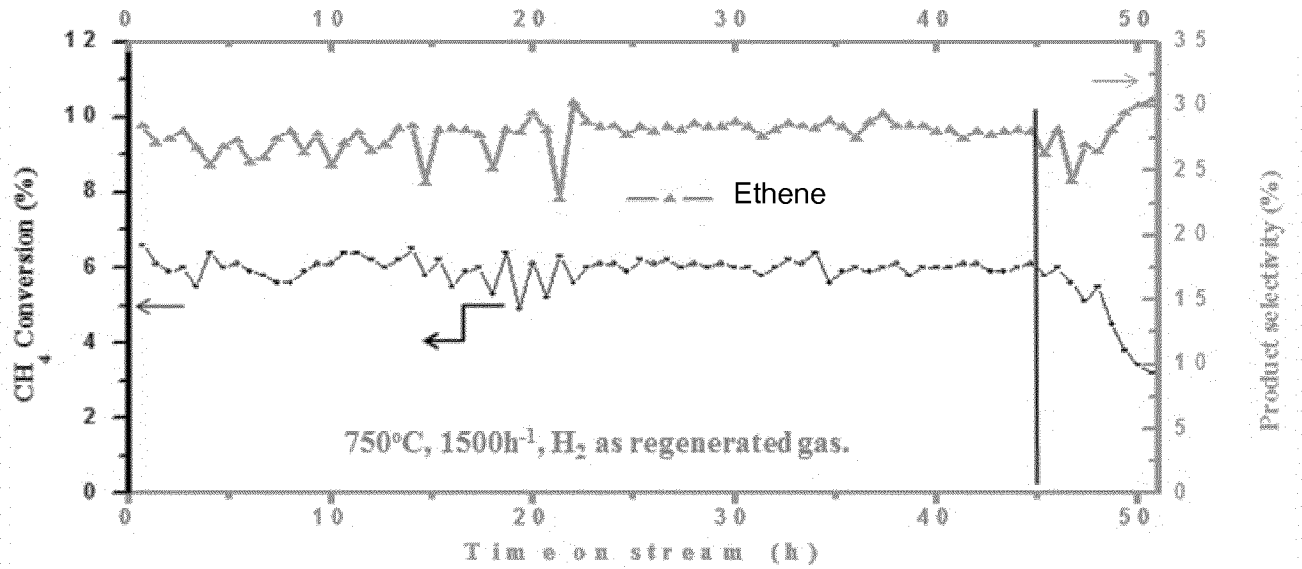


Figure 12



5 Figure 13



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/066788

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C2/84 C07C11/04
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C07C
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHRISTOPHER L. GORDON ET.AL.: "Ethylene production using a Pd and Ag-Pd-Y-Zeolite catalyst in a DC plasma reactor", CATALYSIS TODAY, vol. 84, 2003, pages 51-75, XP002730026, page 52, left column, lines 18-26; figures 1,2,4	1-18
A	----- WO 2005/005042 A1 (HRD CORP [US]; NAT PETROCHEMICAL COMPANY PETR [IR]) 20 January 2005 (2005-01-20) claims 1-27 ----- -/--	1-26

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
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- "&" document member of the same patent family

Date of the actual completion of the international search 22 September 2014	Date of mailing of the international search report 09/10/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Kleidernigg, Oliver

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/066788

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>ALTWASSER ET AL: "Ruthenium-containing small-pore zeolites for shape-selective catalysis", MICROPOROUS AND MESOPOROUS MATERIALS, ELSEVIER SCIENCE PUBLISHING, NEW YORK, US, vol. 104, no. 1-3, 31 July 2007 (2007-07-31), pages 281-288, XP022180612, ISSN: 1387-1811, DOI: 10.1016/J.MICROMESO.2007.02.046 pages 284-286, paragraph 3.1.2; tables 1,5</p> <p style="text-align: center;">-----</p>	19-26
X	<p>WO 2008/132452 A2 (JOHNSON MATTHEY PLC [GB]; ANDERSEN PAUL JOSEPH [US]; BAILIE JILLIAN EL) 6 November 2008 (2008-11-06) table 1</p> <p style="text-align: center;">-----</p>	19

INTERNATIONAL SEARCH REPORT

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International application No

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