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(54) Title: METAL DOPED SILICATE CATALYSTS FOR THE SELECTIVE CONVERSION OF ETHANOL TO BUTADIENE

(57) Abstract: The present invention relates to a process for the preparation of butadiene comprising (i) providing a gas stream G-comprising ethanol; (ii) contacting the gas stream G- provided in (i) with a catalyst, thereby obtaining a gas stream G-2 comprising butadiene; wherein the catalyst comprises a crystalline material supporting one or more catalytically active metals M, as well as to the use of the crystalline material supporting one or more catalytically active metals M.



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Metal doped silicate catalysts for the selective conversion of ethanol to butadiene

The present invention relates to a process for the preparation of butadiene using a catalyst comprising a crystalline material supporting one or more catalytically active metals M. The present invention further relates to a the use of a crystalline material supporting one or more catalytically active metals M, as a catalytically active material for the preparation of butadiene, preferably from a gas stream comprising ethanol and optionally comprising acetaldehyde.

INTRODUCTION

Butadiene is widely used in the chemical industry, for example as monomer and/or comonomer for the polymerization of elastomers. Currently, butadiene is almost entirely produced as a by-product of ethylene stem cracking of naphtha or gas oil feedstock. Due to increasing prices of oil, alternative methods for producing butadiene are of major interest.

In GB 331482 a process for the preparation of butadiene is described, wherein ethanol is contacted with aluminum oxide mixed with zinc oxide. However this process leads to a low yield of butadiene of 18 %.

In Ind. Eng. Chem. 41 (1949), pages 1012-1017, the preparation of butadiene by a two step process is described. In the first step ethanol is dehydrogenated to acetaldehyde. In the second step, the obtained acetaldehyde is mixed with ethanol and converted to butadiene by use of impregnated catalysts. By use of the most efficient catalyst which comprises 2.3 weight % tantalum oxide on amorphous silica, a selectivity of butadiene of up to 69 % and a conversion of the starting material of 34 % were achieved for 8 h on stream. However, due to the price of tantalum, the catalyst is relatively expensive.

Furthermore, US 2421361 discloses a process for the preparation of butadiene which comprises passing an acyclic mono-olefinic aldehyde like crotonaldehyde or acetaldehyde and a monohydric alcohol like ethanol over a catalyst of the group of zirconium oxide, tantalum oxide, columbium oxide and combinations of these oxides with amorphous silica. By use of the catalyst containing 2 weight-% of zirconium oxide, a 47 % single-pass yield of the butadiene fraction was obtained which contained about 93 weight-% butadiene.

In WO 2012/015340 A1 a process for the preparation of butadiene is disclosed by use of a solid catalyst containing metals chosen from the group of silver, gold or copper, and metal oxides, chosen from the group of magnesium, titanium, zirconium, tantalum or niobium oxide. However, only low conversion rates in the range of from 6 to 64 % were achieved in this process, wherein these values were determined during only 3 h time on stream.

The use of a variety of silica impregnated bi- and trimetallic catalysts for the conversion of ethanol and a mixture of ethanol and acetaldehyde to butadiene is described in M.D. Jones et al., Catal. Sci. Technol. 1 (2011), 267-272. However, all catalysts tended to show a reduced conversion rate over a period of 3 h.

DETAILED DESCRIPTION

Thus, it was an object of the present invention to provide a process for the preparation of butadiene which does not exhibit the disadvantages of the methods according to the prior art and wherein a high conversion of the starting material as well as a high selectivity to butadiene is achieved. Furthermore, it was an object of the present invention to improve the long term activity of the catalyst used.

Surprisingly, it was found that by a process for the preparation of butadiene in the presence of a catalyst comprising a crystalline material supporting one or more catalytically active metals M, an unexpectedly high conversion of the starting material and at the same time also a high selectivity towards butadiene is achieved. Further, it was surprisingly found that the catalysts used in the process of the present invention show an improved long time activity compared to the catalysts used in the prior art.

Therefore, the present invention relates to a process for the preparation of butadiene comprising

- (i) providing a gas stream G-1 comprising ethanol;
 - (ii) contacting the gas stream G-1 provided in (i) with a catalyst, thereby obtaining a gas stream G-2 comprising butadiene;
- wherein the catalyst comprises a crystalline material supporting one or more catalytically active metals M.

In the inventive process, a gas stream G-1 comprising ethanol is provided in step (i) and subsequently contacted with a catalyst in step (ii). According to a preferred embodiment of the present invention, the gas stream G-1 further comprises acetaldehyde.

Concerning the gas stream G-1 provided in step (i), no particular restriction applies according to the present invention relative to the composition of the gas stream G-1 regarding ethanol and optionally acetaldehyde contained therein, provided that after contacting the gas stream G-1 with a catalyst in step (ii), a gas stream G-2 comprising butadiene is obtained. Thus, in general, no specific restrictions exist concerning the molar ratio of ethanol to acetaldehyde in the gas stream G-1. According to a preferred embodiment of the present invention, the molar ratio of ethanol to acetaldehyde in the gas stream G-1 is in the range of from 1 : 1 to 6 : 1, preferably from 2 : 1 to 3.5 : 1, more preferably from 2.5 : 1 to 2.9 : 1.

Concerning the composition of the gas stream G-1 provided in (i), prior to contacting with the catalyst, no specific restrictions exist regarding the amount of ethanol or the mixture of ethanol and acetaldehyde comprised in the gas stream G-1, respectively. Thus, according to a preferred embodiment of the present invention, 70 vol.-% or more, preferably 75 vol.-% or more, more preferably 80 vol.-% or more of the gas stream G-1 comprises ethanol or a mixture of ethanol and acetaldehyde. It is further preferred that prior to contacting with the catalyst, 85 vol.-% or more, preferably 90 vol.-% or more, more preferably 95 vol.-% or more of the gas stream G-1 comprises ethanol or of a mixture of ethanol and acetaldehyde. Therefore, according to a preferred embodiment of the present invention, 80 vol.-% or more of the gas stream G-1 comprises ethanol or of a mixture of ethanol and acetaldehyde, wherein preferably 90 vol.-% or more, more preferably 95 vol.-% or more of the gas stream G-1 comprises ethanol or of a mixture of ethanol and acetaldehyde.

As to the content of the one or more catalytically active metals M in the crystalline material comprised in the catalyst, in general, no specific restrictions exist, provided that the catalyst comprising the crystalline material supporting one or more catalytically active metals M can be used as catalytically active material for the preparation of butadiene, preferably from a gas stream comprising ethanol and optionally comprising acetaldehyde. Thus, according to a preferred embodiment of the present invention, the content of the one or more catalytically active metals M in the crystalline material comprised in the catalyst is in the range of from 0.1 to 25 weight-%, preferably from 0.2 to 15 weight-%, more preferably from 0.3 to 10 weight-%, more preferably from 0.4 to 8 weight-%, more preferably from 0.5 to 6 weight-%, wherein M is calculated as the element and based on the total weight of the crystalline material.

Thus, according to a particular preferred embodiment of the present invention, the content of the one or more catalytically active metals M in the crystalline material comprised in the catalyst is in the range of from 0.1 to 25 weight-%, preferably from 0.3 to 10 weight-%, more preferably from 0.5 to 6 weight-%, wherein M is calculated as the element and based on the total weight of the crystalline material.

According to the present invention, the gas stream G-1 comprising ethanol provided in step (i) is subsequently contacted with a catalyst in step (ii), wherein the catalyst comprises a crystalline material supporting one or more catalytically active metals M. In general, no specific restrictions exist concerning the chemical nature of the one or more catalytically active metals M. According to a preferred embodiment of the present invention, M is selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, Ta, Mn, Hf, Nb, Ga, Ge, and combinations of two or more thereof, preferably selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, and combinations of two or more thereof, more preferably selected from the group consisting of Cr, Co, Cu, Zn, Zr, and combinations of two or more thereof.

Therefore, according to a particularly preferred embodiment of the present invention, the gas stream G-1 comprising ethanol provided in step (i) is subsequently contacted with a catalyst in step (ii), wherein the catalyst comprises a crystalline material supporting one or more catalytically active metals M, and wherein the catalytically active metal M selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, Ta, Mn, Hf, Nb, Ga, Ge, and combinations of two or more thereof, preferably selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, and combinations of two or more thereof, more preferably selected from the group consisting of Cr, Co, Cu, Zn, Zr, and combinations of two or more thereof is comprised in the catalyst in the range of from 0.1 to 25 weight-%, preferably from 0.3 to 10 weight-%, more preferably from 0.5 to 6 weight-%, wherein M is calculated as the element and based on the total weight of the crystalline material

As regards the one or more active metals M supported on the crystalline material comprised in the catalyst, no specific restrictions exist concerning the method by which the one or more active metals M are disposed on the crystalline material. Therefore, it may be conceivable to dispose the one or more active metals M on the crystalline material by impregnation, ion-exchange incipient wetness impregnation and/or by dry impregnation. According to a preferred embodiment of the present invention, the one or more active metals M are disposed on the crystalline material by incipient wetness impregnation, dry impregnation and/or by ion exchange. According to the present invention, it is particularly preferred to dispose the one or more active metals M on the crystalline material by incipient wetness impregnation.

As regards the incipient wetness impregnation, no particular restriction exists regarding the number of times said step is repeated. The incipient wetness impregnation is conducted with the aid of a solvent or solvent mixture in which the one or more active metals M to be disposed on the crystalline materials are suitably dissolved. With respect to the type of solvent which may be used, there is again no particular restriction in this respect, provided that the one or more active metals M to be disposed on the crystalline material are may be solvated therein. Thus, by way of example, the solvent or mixture of solvents which may be used include water and alcohols, and in particular short chain alcohols selected among C₁-C₄, and preferably C₁-C₃ alcohols, in particular methanol, ethanol or propanol, including 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 at least one alcohol 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. According to a preferred embodiment of the present invention, however, water or a mixture of water and one or more alcohols is preferred,

wherein a mixture of water and ethanol is further preferred, deionized water being particularly preferred as the solvent for the one or more ion-exchange procedures.

As regards the amount of the one or more solvents preferably used in the incipient wetness impregnation in order to dispose the one or more active metals M on the crystalline material, there is again no particular restriction, provided that the one or more catalytically active metals M are effectively disposed on the crystalline material. According to a preferred embodiment of the present invention, incipient wetness impregnation may be achieved with a volume of solvent or a solvent mixture which slightly exceeds or approximately corresponds to or is slightly inferior to the porous volume of the crystalline material such that catalytically active metals M solvated in the solvent or solvent mixture enters the porous system of the zeolitic material by capillary action.

It is preferred that the impregnation is conducted by use of a liquid to solid weight ratio ranging anywhere from 0.1 to 50. According to said preferred embodiments of the present invention, however, it is preferred that the liquid to solid weight ratio being the weight ratio of the solvent or solvent mixture to the crystalline material, is comprised in the range of from 1 to 45, more preferably of from 5 to 40, more preferably of from 8 to 35, more preferably of from 10 to 25, and even more preferably of from 12 to 22. According to particularly preferred embodiments of the present invention, the liquid to solid weight ratio employed in the impregnation is comprised in the range of from 14 to 21.

According to a preferred embodiment of the present invention, the one or more catalytically active metals M are disposed on the crystalline material by impregnation, preferably by incipient wetness impregnation.

Thus, according to a preferred embodiment of the present invention, wherein the one or more active metals M are disposed on the crystalline material by impregnation, preferably by incipient wetness impregnation, it is particularly preferred that the one or more active metals M which are disposed on the crystalline material are selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, Ta, Mn, Hf, Nb, Ga, Ge, and combinations of two or more thereof, preferably selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, and combinations of two or more thereof, more preferably selected from the group consisting of Cr, Co, Cu, Zn, Zr, and combinations of two or more thereof. Further, according to the present invention, it is preferred that the one or more active metals M selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, Ta, Mn, Hf, Nb, Ga, Ge, and combinations of two or more thereof, preferably selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, and combinations of two or more thereof, more preferably selected from the group consisting of Cr, Co, Cu, Zn, Zr, and combinations of two or more thereof are disposed on the crystalline material by impregnation, preferably by incipient wetness impregnation using water as solvent.

As regards the impregnation, no particular restrictions exist concerning the compounds comprising the one or more catalytically active metals M which are used to dispose the one or more catalytically active metals M on the crystalline material by impregnation, preferably by incipient wetness impregnation. According to the present invention, it is preferred to carry out the impregnation by use of one or more inorganic or organic salts. In general, no specific restrictions exist concerning the one or more inorganic or organic salts used in the impregnation procedure, provided that the one or more catalytically active metals M comprised in the one or more inorganic or organic salts is effectively disposed on the crystalline material. It is preferred according to the present invention that the one or more inorganic or organic salts are selected from the group consisting of halides, nitrates, sulfates, phosphates, hydroxides, carboxylates, alcoholates, and combinations of two or more thereof, more preferably selected from the group consisting of chlorides, nitrates, acetates, and combinations of two or more thereof.

Thus, according to a preferred embodiment of the present invention, impregnation is carried out using one or more inorganic or organic salts, wherein these salts are preferably selected from the group consisting of halides, nitrates, sulfates, phosphates, hydroxides, carboxylates, alcoholates, and combinations of two or more thereof, more preferably selected from the group consisting of chlorides, nitrates, acetates, and combinations of two or more thereof.

According to a particularly preferred embodiment of the present invention, the one or more inorganic or organic salts are selected from the group consisting of copper(II)nitrate, nickel(II)nitrate, cobalt(II)nitrate, chromium(III)nitrate, zinc(II)nitrate, copper (II)acetate, Zr(IV)oxynitrate and tin(IV)chloride, and combinations of two or more thereof.

According to a preferred embodiment of the present invention, the crystalline material comprises a zeolitic material. As regards the zeolitic material comprised in the crystalline material, no specific restrictions exist. Said zeolitic material may be any suitable zeolitic material having an BEA, RRO, MWW, MFI, MEL, MOR, RUT, DOH, MTN, FER, FAU, CDO, LEV, CHA framework structure, provided that the catalyst comprising the crystalline material which comprises the zeolitic material may act as catalyst in the process for the preparation of butadiene. According to a preferred embodiment of the present invention, the crystalline material comprises a zeolitic material having a framework structure selected from the group consisting of BEA, RRO, MWW, MFI, MEL, MOR, RUT, DOH, MTN, FER, FAU, and combinations of two or more thereof, preferably selected from the group consisting of BEA, RRO, MWW, MFI, MEL, and combinations of two or more thereof, more preferably selected from BEA and/or RRO.

Further, according to the present invention, it is preferred that the zeolitic material comprises YO_2 , wherein Y stands for one or more tetravalent elements. According to a preferred embodiment of the present invention, the tetravalent element Y is selected from the group consisting of Si, Sn, Ti, Zr, Ge, and combinations of two or more thereof, wherein Y preferably being Si.

Therefore, according to preferred embodiments of the present invention, the framework structure of the zeolitic material comprises YO_2 , Y standing for one or more tetravalent elements, wherein Y is preferably selected from the group consisting of Si, Sn, Ti, Zr, Ge, and combinations of two or more thereof, Y preferably being Si.

According to a preferred embodiment of the present invention, wherein the zeolitic material comprised in the crystalline material is BEA and/or RRO, the one or more tetravalent element Y comprised in the zeolitic material is Si.

Further, it is preferred according to the present invention that the zeolitic material having a BEA framework structure is zeolite beta and the zeolitic material having a RRO framework structure is RUB-41. Therefore, embodiments of the present invention are preferred, wherein the crystalline material comprises zeolite beta and/or RUB-41.

As regards the one or more tetravalent elements Y comprised in the framework structure of the zeolitic material, it is preferred according to the present invention that at least a portion of the one or more tetravalent element comprised in the framework structure of the zeolitic material is isomorphously substituted by one or more elements X1. According to a preferred embodiment of the present invention, X1 stands for one or more trivalent, tetravalent, and/or pentavalent elements. As regards the one or more trivalent, tetravalent, and/or pentavalent elements elements X1, no particular restrictions exist concerning the chemical nature of the one or more trivalent, tetravalent, and/or pentavalent elements elements X1. In general, all conceivable trivalent, tetravalent, and/or pentavalent elements may be used, provided that at least a portion of the one or more tetravalent elements Y are isomorphously substituted by the one or more trivalent, tetravalent, and/or pentavalent elements elements X1. Further, it is preferred according to the present invention that the one or more trivalent, tetravalent, and/or pentavalent elements X1 are selected from the group consisting of Al, Ti, V, Sn, Zr, Ta, Ge, B, Fe, and combinations of two or more thereof, more preferably selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof, wherein preferably X1 is different from M.

Therefore, according to a particular preferred embodiment of the present invention at least a portion of the one or more tetravalent elements Y in the framework structure of the zeolitic material is isomorphously substituted by one or more elements X1, wherein X1 preferably stands for one or more trivalent, tetravalent, and/or pentavalent elements, wherein the one

or more elements X1 are preferably selected from the group consisting of Al, Ti, V, Sn, Zr, Ta, Ge, B, Fe, and combinations of two or more thereof, more preferably selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof, wherein preferably X1 is different from M.

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According to a particular preferred embodiment of the present invention, wherein the zeolitic material is zeolite beta and Y stands for Si, at least a portion Si comprised in the framework structure of the zeolite beta is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X1. It is further preferred that at least a portion Si comprised in the framework structure of the zeolite beta is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X1, wherein the one or more elements X1 are preferably selected from the group consisting of Al, Ti, V, Sn, Zr, Ta, Ge, B, Fe, and combinations of two or more thereof, more preferably selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof, wherein preferably X1 is different from M.

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Further, according to a particular preferred embodiment of the present invention, the crystalline material comprises zeolite beta, wherein at least a portion of Si comprised in the framework structure of the zeolite beta is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X1 selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof.

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Concerning the molar ratio of the one or more tetravalent elements Y to the one or more trivalent, tetravalent, and/or pentavalent elements X1 in the framework structure, no specific restrictions exist. According to a preferred embodiment of the present invention, the molar ratio of Y : X1 in the framework structure ranges from 10 : 1 to 150 : 1, preferably from 30 : 1 to 100 : 1, more preferably from 45 : 1 to 80 : 1.

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The notation "X-BEA" as used in the context of the present invention describes the isomorphously substituted zeolitic materials having a BEA framework structure, wherein X stands for the element by which the zeolitic material is isomorphously substituted.

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According to a particularly preferred embodiment of the present invention, the crystalline material comprised in the catalyst used in (ii) comprises isomorphously substituted zeolite beta preferably selected from the group consisting of Sn-BEA, Zr-BEA, Ta-BEA and combinations of two or more thereof.

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Further, according to the present invention, it is preferred that the crystalline material comprising isomorphously substituted zeolite beta preferably selected from the group consisting of Sn-BEA, Zr-BEA, Ta-BEA and combinations of two or more thereof supports one or more active metals M selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, Ta, Mn, Hf,

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Nb, Ga, Ge, and combinations of two or more thereof, preferably selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, and combinations of two or more thereof, more preferably selected from the group consisting of Cr, Co, Cu, Zn, Zr. According to a particularly preferred embodiment of the present invention, crystalline material comprising isomorphously substituted zeolite beta preferably selected from the group consisting of Sn-BEA, Zr-BEA, Ta-BEA and combinations of two or more thereof supports one or more active metals M selected from the group consisting of Cr, Co, Ni, Cu, Zn and combinations of two or more thereof.

According to a preferred embodiment of the present invention, wherein the crystalline material comprises a zeolitic material having a BEA framework structure comprising YO_2 , wherein Y stands for one or more tetravalent elements, and wherein at least a portion of Y is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X1, the zeolitic material having a BEA framework structure comprised in the crystalline material is preferably provided by a process comprising

- (a) preparing an aqueous synthesis mixture comprising a Y source, a X1 source, and optionally a template compound, preferably selected from the group consisting of piperidine, hexamethylene imine, N,N,N-trimethyl-1-adamantan ammonium hydroxide, piperidine, hexamethylene imine, dibenzyl-1,4-diazabicyclo[2,2,2]octane, dibenzylmethylammonium, tetraethylammonium hydroxide, and combinations of two or more thereof;
- (b) optionally adding seed crystals and/or an acid to the mixture prepared in (a), wherein an aqueous HF solution is preferably used as the acid;
- (c) hydrothermally synthesizing a zeolitic material having a BEA framework structure comprising one or more tetravalent elements Y and one or more trivalent, tetravalent, and/or pentavalent elements X1 from the aqueous synthesis mixture prepared in (a), optionally after step (b).

According to a preferred embodiment of the present invention, wherein the zeolitic material comprised in the crystalline material has a BEA framework structure comprising YO_2 , Y stands for one or more tetravalent elements preferably selected from the group consisting of Si, Sn, Ti, Zr, Ge, and combinations of two or more thereof, Y preferably being Si.

Further, according to the present invention, it is preferred that at least a portion of the one or more tetravalent elements Y is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X1 preferably selected from the group consisting of Al, Ti, V, Sn, Zr, Ta, Ge, B, Fe, and combinations of two or more thereof, more preferably selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof.

Therefore, embodiments of the present invention are preferred, wherein the zeolitic material comprised in the crystalline material has a BEA framework structure, and wherein Y stands

for Si and X1 is selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof.

According to a preferred embodiment of the present invention, wherein Y stands for Si, any suitable silicon source may be used to prepare the aqueous synthesis mixture in (a), wherein preferably, the silicon source is selected from the group consisting of tetraethylorthosilicate, a fumed silica, a colloidal silica such as ammonia-stabilized colloidal silica, and combinations of two or more thereof, more preferably, the silicon source is tetraethylorthosilicate.

As regards the X1 source, all conceivable sources for the one or more trivalent, tetravalent, and/or pentavalent elements X1 may be used. According to a particular preferred embodiment of the present invention, wherein X1 is Sn, the Sn source used in (a) is preferably selected from the group consisting of SnCl_4 , Sn(IV)-acetate, Sn(IV)-tert-butoxide, SnBr_4 , SnCl_4 , SnF_4 , Sn(IV)-bisacetylacetonate dichloride; Sn(IV)-bisacetylacetonate dibromide, Sn(II)-acetate, Sn(II)acetylacetonate, Sn(II)-citrate, SnCl_2 , SnF_2 , SnI_2 , SnSO_4 , and a mixture of two or more thereof. More preferably, the tin source is Sn(IV)-tert-butoxide.

According to a particular preferred embodiment of the present invention, wherein X1 is Zr, the Zr source used in (a) is preferably selected from the group consisting of zirconium and zirconyl salts, more preferably from the group consisting of zirconium and zirconyl halides, zirconium hydroxide, zirconyl nitrate, zirconium alkoxides, and mixtures of two or more thereof, more preferably from the group consisting of zirconium and zirconyl bromide, chloride, fluoride, zirconyl nitrate, C1-C4 alkoxides of Zr, and mixtures of two or more thereof, more preferably from the group consisting of zirconium and zirconyl chloride, fluoride, zirconyl nitrate, C2-C3 alkoxides of Zr, and mixtures of two or more thereof, more preferably from the group consisting of zirconium and zirconyl chloride, zirconyl nitrate, C3 alkoxides of Zr, and mixtures of two or more thereof, more preferably from the group consisting of zirconyl chloride, zirconyl nitrate, Zn-n-propoxide, and mixtures of two or more thereof, wherein more preferably the Zr source is Zr-(IV) oxychloride octahydrate.

According to a preferred embodiment of the present invention, wherein the aqueous synthesis mixture prepared in (a) comprises an alcohol, the aqueous synthesis mixture prepared in (a) is heated at a temperature in the range of from 40 to 120 °C, preferably from 45 to 100 °C, more preferably from 55 to 70 °C prior to optionally adding seed crystals and/or an acid and preferably an aqueous HF solution to the mixture prepared in (a) according to (b) and prior to hydrothermally synthesizing a zeolitic material having a BEA framework structure from the aqueous synthesis mixture prepared in (a) according to (c) for removing one or more alcohols and in particular propanol and/or ethanol, and preferably for removing ethanol from the synthesis mixture by distillation.

Further, according to a preferred embodiment of the present invention, wherein the crystalline material comprises a zeolitic material having a BEA framework structure comprising YO_2 , wherein Y stands for one or more tetravalent elements, and wherein at least a portion of Y is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X1, the zeolitic material having a BEA framework structure comprised in the crystalline material is preferably provided by a process comprising

- (a) providing a zeolitic material having a BEA framework structure comprising YO_2 and Z_2O_3 , wherein Y stands for one or more tetravalent elements and Z stands for a trivalent element;
- (b) removing at least a portion of Z by treating the zeolitic material provided in (a) with a liquid solvent system having a pH of at most 5;
- (c) preparing a synthesis mixture comprising the zeolitic material obtained from (b), a solvent and a X1 source;
- (d) evaporating the mixture obtained in (c) to dryness, thereby obtaining a zeolitic material having a BEA framework structure comprising YO_2 , wherein Y stands for one or more tetravalent elements, and wherein at least a portion of Y is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X1.

According to a preferred embodiment of the present invention, YO_2 and Z_2O_3 comprised in the framework structure of the zeolitic materials provided in step (a) are contained in the framework structure as framework-forming elements, as opposed to non-framework elements which can be present in the pores and cavities formed by the framework structure and which can be typical for zeolitic materials in general.

As far as the chemical nature of Z is concerned, no specific restrictions exist. In particular Z can be any conceivable trivalent element or mixture of two or more trivalent elements. Preferred trivalent elements according to the present invention include, but are not restricted to, Al, B, In, Ga and Fe. Preferably, Z is selected from the group consisting of Al, B, In, Ga, Fe and combinations of two or more thereof, Z preferably being Al.

Also no specific restrictions exist concerning the one or more tetravalent element Y comprised in the framework structure of the zeolitic material provided in (a). According to a preferred embodiment of the present invention, Y is selected from the group consisting of Si, Sn, Ti, Zr, Ge and combinations of two or more thereof, preferably selected from the group consisting of Si, Ti, Ge, and combinations of two or more thereof, more preferably Y stands for Si.

Therefore, according to a particularly preferred embodiment of the present invention, Y stands for Si and Z stands for Al.

According to a preferred embodiment of the present invention, wherein Y stands for Si, any suitable silicon source may be used to prepare the aqueous synthesis mixture in (a), wherein preferably, the silicon source is selected from the group consisting of tetraethylorthosilicate, a fumed silica, a colloidal silica such as ammonia-stabilized colloidal silica, and combinations of two or more thereof, more preferably, the silicon source is fumed silica.

Further, according to a preferred embodiment of the present invention, wherein Z stands for Al, any suitable aluminium source may be used to provide the zeolitic material in (a), wherein preferably the aluminium source is aluminium nitrate, aluminium oxide, an aluminium halide, an aluminium hydroxide, or a mixture of two or more thereof, with aluminium nitrate being especially preferred.

Further, according to the present invention, it is preferred that (a) comprises crystallizing the zeolitic material having a BEA framework structure comprising YO_2 and Z_2O_3 . Preferably, crystallization is carried out at a temperature in the range of from 80 to 200°C, more preferably from 90 to 180°C, more preferably from 100 to 170°C, more preferably from 110 to 160°C, more preferably from 120 to 150°C, and even more preferably from 130 to 145°C.

Concerning the synthesis mixture prepared in (c), no specific restrictions exist regarding the used solvent. Therefore, any conceivable solvent may be used in (c), provided a zeolitic material having a BEA framework structure comprising one or more tetravalent elements Y and one or more trivalent, tetravalent, and/or pentavalent elements X1 is obtained in (d). Solvents which may be used are, for example, 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 at least one alcohol, 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. According to a preferred embodiment of the present invention, propanol is used as solvent in (c).

As regards the X1 source used in (c), all conceivable sources for the one or more trivalent, tetravalent, and/or pentavalent elements X1 may be used. According to a particular preferred embodiment of the present invention, wherein X1 is Ta, the Ta source used in (c) is preferably selected from the group consisting of tantalum and tantalum salts, more preferably from the group consisting of tantalum and tantalum halides, tantalum hydroxide, tantalum alkoxides, and mixtures of two or more thereof, more preferably the Ta source is pentaethoxytantalum(V).

According to a preferred embodiment of the present invention, the crystalline material comprised in the catalyst comprises a layered silicate. As regards the layered silicate comprised

in the crystalline material, no specific restrictions exist concerning the type of the layered silicate, provided that the catalyst comprises the crystalline material comprising the layered silicate allows to obtain a gas stream G-2 comprising butadiene. According to the present invention, it is preferred that the layered silicate comprised in the crystalline material is selected from the group consisting of MCM-22, PREFER, Nu-6(2), CDS-1, PLS-1, MCM-47, ERS-12, MCM-65, RUB-15, RUB-18, RUB-20, RUB-36, RUB-38, RUB-39, RUB-40, RUB-42, RUB-51, BLS-1, BLS-3, ZSM-52, ZSM-55, kanemite, makatite, magadiite, kenyaite, revdite, montmorillonite, and combinations of two or more thereof, preferably selected from RUB-36 and/or RUB-39.

Therefore, according to a preferred embodiment of the present invention, the crystalline material comprised in the catalyst is a layered silicate, wherein the layered silicate is preferably selected from the group consisting of MCM-22, PREFER, Nu-6(2), CDS-1, PLS-1, MCM-47, ERS-12, MCM-65, RUB-15, RUB-18, RUB-20, RUB-36, RUB-38, RUB-39, RUB-40, RUB-42, RUB-51, BLS-1, BLS-3, ZSM-52, ZSM-55, kanemite, makatite, magadiite, kenyaite, revdite, montmorillonite, and combinations of two or more thereof, preferably selected from RUB-36 and/or RUB-39.

According to a particularly preferred embodiment of the present invention, the layered silicate comprised in the crystalline material is selected from the group consisting of RUB-36, RUB-39, RUB-15, BLS-1, BLS-3, and combinations of two or more thereof. According to the present invention, there is no particular restriction as to the method according to which the materials RUB-36, RUB-39, RUB-15, BLS-1, and BLS-3 may be obtained, wherein preferably, the materials are obtained according to the particular and preferred embodiments as defined in WO 2010/100191 A2.

According to a further preferred embodiment of the present invention, the crystalline material comprised in the catalyst comprises a pillared silicate.

Within the meaning of the present invention, the term "pillared silicate" generally refers to any conceivable layered silicate structure, wherein the silicate layers are covalently bound to one another by suitable bridging elements. Furthermore, according to said definition, bridging is achieved between the surfaces of neighboring silicate layers of a layered silicate structure, wherein a sufficient portion of the respective surfaces forms covalent bonds to said bridging elements. Within the meaning of the present invention, a sufficient portion of a silicate layer surface is covalently bound to bridging elements, preferably when 10 % or more of the atoms or chemical moieties located on the silicate layer surface which is capable of forming covalent bonds to said bridging elements actually engage in such chemical bonding, thus forming a covalent bridge to the neighboring silicate layers. Preferably, a sufficient portion of the silicate layer refers to pillared silicate compounds wherein 30% or more of said surface atoms or chemical moieties of the respective silicate layer surfaces engage

in such covalent bonds, more preferably 50% or more, more preferably 70% or more, more preferably 80% or more, more preferably 90% or more, more preferably 95% or more, more preferably 98% or more, more preferably 99% or more, more preferably 99.9% or more and even more preferably 99.99% or more.

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As regards the pillared silicate comprised in the crystalline material, no specific restrictions exist concerning the type of the pillared silicate, provided that the catalyst comprises the crystalline material comprising the pillared silicate allows to obtain a gas stream G-2 comprising butadiene. According to the present invention, it is preferred that the pillared silicate comprised in the crystalline material is a pillared silicate having a layered silicate structure, wherein the layered silicate structure is preferably selected from the group consisting of RUB-36, RUB-39, RUB-15, BLS-1, BLS-3, and combinations of two or more thereof, more preferably selected from RUB-36, RUB-39, RUB-15, and combinations of two or more thereof, wherein more preferably the layered silicate structure is RUB-36.

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Thus, according to a preferred embodiment of the present invention, the crystalline material comprised in the catalyst is a pillared silicate having a layered silicate structure, wherein the layered silicate structure is preferably selected from the group consisting of RUB-36, RUB-39, RUB-15, BLS-1, BLS-3, and combinations of two or more thereof, more preferably selected from RUB-36, RUB-39, RUB-15, and combinations of two or more thereof, wherein more preferably the layered silicate structure is RUB-36.

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As regards the bridging elements comprised in the pillared silicate by which the silicate layers are covalently bound to one another, no particular restrictions exist. Therefore, any bridging elements suitable to covalently bound the silicate layers to one another are conceivable. According to a preferred embodiment of the present invention, the silicate layers are covalently bound to one another by one or more bridging elements selected from the group consisting of Si, B, Mg, Ca, Ti, Zr, Zn, Al, Ga, In, Ge, Sn, Pb, Cu, Fe, and combinations of two or more thereof, preferably selected from the group consisting of Si, B, Ti, Al, Ga, In, Ge, Sn, and combinations of two or more thereof, more preferably Si, B, Al, Ga, Ge, and combinations of two or more thereof. According to a particularly preferred embodiment of the present invention, the silicate layers are covalently bound to one another by Si.

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Thus, according to a preferred embodiment of the present invention, the pillared silicate comprises one or more bridging elements selected from the group consisting of Si, B, Mg, Ca, Ti, Zr, Zn, Al, Ga, In, Ge, Sn, Pb, Cu, Fe, and combinations of two or more thereof, preferably selected from the group consisting of Si, B, Ti, Al, Ga, In, Ge, Sn, and combinations of two or more thereof, more preferably Si, B, Al, Ga, Ge, and combinations of two or more thereof, wherein more preferably the bridging element is Si.

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Therefore, according to a particularly preferred embodiment of the present invention, the pillared silicate is a pillared silicate having a layered silicate structure, wherein the silicate layers are covalently bound to one another via bridging silicon atoms thus forming a three dimensional framework.

Further, according to a particularly preferred embodiment of the present invention, wherein the crystalline material comprised in the catalyst is a pillared silicate having a RUB-36 structure, it is preferred that the silicate layers of the RUB-36 structure are covalently bound bound to one another via bridging silicon atoms thus forming a three dimensional framework.

According to the present invention, it is preferred that at least a portion of Si comprised in the layered silicate or in the layered silicate structure of the pillared silicate is isomorphously substituted by one or more elements X₂. According to a preferred embodiment of the present invention, X₂ stands for one or more trivalent, tetravalent, and/or pentavalent elements. As regards the one or more trivalent, tetravalent, and/or pentavalent elements elements X₂, no particular restrictions exist concerning the chemical nature of the one or more trivalent, tetravalent, and/or pentavalent elements elements X₂. In general, all conceivable trivalent, tetravalent, and/or pentavalent elements may be used, provided that at least a portion of Si is isomorphously substituted by the one or more trivalent, tetravalent, and/or pentavalent elements elements X₂. Further, it is preferred according to the present invention that the one or more trivalent, tetravalent, and/or pentavalent elements X₂ are selected from the group consisting of Al, Ti, V, Sn, Zr, Ta, Ge, B, Fe, and combinations of two or more thereof, more preferably selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof, wherein preferably X₂ is different from M.

Therefore, according to a particular preferred embodiment of the present invention, at least a portion of Si in the layered silicate or in the layered silicate structure of the pillared silicate is isomorphously substituted by one or more elements X₂, wherein X₂ preferably stands for one or more trivalent, tetravalent, and/or pentavalent elements, wherein the one or more elements X₂ are preferably selected from the group consisting of Al, Ti, V, Sn, Zr, Ta, Ge, B, Fe and combinations of two or more thereof, more preferably selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof, wherein preferably X₂ is different from M.

According to a particular preferred embodiment of the present invention, wherein the layered silicate is RUB-36 and/or RUB-39, at least a portion Si comprised in RUB-36 and/or RUB-39 is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X₂. It is further preferred that at least a portion Si comprised in RUB-36 and/or RUB-39 is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X₂, wherein the one or more elements X₂ are preferably selected

from the group consisting of Al, Ti, V, Sn, Zr, Ta, Ge, B, Fe, and combinations of two or more thereof, more preferably selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof, wherein preferably X2 is different from M.

- 5 Further, according to a particularly preferred embodiment of the present invention, the crystalline material comprises RUB-36 and/or RUB-39, wherein at least a portion of Si is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X1 selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof.

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- According to a preferred embodiment of the present invention, wherein the crystalline material comprised in the catalyst is a pillared silicate having a layered silicate structure, wherein the layered silicate structure is preferably selected from the group consisting of RUB-36, RUB-39, RUB-15, BLS-1, BLS-3, and combinations of two or more thereof, more preferably selected from RUB-36, RUB-39, RUB-15, and combinations of two or more thereof, wherein more preferably the layered silicate structure is RUB-36, it is preferred that at least a portion Si comprised in RUB-36 and/or RUB-39 is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X2. It is further preferred that at least a portion Si comprised in the pillared silicate having a layered silicate structure, wherein the layered silicate structure is preferably selected from the group consisting of RUB-36, RUB-39, RUB-15, BLS-1, BLS-3, and combinations of two or more thereof, is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X2, wherein the one or more elements X2 are preferably selected from the group consisting of Al, Ti, V, Sn, Zr, Ta, Ge, B, Fe, and combinations of two or more thereof, more preferably selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof, wherein preferably X2 is different from M.

- Thus, according to a particularly preferred embodiment of the present invention wherein the crystalline material comprised in the catalyst is a pillared having a RUB-36 structure, at least a portion of Si comprised in RUB-36 is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X1 selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof.

- Concerning the molar ratio of Si to the one or more trivalent, tetravalent, and/or pentavalent elements X2, no specific restrictions exist. According to a preferred embodiment of the present invention, molar ratio of Si : X2 in the framework structure ranges from 10 : 1 to 160 : 1, preferably from 60 : 1 to 130 : 1, more preferably from 90 : 1 to 110 : 1.

- According to the present invention, it is preferred that the crystalline material comprising RUB-36 and/or RUB 39 supports one or more active metals M selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, Ta, Mn, Hf, Nb, Ga, Ge, and combinations of two or

more thereof, preferably selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, and combinations of two or more thereof, more preferably selected from the group consisting of Cr, Co, Cu, Zn, Zr. Further, according to a preferred embodiment of the present invention, the crystalline material comprising RUB-36 and/or RUB 39 supports one or more
5 active metals M selected from the group consisting of Cr, Co, Cu, Zn, Zr and combinations of two or more thereof. According to a particular preferred embodiment of the present invention, the crystalline material comprising RUB-36 and/or RUB 39 supports one or more active metals M selected from the group consisting of Cu, Zn, Zr, and combinations of two or more thereof.

10 Further, it is preferred according to the present invention, that the crystalline material comprising a pillared silicate having a layered silicate structure, wherein the layered silicate structure is preferably selected from the group consisting of RUB-36, RUB-39, RUB-15, BLS-1, BLS-3, and combinations of two or more thereof, supports one or more active met-
15 als M selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, Ta, Mn, Hf, Nb, Ga, Ge, and combinations of two or more thereof, preferably selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, and combinations of two or more thereof, more preferably selected from the group consisting of Cr, Co, Cu, Zn, Zr. Further, according to a preferred embodiment of the present invention, the crystalline material comprising a pillared silicate
20 having a layered silicate structure, wherein the layered silicate structure is preferably selected from the group consisting of RUB-36, RUB-39, RUB-15, BLS-1, BLS-3, and combinations of two or more thereof, supports one or more active metals M selected from the group consisting of Cr, Co, Cu, Zn, Zr and combinations of two or more thereof. According to a particular preferred embodiment of the present invention, the crystalline material comprising
25 a pillared silicate having a layered silicate structure, wherein the layered silicate structure is preferably selected from the group consisting of RUB-36, RUB-39, RUB-15, BLS-1, BLS-3, and combinations of two or more thereof, supports one or more active metals M selected from the group consisting of Cu, Zn, Zr, and combinations of two or more thereof.

30 According to a particularly preferred embodiment of the present invention, the pillared silicate comprised in the crystalline material having a RUB-36 structure supports one or more active metals M selected from the group consisting of Cu, Zn, Zr, and combinations of two or more thereof.

35 According to a preferred embodiment of the present invention, the layered silicate or the layered silicate structure of the pillared silicate is RUB-36 and/or RUB-39, wherein neither RUB-36 nor RUB-39 is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X₂.

In general, there are no specific restrictions how the layered silicate is provided. For example, it may be conceivable to prepare RUB-36 and/or RUB-39 according to WO 2010/100203 A2 or WO 2010/100191 A2.

5 According to a preferred embodiment of the present invention, wherein the crystalline material comprises a layered silicate, the layered silicate comprised in the crystalline material is preferably provided by a process comprising

- 10 (1) providing a mixture containing silica, preferably amorphous silica, and/or at least one silica precursor, water, at least one tetraalkylammonium compound selected from the group consisting of a diethyldimethylammonium compound, a dimethyldipropylammonium compound, a triethylmethylammonium compound, and a mixture of a diethyldimethylammonium and a triethylmethylammonium compound, optionally one or more bases,
- 15 (2) heating the mixture obtained according to (1) under hydrothermal conditions to give a suspension containing the layered silicate,
- (3) separating and optionally (4) washing and/or (5) drying the layered silicate from the suspension obtained according to (2).

20 According to a preferred embodiment of the present invention, the one or more optional bases comprised in the mixture according to (1) is one or more inorganic bases, preferably one or more alkali or earth alkali hydroxides, more preferably sodium hydroxide.

According to a preferred embodiment of the present invention, wherein the layered silicate comprised in the crystalline material is RUB-36, the tetraalkylammonium compound used in 25 (1) is a diethyldimethylammonium compound, preferably diethyldimethylammonium hydroxide.

30 According to a preferred embodiment of the present invention, wherein the layered silicate comprised in the crystalline material is isomorphously substituted RUB-36, in the above described process for providing the layered silicate either the mixture according to (1) contains one or more sources of at least one element suitable for isomorphous substitution of at least a portion of the Si atoms in the silicate; and/or the separated and optionally washed and/or dried RUB-36 silicate according to (3) is post-treated, thereby isomorphously substituting at least a portion of the Si atoms in the silicate with at least one suitable element.

35 According to a preferred embodiment of the present invention, wherein the layered silicate is isomorphously substituted RUB-36, at least a portion Si comprised in RUB-36 is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X₂, wherein the one or more elements X₂ are preferably selected from the group consisting of 40 Al, Ti, V, Sn, Zr, Ta, Ge, B, Fe, and combinations of two or more thereof, more preferably selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof.

According to a preferred embodiment of the present invention, wherein the layered silicate comprised in the crystalline material is RUB-39, the mixture according to (j) comprises one or more bases, preferably one or more inorganic bases, more preferably one or more alkali or earth alkali hydroxides, more preferably sodium hydroxide. It is further preferred according to the present invention that the mixture according to (j) comprising one or more inorganic bases, preferably one or more alkali or earth alkali hydroxides, more preferably sodium hydroxide further comprises seed crystals.

Further, according to a preferred embodiment of the present invention, wherein the layered silicate comprised in the crystalline material is isomorphously substituted RUB-39, the isomorphously substituted RUB-39 is preferably provided by a process comprising

- (1) providing a mixture containing silica, preferably amorphous silica, and/or at least one silica precursor, water, at least one tetraalkylammonium compound selected from the group consisting of a diethyldimethylammonium compound, a dimethyldipropylammonium compound, a triethylmethylammonium compound, and a mixture of a diethyldimethylammonium and a triethylmethylammonium compound, optionally one or more bases,
- (2) heating the mixture obtained according to (1) under hydrothermal conditions to give a suspension containing the layered silicate,
- (3) separating and optionally (4) washing and/or (5) drying the layered silicate from the suspension obtained according to (2).
- (6) adding at least one source at least one element suitable for isomorphous substitution of at least a portion of the Si atoms in the layered silicate to the mixture obtained from (2);
- (7) heating the mixture obtained according to (6) under hydrothermal conditions to give the layered silicate.

According to a preferred embodiment of the present invention, wherein the layered silicate comprised in the crystalline material is RUB-39, at least a portion of Si at least a portion Si comprised in RUB-39 is isomorphously substituted by one or more trivalent, tetravalent, and/or pentavalent elements X₂, wherein the one or more elements X₂ are preferably selected from the group consisting of Al, Ti, V, Sn, Zr, Ta, Ge, B, Fe, and combinations of two or more thereof, more preferably selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof.

Furthermore, according to the present invention, there is no particular restriction as to the method according to which the pillared silicate preferably comprised in the crystalline material is provided. Thus, the pillared silicates may be provided as such or may be prepared according to any suitable method. It is, however, preferred according to the present invention that the pillared silicate according to particular and preferred embodiments of the in-

ventive process is prepared according to the method described in WO 2010/100191 A2 and/or in WO 2012/001663 A1, explicitly including any one of the particular and preferred embodiments described in said documents. This applies in particular according to particularly preferred embodiments of the present invention, wherein the pillared silicate has a layered silicate structure, wherein the layered silicate structure is RUB-36 and/or RUB-39. According to particular embodiments thereof which are yet further preferred, wherein the layered silicate structure is RUB-36 and/or RUB-39 and the bridging element is Si, it is preferred that said particularly preferred pillared silicate employed in the inventive process is prepared according to the method described in WO 2010/100191 A2, explicitly including any one of the particular and preferred embodiments described in said document.

As regards the particular conditions under which the gas stream G-1 is contacted with a catalyst according to the present invention in step (ii), no particular restrictions exist provided that a gas stream G-2 comprising butadiene is obtained. This, for example, applies to the temperature at which the contacting in step (ii) takes place. Accordingly, said contacting of the gas stream in step (ii) may be conducted according to the inventive process at a temperature in the range of from 150 to 600 °C, preferably from 200 to 500 °C, preferably from 220 to 470 °C, more preferably from 250 to 450 °C, more preferably from 270 to 420 °C, more preferably from 300 to 400 °C. According to a particular preferred embodiment of the present invention, contacting the gas stream G-1 with the catalyst is carried out at a temperature in the range of from 200 to 500 °C, preferably from 250 to 450 °C, more preferably from 300 to 400 °C.

Same applies accordingly to the pressure under which the gas stream G-1 is contacted with a catalyst according to the present invention in step (ii) of the inventive process. Thus, in principle, said contacting may be conducted at any conceivable pressure, provided that a gas stream G-2 comprising butadiene is obtained. According to a preferred embodiment of the present invention, contacting of the gas stream G-1 with the catalyst is carried out at a pressure in the range of from 1 to 5 bar, preferably from 1 to 2 bar.

According to a particularly preferred embodiment of the present invention, the gas stream G-1 is contacted with a catalyst according to the present invention in step (ii) at a temperature in the range of from 200 to 500 °C, preferably from 250 to 450 °C, more preferably from 300 to 400 °C at a pressure in the range of from 1 to 5 bar, preferably from 1 to 2 bar.

Furthermore, no particular restriction applies relative to the manner in which the inventive process for the preparation of butadiene is conducted, such that both a non-continuous mode as well as a continuous mode may be applied to the inventive process, wherein the non-continuous process may for example be conducted as a batch-process.

According to a preferred embodiment of the present invention, contacting gas stream G-1 with the catalyst is carried out in a continuous mode.

No specific restrictions exist concerning the set-up of the continuous process. Preferred continuous process set-ups include the use of one or more fixed-bed reactor. Thus, according to a preferred embodiment of the present invention, contacting the gas stream G-1 with the catalyst is carried out in one or more reactors, wherein preferably the one or more reactors contain the catalyst in the form of a fixed bed.

Further, according to the present invention, it is preferred that prior to contacting the gas stream G-1 with the catalyst, the gas stream is heated. According to a preferred embodiment, the heating of the gas stream G-1 prior to contacting with the catalyst may be conducted at a temperature in the range of from 50 to 300 °C, preferably from 100 to 250 °C, and more preferably from 120 to 180 °C. Thus, according to a preferred embodiment of the present invention, prior to reacting the gas stream G-1 with the catalyst, the gas stream G-1 is heated, preferably to a temperature in the range of from 100 to 250 °C, more preferably from 120 to 180°C.

Further, according to a preferred embodiment of the present invention an activation of the catalyst takes place prior to contacting the gas stream G-1 with the catalyst, wherein, for example, the activation may be conducted by heating of the catalyst. Thus, according to a preferred embodiment of the present invention, prior to contacting the gas stream G-1 with the catalyst, the catalyst is activated, preferably by heating.

As regards the specific conditions under which the catalyst is activated, no particular restrictions exist, provided that by use of the activated catalyst a gas stream G-2 is obtained. Accordingly, said activation of the catalyst prior to contacting with the gas stream G-1 may be conducted according a preferred embodiment of the inventive process at a temperature in the range of from 250 to 700 °C, preferably from 350 to 600 °C, more preferably from 440 to 510 °C. The same applies to the duration of the activation. Thus, according to a preferred embodiment of the present invention, the activation prior to contacting with the gas stream G-1 is conducted for a period in the range of from 0.5 to 10 h, more preferably from 1 to 7 h, more preferably from 2 to 5 h. Thus, according to a preferred embodiment of the present invention, the catalyst is activated by heating to a temperature in the range of from 250 to 700 °C, preferably from 350 to 600 °C, more preferably from 440 to 510 °C, preferably for a period in the range of from 0.5 to 10 h, more preferably from 1 to 7 h, more preferably from 2 to 5 h.

According to a preferred embodiment of the present invention, a heating ramp is used for reaching the temperature of activation, wherein the heating rate preferably ranges from 0.5 to 10 K/min, preferably 1 to 5 K/min, preferably from 1 to 3 K/min. Thus, according to a pre-

ferred embodiment of the present invention, the catalyst is heated with a temperature ramp in the range of from 0.5 to 10 K/min, preferably 1 to 5 K/min, more preferably from 1 to 3 K/min.

- 5 Generally, no specific restrictions exist concerning the set-up in which the activation is conducted. According to a particularly preferred embodiment of the present invention, the catalyst is activated in the one or more reactors.

10 It is preferred that during heating the catalyst is flushed with an inert gas. As to the chemical nature of the inert gas, no particular restrictions exist. According to a particularly preferred embodiment of the present invention that during heating the catalyst is flushed with an inert gas, preferably with an inert gas selected from the group consisting of helium, nitrogen, argon, and mixtures of two or more thereof, wherein the inert gas is more preferably nitrogen.

15 As to the amount of butadiene comprised in the gas stream G-2 obtained from the contacting of the gas stream G-1 with the catalyst in step (ii) of the present invention, no particular restrictions exist. However, it was surprisingly found that by a process for the preparation of butadiene according to the inventive process, a gas stream G-2 is obtained containing butadiene in an amount of from 10 to 90 vol-%, preferably from 20 to 80 vol-%, more preferably from 30 to 70 vol-%, based on the total volume of the gas stream G-2. Therefore, embodiments of the present invention are preferred wherein the gas stream G-2 contains butadiene in an amount of from 10 to 90 vol-%, preferably from 20 to 80 vol-%, more preferably from 30 to 70 vol-%, based on the total volume of the gas stream G-2.

25 According to preferred embodiments of the present invention, the process for the preparation of butadiene further comprises a separation of butadiene from the gas stream G-2 obtained from step (ii) of the present invention, wherein a purified gas stream G-3 comprising butadiene is obtained. Generally, there are no restrictions concerning the method for the separation of butadiene from the gas stream G-2, provided that a purified gas stream G-3 comprising butadiene is obtained. Such methods may include thermal separation. Preferably, the separation of butadiene from the gas stream G-2 is achieved by thermal separation, more preferably by distillation.

35 Thus, embodiments of the present invention are preferred, wherein the process for the preparation of butadiene further comprises

- (iii) separating butadiene from the gas stream G-2, thereby obtaining a purified gas stream G-3 comprising butadiene, wherein the separation is preferably achieved by thermal separation, more preferably by distillation.

40 According to a preferred embodiment of the present invention, the gas stream G-2 comprising butadiene obtained from step (ii) of the present invention may comprise further com-

pounds resulting from contacting the gas stream G-1 with the catalyst. Thus, according to preferred embodiments of the invention the gas stream G-2 comprising butadiene further comprises diethyl ether. If the gas stream G-2 comprising butadiene further comprises diethyl ether, it is preferred that the diethyl ether is separated from the gas stream G-2 comprising butadiene. It is further preferred that the separation is carried out by thermal separation, preferably by distillation.

Further, it was found that the separated diethyl ether may be recycled to the gas-phase process for the preparation of butadiene according to the present invention, wherein it is preferred to recycle the separated diethyl ether as a component of the gas stream G-1 which is contacted with a catalyst in step (ii). Therefore, according to a preferred embodiment of the present invention, the separated diethyl ether is recycled to the gas-phase process for the preparation of butadiene according to the present invention, wherein the separated diethyl ether is preferably recycled as a component of the gas stream G-1 which is contacted with the catalyst in step (ii) to obtain butadiene. Thus, according to a preferred embodiment of the present invention, the gas stream G-2 further comprises diethyl ether, and wherein the diethyl ether is separated from the gas stream G-2, preferably by thermal separation, more preferably by distillation, and recycling the separated diethyl ether to the gas-phase process for the preparation of butadiene, preferably as component of the gas stream G-1.

According to preferred embodiments of the present invention, wherein G-2 further comprises diethyl ether which is preferably separated from G-2 and recycled preferably as component of the gas stream G-1, it is preferred that the gas stream G-2 prior to separating the diethyl ether contains diethyl ether in an amount of from 1 to 65 vol.-%, preferably from 2 to 35 vol.-%, more preferably from 5 to 30 vol.-%, based on the total volume of the gas stream G-2. Thus, according to a particularly preferred embodiment of the present invention, the gas stream G-2 contains the diethyl ether in an amount of from 1 to 65 vol.-%, preferably from 2 to 35 vol.-%, more preferably from 5 to 30 vol.-%, based on the total weight of the gas stream G-2.

As regards the separated diethyl ether from the gas stream G-1, according to a preferred embodiment of the present invention, at least a portion of the separated diethyl ether is hydrolyzed to ethanol prior to its recycling to the gas-phase process for the preparation of butadiene, preferably as component of the gas stream G-1. Thus, according to a preferred embodiment of the present invention, the process for the preparation of butadiene further comprises hydrolyzing at least a portion of the separated diethyl ether to ethanol prior to its recycling to the gas-phase process for the preparation of butadiene, preferably as component of the gas stream G-1.

As to the conditions under which hydrolyzation is conducted, according to a preferred embodiment of the present invention, the separated diethyl ether is hydrolyzed under acidic conditions, more preferably in the presence of a solid catalyst.

- 5 According to a preferred embodiment of the present invention, wherein the gas stream G-2 further comprises diethyl ether, the gas stream G-2 may further comprise crotonaldehyde. Thus, according to a preferred embodiment of the present invention, the gas mixture G-2 further comprises crotonaldehyde.
- 10 According to a preferred embodiment of the embodiment of the present invention, wherein the gas stream G-2 further comprises crotonaldehyde, it is preferred that the gas stream G-2 contains crotonaldehyde in an amount of from 0.1 to 15 vol.-%, preferably from 0.5 to 10 vol.-%, more preferably from 1 to 5 vol.-%, based on the total weight of the gas stream G-2.
- 15 According to a particularly preferred embodiment of the present invention, the gas stream G-2 comprising butadiene is free of crotonaldehyde or essentially free of crotonaldehyde, i.e. contains crotonaldehyde only in traces. Therefore, according to a particularly preferred embodiment of the present invention, the gas stream G-2 comprising butadiene contains 0.1 vol.-% or less crotonaldehyde, preferably contains crotonaldehyde in an amount of 0.05
- 20 vol.-% or less, preferably 0.01 vol.-% or less, more preferably 0.001 vol.-% or less, more preferably 0.0001 vol.-% or less.

- According to a preferred embodiment of the present invention, the catalyst is subjected to regeneration, wherein regeneration may be conducted by any suitable method. Conceivable
- 25 methods are, for example to regenerate the catalyst by thermal treatment, preferably in the presence of oxygen. Further, there are no particular restrictions concerning the temperature under which the regeneration is conducted. According to a preferred embodiment of the present invention, the thermal treatment is conducted, for example, at a temperature in the range of from 100 to 700 °C, preferably from 350 to 600 °C, more preferably from 450 to
- 30 570 °C.

- Therefore, according to a preferred embodiment of the present invention the process for the preparation of butadiene according to the present invention further comprises regenerating the catalyst, preferably by thermal treatment in the presence of oxygen, wherein the thermal
- 35 treatment is preferably performed at a temperature in the range of from 100 to 700 °C, preferably from 350 to 600 °C, more preferably from 450 to 570 °C.

- It was surprisingly found that the crystalline materials supporting one or more catalytically active materials obtained or obtainable according to the present invention can be used as
- 40 such for any suitable purpose and in particular as a catalytically active materials, such as a

catalytically active material in a process for the preparation of butadiene according to the present invention.

5 Thus, the present invention also relates to the use of a crystalline material supporting one or more catalytically active metals M, as a catalytically active material in a process for the preparation of butadiene, preferably from a gas stream comprising ethanol and optionally comprising acetaldehyde.

10 According to a preferred embodiment of the present invention, the crystalline material is used as a catalytically active material in a process for the preparation of butadiene, preferably from a gas stream comprising ethanol and optionally acetaldehyde. According to a particularly preferred embodiment of the present invention, the crystalline material used as catalytically active material in a process for the preparation of butadiene, preferably from a gas stream comprising ethanol and optionally acetaldehyde, is a crystalline material supporting
15 one or more catalytically active metals M as defined according to any of the particular and preferred embodiments of the present invention.

Thus, quite unexpectedly it was found that the zeolitic materials obtained or obtainable according to the present invention can be used in a process for the preparation of butadiene
20 according to the present invention, wherein the selectivity of the process relative to butadiene is at least 10 %, preferably in the range of from 10 to 90 %, more preferably from 20 to 80 %, and more preferably from 30 to 70 %.

Therefore, according to a particularly preferred embodiment of the present invention, the
25 zeolitic materials according to the present invention are used in a process for the preparation of butadiene according to the present invention, wherein the selectivity of the process relative to butadiene is at least 10 %, preferably in the range of from 10 to 90 %, more preferably from 20 to 80 %, more preferably from 30 to 70 %. Within the meaning of the present invention, the selectivity of the process relative to butadiene generally designates any suitable process for the preparation of butadiene, and accordingly the selectivity relative to butadiene obtained by such a process. It is, however, preferred according to the present invention, that the selectivity relative to butadiene designates a selectivity as obtained according to any of the particular and preferred embodiments of the process for the preparation of butadiene according to present invention as defined in the present application.
35

The present invention includes the following embodiments, wherein these include the specific combinations of embodiments as indicated by the respective interdependencies defined therein:

- 40 1. A process for the preparation of butadiene comprising
(i) providing a gas stream G-1 comprising ethanol;

(ii) contacting the gas stream G-1 provided in (i) with a catalyst, thereby obtaining a gas stream G-2 comprising butadiene;
wherein the catalyst comprises a crystalline material supporting one or more catalytically active metals M.

- 5
2. The process of embodiment 1, wherein the gas stream G-1 further comprises acetaldehyde.
- 10
3. The process of embodiment 2, wherein the molar ratio of ethanol to acetaldehyde in the gas stream G-1 is in the range of from 1 : 1 to 6 : 1, preferably from 2 : 1 to 3.5 : 1, more preferably from 2.5 : 1 to 2.9 : 1.
- 15
4. The process of embodiment 2 or 3, wherein 80 vol.-% or more of the gas stream G-1 consists of ethanol or of a mixture of ethanol and acetaldehyde, wherein preferably 90 vol.-% or more, more preferably 95 vol.-% or more of the gas stream G-1 consists of ethanol or of a mixture of ethanol and acetaldehyde.
- 20
5. The process of any of embodiments 1 to 4, wherein the content of the one or more catalytically active metals M in the crystalline material comprised in the catalyst is in the range of from 0.1 to 25 weight-%, preferably from 0.3 to 10 weight-%, more preferably from 0.5 to 6 weight-%, wherein M is calculated as the element and based on the total weight of the crystalline material.
- 25
6. The process of any of embodiments 1 to 5, wherein M is selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, Ta, Mn, Hf, Nb, Ga, Ge, and combinations of two or more thereof, preferably selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, and combinations of two or more thereof, more preferably selected from the group consisting of Cr, Co, Cu, Zn, Zr, and combinations of two or more thereof.
- 30
7. The process of any of embodiments 1 to 6, wherein the one or more catalytically active metals M are disposed on the crystalline material by impregnation, preferably by incipient wetness impregnation.
- 35
8. The process of embodiment 7, wherein impregnation is carried out using one or more inorganic or organic salts, wherein these salts are preferably selected from the group consisting of halides, nitrates, sulfates, phosphates, hydroxides, carboxylates, alcoholates, and combinations of two or more thereof, more preferably selected from the group consisting of chlorides, nitrates, acetates, and combinations of two or more thereof.
- 40

9. The process of embodiment 8, wherein the one or more inorganic or organic salts are selected from the group consisting of copper(II)nitrate, nickel(II)nitrate, cobalt(II)nitrate, chromium(III)nitrate, zinc(II)nitrate, copper (II)acetate, Zr(IV)oxynitrate and tin(IV)chloride, and combinations of two or more thereof.
- 5
10. The process of any of embodiments 1 to 9, wherein the crystalline material comprises a zeolitic material having a framework structure selected from the group consisting of BEA, RRO, MWW, MFI, MEL, MOR, RUT, DOH, MTN, FER, FAU, CDO, LEV, CHA, and combinations of two or more thereof, preferably selected from the group consisting of BEA, RRO, MWW, MFI, MEL, and combinations of two or more thereof, more preferably selected from BEA and/or RRO.
- 10
11. The process of embodiment 10, wherein the framework structure of the zeolitic material comprises YO_2 , Y standing for one or more tetravalent elements, wherein Y is preferably selected from the group consisting of Si, Sn, Ti, Zr, Ge, and combinations of two or more thereof, Y preferably being Si.
- 15
12. The process of embodiment 10 or 11, wherein the crystalline material comprises zeolite beta and/or RUB- 41.
- 20
13. The process of embodiment 12, wherein at least a portion of the one or more tetravalent elements Y in the framework structure of the zeolitic material is isomorphously substituted by one or more elements X1, wherein X1 preferably stands form one or more trivalent, tetravalent, and/or pentavalent elements, wherein the one or more elements X1 are preferably selected from the group consisting of Al, Ti, V, Sn, Zr, Ta, Ge, B, Fe, and combinations of two or more thereof, more preferably selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof, wherein preferably X1 is different from M.
- 25
14. The process of embodiment 13, wherein the molar ratio of Y : X1 in the framework structure ranges from 10 : 1 to 150 : 1, preferably from 30 : 1 to 100 : 1, more preferably from 45 : 1 to 80 : 1.
- 30
15. The process of any of embodiments 1 to 7, wherein the crystalline material comprised in the catalyst is a layered silicate, wherein the layered silicate is preferably selected from the group consisting of MCM-22, PREFER, Nu-6(2), CDS-1, PLS-1, MCM-47, ERS-12, MCM-65, RUB-15, RUB-18, RUB-20, RUB-36, RUB-38, RUB-39, RUB-40, RUB-42, RUB-51, BLS-1, BLS-3, ZSM-52, ZSM-55, kanemite, makatite, magadiite, kenyaite, revdite, montmorillonite, and combinations of two or more thereof, preferably selected from RUB-36 and/or RUB-39.
- 35
- 40

16. The process of any of embodiments 1 to 7, wherein the crystalline material comprised in the catalyst is a pillared silicate having a layered silicate structure, wherein the layered silicate structure is preferably selected from the group consisting of RUB-36, RUB-39, RUB-15, BLS-1, BLS-3, and combinations of two or more thereof, more preferably selected from RUB-36, RUB-39, RUB-15, and combinations of two or more thereof, wherein more preferably the layered silicate structure is RUB-36.
17. The process of embodiment 16, wherein the bridging elements in the pillared silicate are selected from the group consisting of Si, B, Mg, Ca, Ti, Zr, Zn, Al, Ga, In, Ge, Sn, Pb, Cu, Fe, and combinations of two or more thereof, preferably selected from the group consisting of Si, B, Ti, Al, Ga, In, Ge, Sn, and combinations of two or more thereof, more preferably Si, B, Al, Ga, Ge, and combinations of two or more thereof, wherein more preferably the bridging element is Si.
18. The process of any of embodiments 15 to 17, wherein at least a portion of Si in the layered silicate or in the layered silicate structure of the pillared silicate is isomorphously substituted by one or more elements X2, wherein X2 preferably stands for one or more trivalent, tetravalent, and/or pentavalent elements, wherein the one or more elements X2 are preferably selected from the group consisting of Al, Ti, V, Sn, Zr, Ta, Ge, B, Fe and combinations of two or more thereof, more preferably selected from the group consisting of Sn, Zr, Ta, and combinations of two or more thereof, wherein preferably X2 is different from M.
19. The process of embodiment 18, wherein the molar ratio of Si : X2 in the framework structure ranges from 10 : 1 to 160 : 1, preferably from 60 : 1 to 130 : 1, more preferably from 90 : 1 to 110 : 1.
20. The process of any of embodiments 1 to 19, wherein contacting the gas stream G-1 with the catalyst is carried out at a temperature in the range of from 200 to 500 °C, preferably from 250 to 450 °C, more preferably from 300 to 400 °C.
21. The process of any of embodiments 1 to 20, wherein contacting of the gas stream G-1 with the catalyst is carried out at a pressure in the range of from 1 to 5 bar, preferably from 1 to 2 bar.
22. The process of any of embodiments 1 to 21, wherein contacting gas stream G-1 with the catalyst is carried out in a continuous mode.
23. The process of any of embodiments 1 to 22, wherein contacting the gas stream G-1 with the catalyst is carried out in one or more reactors, wherein preferably the one or more reactors contain the catalyst in the form of a fixed bed.

24. The process of any of embodiments 1 to 23, wherein prior to reacting the gas stream G-1 with the catalyst, the gas stream G-1 is heated, preferably to a temperature in the range of from 100 to 250 °C, more preferably from 120 to 180°C.
- 5
25. The process of any of embodiments 1 to 24, wherein prior to contacting the gas stream G-1 with the catalyst, the catalyst is activated, preferably by heating.
26. The process of embodiment 25, wherein the catalyst is activated by heating to a temperature in the range of from 250 to 700 °C, preferably from 350 to 600 °C, more preferably from 440 to 510 °C, preferably for a period in the range of from 0.5 to 10 h, more preferably from 1 to 7 h, more preferably from 2 to 5 h.
- 10
27. The process of embodiment 25 or 26, wherein the catalyst is heated with a temperature ramp in the range of from 0.5 to 10 K/min, preferably 1 to 5 K/min, more preferably from 1 to 3 K/min.
- 15
28. The process of any of embodiments 25 to 27, wherein during heating the catalyst is flushed with an inert gas, preferably with an inert gas selected from the group consisting of helium, nitrogen, argon, and mixtures of two or more thereof, wherein the inert gas is more preferably nitrogen.
- 20
29. The process of any of embodiments 1 to 28, wherein the gas stream G-2 contains butadiene in an amount of from 10 to 90 vol.-%, preferably from 20 to 80 vol.-%, more preferably from 30 to 70 vol.-%, based on the total weight of the mixture G-2.
- 25
30. The process of any of embodiments 1 to 29, further comprising
(iii) separating butadiene from the gas stream G-2, thereby obtaining a purified gas stream G-3 comprising butadiene, wherein the separation is preferably achieved by thermal separation, more preferably by distillation.
- 30
31. The process of any of embodiments 1 to 30, wherein the gas stream G-2 further comprises diethyl ether, and wherein the diethyl ether is separated from the gas stream G-2, preferably by thermal separation, more preferably by distillation, and recycling the separated diethyl ether to the gas-phase process for the preparation of butadiene, preferably as component of the gas stream G-1.
- 35
32. The process of embodiment 31, wherein the gas stream G-2 contains the diethyl ether in an amount of from 1 to 65 vol.-%, preferably from 2 to 35 vol.-%, more preferably from 5 to 30 vol.-%, based on the total weight of the gas stream G-2.
- 40

33. The process of embodiment 31 or 32, further comprising hydrolyzing at least a portion of the separated diethyl ether to ethanol prior to its recycling to the gas-phase process for the preparation of butadiene, preferably as component of the gas stream G-1.
- 5 34. The process of embodiment 33, wherein the separated diethyl ether is hydrolyzed under acidic conditions, more preferably in the presence of a solid catalyst.
35. The process of any of embodiments 1 to 34, wherein the gas mixture G-2 further comprises crotonaldehyde.
- 10 36. The process of embodiment 35, wherein the gas stream G-2 contains crotonaldehyde in an amount of from 0.1 to 15 vol.-%, preferably from 0.5 to 10 vol.-%, more preferably from 1 to 5 vol.-%, based on the total weight of the gas stream G-2.
- 15 37. The process of any of embodiments 1 to 36, further comprising regenerating the catalyst, preferably by thermal treatment in the presence of oxygen, wherein the thermal treatment is preferably performed at a temperature in the range of from 100 to 700 °C, preferably from 350 to 600 °C, more preferably from 450 to 570 °C.
- 20 38. Use of a crystalline material supporting one or more catalytically active metals M, as a catalytically active material in a process for the preparation of butadiene, preferably from a gas stream comprising ethanol and optionally comprising acetaldehyde.
- 25 39. The use of embodiment 38, wherein the crystalline material is a crystalline material supporting one or more catalytically active metals M as defined in any one of embodiments 5 to 19.
- 30 40. The use of embodiment 38 or 39, wherein the selectivity to butadiene is in the range of from 10 to 90 %, preferably from 20 to 80 %, more preferably from 30 to 70 %.

DESCRIPTION OF THE FIGURES

- 35 Figure 1 shows the UV-VIS spectra of Zr-BEA (middle) obtained according to Reference Example 1, of Sn-BEA (bottom) obtained according to Reference Example 2, and of Ta-BEA (top) obtained according to Reference Example 3. On the x axis, the wavelength values (nanometer) are shown, and the Kubelka-Munk "K/M" axis is plotted along the y-axis.
- 40 Figure 2 shows the product formation and ethanol conversion as function of time by use of the pillared silicate obtained from Example 13 a) impregnated with zinc and

zirconium obtained from Example 13 c), according to the present invention. On the y axis, the percentage values are shown, on the x axis, the time.

Figure 3 shows the product formation and ethanol conversion as function of time by use of the pillared silicate obtained from Example 14 a) impregnated with copper, zinc and zirconium obtained from Example 14 c), according to the present invention. On the y axis, the percentage values are shown, on the x axis, the time.

Figure 4 shows the X-ray diffraction (XRD) pattern (measured using Cu K alpha-1 radiation) of the crystalline zirconium-containing zeolitic material (Zr-BEA) obtained from Reference Example 1. In the figure, the diffraction angle 2 theta in ° is shown along the abscissa and the intensities are plotted along the ordinate.

Figure 5 shows the X-ray diffraction (XRD) pattern (measured using Cu K alpha-1 radiation) of the crystalline tin-containing zeolitic material (Sn-BEA) obtained from Reference Example 2. In the figure, the diffraction angle 2 theta in ° is shown along the abscissa and the intensities are plotted along the ordinate.

Figure 6 shows the X-ray diffraction (XRD) pattern (measured using Cu K alpha-1 radiation) of the crystalline tantalum-containing zeolitic material (Ta-BEA) obtained from Reference Example 3. In the figure, the diffraction angle 2 theta in ° is shown along the abscissa and the intensities are plotted along the ordinate.

EXAMPLES

Reference Example 1: Preparation of zirconium-containing zeolitic material having a BEA framework structure (Zr-BEA)

Zr-BEA was prepared according to the description from Y. Zhu, S. Jaenicke and G.K. Chuah Chem. Commun. (2003), p. 2734. For the synthesis 41.7g tetraethylorthosilicate (TEOS) was hydrolyzed in 42.1 g tetraethylammoniumhydroxide (TEAOH) (35 weight-% in water) and 0.86 g zirconium(IV)oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) with stirring. The mixture was stirred until the ethanol formed upon hydrolysis of TEOS was evaporated at 60 °C. 4.4 g hydrofluoric acid (HF) (48% weight-% in water) was added to the reaction mixture and a solid was formed. Crystallization was carried out in a teflon-lined stainless steel autoclave at 140 °C for 30 days with tumbling at 40 rpm. The solid product obtained was filtered, washed with deionized water, dried at 100 °C and calcined at 550 °C for 10 h.

Characterization

The obtained zeolitic material had a molar ratio Si : Zr was 103 : 1, a BET specific surface area determined via nitrogen adsorption at 77 K according to DIN 66134 was 631 m²/g and a micropore volume of 0.23 cm³/g, determined by application of the t-Plot method. The solids were further characterized by UV-VIS measurements (see Figure 1), indicating solely tetrahedral coordinated Zr sites. The XRD of the obtained zeolitic material is shown in Figure 4.

Reference Example 2: Preparation of tin-containing zeolitic material having a BEA framework structure (Sn-BEA)

Zr-BEA was prepared according to the description from A. Corma, M.E. Domine, S. Valencia J. Catal., 215 (2003), pp. 294. For the synthesis 41.7g tetraethylorthosilicate (TEOS) was hydrolyzed in 42.1 g tetraethylammoniumhydroxide (TEAOH) (35 weight-% in water) together with 0.70 g and tin(IV)chloride pentahydrate (SnCl₄ · 5H₂O) with stirring. The mixture was stirred until the ethanol formed upon hydrolysis of TEOS was evaporated at 60 °C. 4.4 g hydrofluoric acid (HF) (48% weight-% in water) was added to the reaction mixture and a solid was formed. Crystallization was carried out in a teflon-lined stainless steel autoclave at 140°C for 21 days with tumbling at 40 rpm. The solid product obtained was filtered, washed with deionized water, dried at 100°C and calcined at 550°C for 10 h.

Characterization

The obtained zeolitic material had a molar ratio Si : Sn was 95 : 1, a BET specific surface area determined via nitrogen adsorption at 77 K according to DIN 66134 was 620 m²/g and a micropore volume of 0.22 cm³/g, determined by application of the t-Plot method. The solids were further characterized by UV-VIS measurements (see Figure 1), indicating solely tetrahedral coordinated Sn sites. The XRD of the obtained zeolitic material is shown in Figure 5.

Reference Example 3: Preparation of tantalum-containing zeolitic material having a BEA framework structure (Ta-BEA)

For the preparation of Ta-BEA, a dealuminated BEA structure was used as a precursor. For the preparation of the precursor 20 g SiO₂ (commercial product: Cabo-sil M5) was hydrolyzed in 28 g tetraethylammoniumhydroxide (TEAOH) (35 weight-% in water). Afterwards 3.4 g aluminium(III)nitrate nonahydrate (Al(NO₃)₃ · 9H₂O) and 0.1 g sodiumhydroxide (NaOH) were added to the reaction mixture. The crystallization was carried out in a teflon-lined stainless steel autoclave at 140°C for 3 days with tumbling at 40 rpm. The obtained solid product was filtered, washed with deionized water, and dried at 100°C for 10 h. The product was named: Al-Beta-as.

To remove the Al-sites from the zeolite framework 15 g Al-Beta-as was dispersed in 500 mL nitric acid (13 N, aqueous solution). The dispersion was stirred for 24 h under reflux conditions with stirring. After this acid treatment, the solid was filtered, washed with deionized water until a pH of 7 was reached and dried at 100°C. The obtained product was named:

De-Al-Beta.

Ta-BEA was prepared according to S. Dzwigaj, Y. Millot, M. Che Catal. Lett., 135 (2010), p. 169. For the synthesis 6 g of De-Al-Beta were added to 300 ml 2-propanol containing 0.54 g Pentaethoxytantalum(V). Thus prepared suspension was stirred for 2 h at 60 °C under argon atmosphere. Afterwards 2-propanol was evaporated at 80°C under air. Then, the obtained Ta-BEA was washed three times in distilled water and dried in air at 100 °C for 12 h.

Characterization

The obtained zeolitic material had a molar ratio Si : Ta was 77 : 1, a BET specific surface area determined via nitrogen adsorption at 77 K according to DIN 66134 was 489 m²/g and a micropore volume of 0.19 cm³/g, determined by application of the t-Plot method. The solids were further characterized by UV-VIS measurements (see Figure 1), indicating prevalent tetrahedral coordinated Ta sites. The XRD of the obtained zeolitic material is shown in Figure 6.

Reference Example 4: Measurement of the UV-VIS spectra

The measurement of the UV-VIS spectra were performed using a Lambda 950 spectrophotometer from PerkinElmer with 150 mm integrating spheres, wherein a spectralon white standard from the firm Labsphere was used as reference.

Example 1: Preparation of Zr-BEA impregnated with Cr

0.38 g chromium(II) nitrate nonahydrate were dissolved in 20 mL deionized water. 1 g of Zr-BEA obtained according to Reference Example 1 was added and water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min.

Example 2: Preparation of Zr-BEA impregnated with Co

0.25 g cobalt(II) nitrate hexahydrate were dissolved in 20 mL deionized water. 1 g of Zr-BEA obtained according to Reference Example 1 was added and water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min.

Example 3: Preparation of Zr-BEA impregnated with Ni

0.25 g nickel(II) nitrate hexahydrate were dissolved in 20 mL deionized water. 1 g of Zr-BEA obtained according to Reference Example 1 was added and water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min.

Example 4: Preparation of Zr-BEA impregnated with Cu

0.19 g copper(II) nitrate trihydrate were dissolved in 20 mL deionized water. 1 g of Zr-BEA obtained according to Reference Example 1 was added and water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min.

Example 5: Preparation of Zr-BEA impregnated with Zn

0.25 g zinc(II) nitrate hexahydrate were dissolved in 20 mL deionized water. 1 g of Zr-BEA obtained according to Reference Example 1 was added and water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min.

Example 6: Preparation of Sn-BEA impregnated with Cr

0.38 g chromium(II) nitrate nonahydrate were dissolved in 20 mL deionized water. 1 g of Sn-BEA obtained according to Reference Example 2 was added and water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min.

Example 7: Preparation of Sn-BEA impregnated with Co

0.25 g cobalt(II) nitrate hexahydrate were dissolved in 20 mL deionized water. 1 g of Sn-BEA obtained according to Reference Example 2 was added and water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min.

Example 8: Preparation of Sn-BEA impregnated with Zn

0.25 g zinc(II) nitrate hexahydrate were dissolved in 20 mL deionized water. 1 g of Sn-BEA obtained according to Reference Example 2 was added and water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min.

Example 9: Preparation of Ta-BEA impregnated with Cr

0.38 g chromium(II) nitrate nonahydrate were dissolved in 20 mL deionized water. 1 g of Ta-BEA obtained according to Reference Example 3 was added and water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min.

Example 10: Preparation of Ta-BEA impregnated with Co

0.25 g cobalt(II) nitrate hexahydrate were dissolved in 20 mL deionized water. 1 g of Ta-BEA obtained according to Reference Example 3 was added and water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min.

Example 11: Preparation of Ta-BEA impregnated with Cu

0.19 g copper(II) nitrate trihydrate were dissolved in 20 mL deionized water. 1 g of Ta-BEA obtained according to Reference Example 3 was added and water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min.

Example 12: Preparation of Ta-BEA impregnated with Zn

0.25 g zinc(II) nitrate hexahydrate were dissolved in 20 mL deionized water. 1 g of Ta-BEA obtained according to Reference Example 3 was added and water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min.

Example 13: Preparation of pillared RUB-36 impregnated with zinc and zirconium

0.023 g zinc nitrate hexahydrate and 0.038 g zirconium(IV) oxynitratehydrate were dissolved in 20 mL deionized water. 1 g of pillared RUB-36 containing Si as bridging elements obtained according to WO 2010/100191 A2 was added into the solution and the water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min. The obtained calcined material had a zinc loading of 0.5 weight-% and a zirconium loading of 1.5 weight-%.

Example 14: Preparation of pillared RUB-36 impregnated with copper, zinc and zirconium

0.031 g copper(II)acetate monohydrate, 0.023 g zinc nitrate hexahydrate and 0.025 g zirconium(IV) oxynitratehydrate were dissolved in 20 mL deionized water, 1 g of pillared RUB-36 containing Si as bridging elements obtained according to WO 2010/100191 A2 was added and the water was slowly evaporated under stirring. The obtained material was calcined in air at 500 °C for 6 h with a heating rate of 1 K/min. The obtained calcined material had a copper loading of 1 weight-%, a zinc loading of 0.5 weight-% and a zirconium loading of 1 weight-%.

Example 15: General method for the conversion of ethanol to butadiene

Experiments were conducted in a fixed bed reactor. Before testing, the catalyst obtained from Examples 1 to 14 were heated to a temperature in the range of from 450 to 500 °C with a heating ramp of 7.5 K/min in a nitrogen flow of 20 mL/min. Ethanol was evaporated and the thus obtained feed stream was converted over the catalyst at a helium flow rate of 18 mL/min and a ethanol feed rate of 2.5 microL/min, wherein the pressure of ethanol was 5kPa with 0.22 g feed per g catalyst per hour. The gaseous product mixture was analyzed by on-line gas chromatography. The temperature at which the feed stream was converted over the catalyst, the conversion of ethanol and the selectivity to butadiene are given in table 1, wherein the selectivity is calculated on the total amount of obtained products and given in percentage values.

Table 1: Results obtained from Example 15

catalyst obtained from	Catalyst substrate	impregnated with	Temp. [°C]	Conversion of ethanol [%]	Selectivity to butadiene [%]	Selectivity to diethylether [%]
Example 1	Zr-BEA	Cr	400	94.3	32.4	4.0
Example 2	Zr-BEA	Co	400	95.8	43.8	1.5
Example 3	Zr-BEA	Ni	400	99.2	19.3	1.8
Example 4	Zr-BEA	Cu	400	98.4	47.4	3.0
Example 5	Zr-BEA	Zn	400	98.7	38.4	1.6
Example 6	Sn-BEA	Cr	400	75.2	20.1	8.9
Example 7	Sn-BEA	Co	400	86.9	26.3	5.1
Example 8	Sn-BEA	Zn	400	96.4	29.8	1.2
Example 9	Ta-BEA	Cr	400	97.0	20.6	1.6
Example 10	Ta-BEA	Co	400	92.3	32.4	4.2
Example 11	Ta-BEA	Cu	400	98.5	28.7	0.6
Example 12	Ta-BEA	Zn	400	99.1	37.8	1.5
Example 13	pillared RUB-36	Zn, Zr	300	98.5*	37.2*	4.5*
Example 14	pillared RUB-36	Cu, Zn, Zr	300	50.4*	30.8*	15.5*

* After 720 min TOS

Summary and comparison of the results of Example 15 by use of the materials obtained according to Examples 1 to 14

As may be taken from the results displayed in Table 1 in Examples which are carried out according to the present invention by use of the catalysts obtained from Examples 1 to 5, i.e. catalysts comprising a zeolitic material having a BEA framework structure which is isomorphously substituted by Zr, wherein the zeolitic material is impregnated with Cr, Co, Ni, Cu or Zn, respectively, unexpectedly high conversions of ethanol in the range of from 94.3 to 99.2 vol.-% were achieved, wherein at the same time high selectivities to butadiene in the range of from 19.3 to 47.4 vol.-% were achieved. Further, it was surprisingly found that by use of a zeolitic material impregnated with Co or Cu, selectivities above 40 vol.-% to butadiene are achieved, wherein by use of the zeolitic material which is impregnated with Cu an unexpectedly high selectivity of 47 vol.-% to butadiene and at the same time an unexpectedly high conversion of ethanol of 98.4 vol.-% were achieved.

Experiments which are carried out according to the present invention by use of the catalysts obtained from Examples 6 to 8, i.e. catalysts comprising a zeolitic material having a BEA framework structure which is isomorphously substituted by Sn, wherein the zeolitic material is impregnated with Cr, Co, or Zn, respectively, leads to high selectivities to butadiene in the range of from 20.1 to 29.8 vol.-% are achieved and at the same time unexpectedly high conversions in the range of from 75.2 to 96.4 % are achieved. Furthermore, by use of the catalyst obtained from Example 6, which is impregnated with Cr, the lowest selectivity to butadiene and the lowest conversion of ethanol is achieved, however, by use of this catalyst the selectivity to diethyl ether is 8.9 vol.-%. Diethyl ether is a product of the present invention which can be hydrolyzed and recycled into the gas-phase process to obtain butadiene. Therefore, it was found that although by use of the Ta-BEA impregnated with Cr a lower selectivity to butadiene and a lower conversion of ethanol is achieved compared with the Ta-BEA impregnated with Co or Zn, the Ta-BEA impregnated with Cr leads to good yields, since the process of the present invention has the advantage that diethyl ether is obtained in a relatively high amount which can be hydrolyzed and recycled into the gas-phase process according to the present invention.

Further, in Examples which are carried out according to the present invention by use of the catalysts obtained from Examples 9 to 12, i.e. catalysts comprising a zeolitic material having a BEA framework structure which is isomorphously substituted by Ta, wherein the zeolitic material is impregnated with Cr, Co, Cu, or Zn, respectively, unexpectedly high conversions of ethanol in the range of from 92.3 to 99.1 vol.-% were achieved, wherein at the same time high selectivities to butadiene in the range of from 20.6 to 37.8 vol.-% were achieved. Further, it was surprisingly found that by use of a zeolitic material impregnated with Cr or Zn, selectivities above 30 vol.-% to butadiene are achieved, wherein by use of the zeolitic material which is impregnated with Zn an unexpectedly high selectivity of 37.2

vol.-% to butadiene and at the same time an unexpectedly high conversion of ethanol of 99.1 vol.-% were achieved.

Also, in Examples which are carried out according to the present invention by use of the catalysts obtained from Examples 13 and 14, i.e. catalysts comprising a layered silicate impregnated with Zn and Zr or with Cu, Zn and Zr, unexpected high selectivities to butadiene above 30 vol.-% are achieved. Furthermore, by use of the catalyst obtained from Example 13, i.e. a layered silicate impregnated with Zn and Zr, a conversion of ethanol of 98.5 vol.-% is achieved. Although by use of the catalyst obtained from Example 14 a lower conversion of ethanol and a lower selectivity to butadiene is achieved compared to the catalyst obtained from Example 13, the catalyst obtained from Example 14 leads to good yields, since by use of this catalyst a selectivity to diethyl ether of 15.5 vol.-% is achieved, wherein the diethyl ether can be hydrolyzed and recycled into the gas-phase process according to the present invention.

Cited Prior Art

- GB 331482
- US 2421361
- WO 2012/015340 A1
- WO 2010/100191 A2
- Ind. Eng. Chem. 41 (1949), pages 1012-1017
- Catal. Sci. Technol. 1 (2011), 267-272
- WO 2010/100191 A2

Claims

1. A process for the preparation of butadiene comprising
 - (i) providing a gas stream G-1 comprising ethanol;
 - (ii) contacting the gas stream G-1 provided in (i) with a catalyst, thereby obtaining a gas stream G-2 comprising butadiene;wherein the catalyst comprises a crystalline material supporting one or more catalytically active metals M.
2. The process of claim 1, wherein the gas stream G-1 further comprises acetaldehyde.
3. The process of claim 2, wherein the molar ratio of ethanol to acetaldehyde in the gas stream G-1 is in the range of from 1 : 1 to 6 : 1.
4. The process of claim 2 or 3, wherein 80 vol.-% or more of the gas stream G-1 consists of ethanol or of a mixture of ethanol and acetaldehyde.
5. The process of any of claims 1 to 4, wherein the content of the one or more catalytically active metals M in the crystalline material comprised in the catalyst is in the range of from 0.1 to 25 weight-%, wherein M is calculated as the element and based on the total weight of the crystalline material.
6. The process of any of claims 1 to 5, wherein M is selected from the group consisting of Cr, Co, Ni, Cu, Zn, Zr, Sn, Ta, Mn, Hf, Nb, Ga, Ge, and combinations of two or more thereof.
7. The process of any of claims 1 to 6, wherein the one or more catalytically active metals M are disposed on the crystalline material by impregnation.
8. The process of claim 7, wherein impregnation is carried out using one or more inorganic or organic salts.
9. The process of claims 8, wherein the one or more inorganic or organic salts are selected from the group consisting of copper(II)nitrate, nickel(II)nitrate, cobalt(II)nitrate, chromium(III)nitrate, zinc(II)nitrate, copper (II)acetate, Zr(IV)oxynitrate and tin(IV)chloride, and combinations of two or more thereof.
10. The process of any of claims 1 to 9, wherein the crystalline material comprises a zeolitic material having a framework structure selected from the group consisting of BEA,

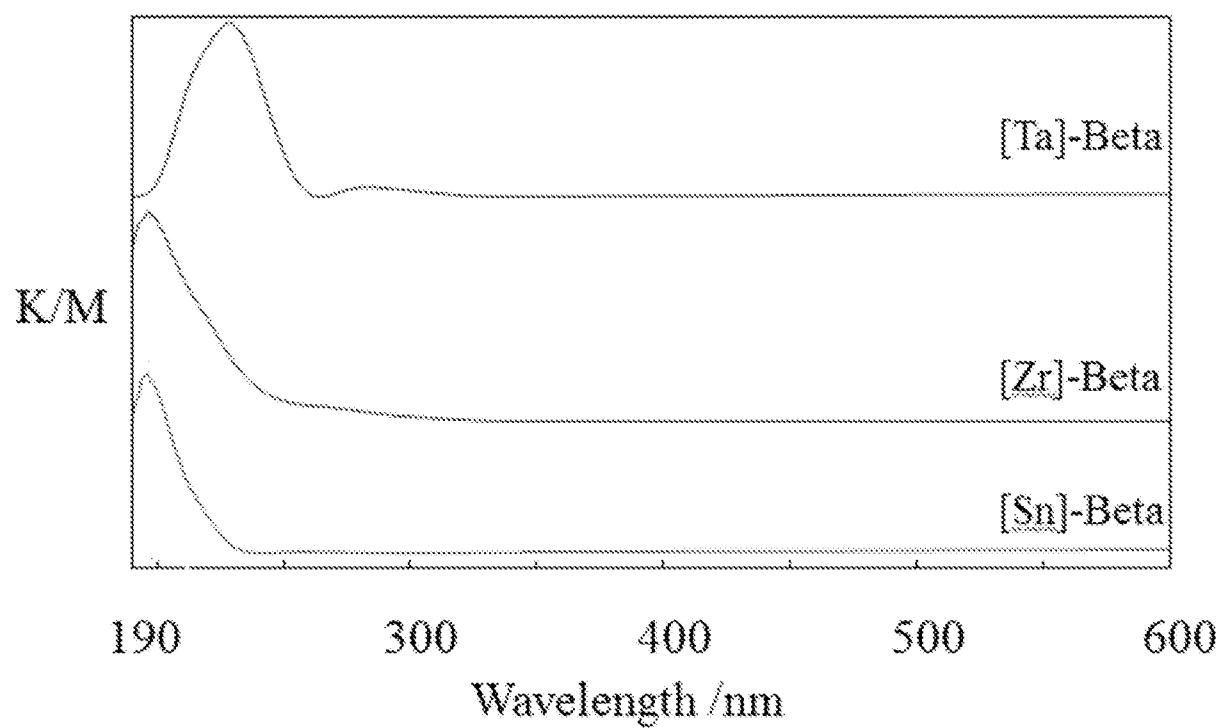
RRO, MWW, MFI, MEL, MOR, RUT, DOH, MTN, FER, FAU, CDO, LEV, CHA, and combinations of two or more thereof.

- 5 11. The process of claim 10, wherein the framework structure of the zeolitic material comprises YO_2 , Y standing for one or more tetravalent elements.
12. The process of claim 10 or 11, wherein the crystalline material comprises zeolite beta and/or RUB- 41.
- 10 13. The process of claim 12, wherein at least a portion of the one or more tetravalent elements Y in the framework structure of the zeolitic material is isomorphously substituted by one or more elements X1.
- 15 14. The process of claim 13, wherein the molar ratio of Y : X1 in the framework structure ranges from 10 : 1 to 150 : 1.
15. The process of any of claims 1 to 7, wherein crystalline material comprised in the catalyst is a layered silicate.
- 20 16. The process of any of claims 1 to 7, wherein the crystalline material comprised in the catalyst is a pillared silicate having a layered silicate structure.
- 25 17. The process of claim 16, wherein the bridging elements in the pillared silicate are selected from the group consisting of Si, B, Mg, Ca, Ti, Zr, Zn, Al, Ga, In, Ge, Sn, Pb, Cu, Fe, and combinations of two or more thereof.
18. The process of any of claims 15 to 17, wherein at least a portion of Si in the layered silicate is isomorphously substituted by one or more elements X2.
- 30 19. The process of claim 18, wherein the molar ratio of Si : X2 in the framework structure ranges from 10 : 1 to 160 : 1.
20. The process of any of claims 1 to 19, wherein contacting the gas stream G-1 with the catalyst is carried out at a temperature in the range of from 200 to 500 °C.
- 35 21. The process of any of claims 1 to 20, wherein contacting of the gas stream G-1 with the catalyst is carried out at a pressure in the range of from 1 to 5 bar.
- 40 22. The process of any of claims 1 to 21, wherein contacting gas stream G-1 with the catalyst is carried out in a continuous mode.

23. The process of any of claims 1 to 22, wherein contacting the gas stream G-1 with the catalyst is carried out in one or more reactors.
24. The process of any of claims 1 to 23, wherein prior to reacting the gas stream G-1 with the catalyst, the gas stream G-1 is heated.
25. The process of any of claims 1 to 24, wherein prior to contacting the gas stream G-1 with the catalyst, the catalyst is activated.
26. The process of claim 25, wherein the catalyst is activated by heating to a temperature in the range of from 250 to 700 °C.
27. The process of claim 25 or 26, wherein the catalyst is heated with a temperature ramp in the range of from 0.5 to 10 K/min.
28. The process of any of claims 25 to 27, wherein during heating the catalyst is flushed with an inert gas.
29. The process of any of claims 1 to 28, wherein the gas stream G-2 contains butadiene in an amount of from 10 to 90 vol.-%, based on the total weight of the mixture G-2.
30. The process of any of claims 1 to 29, further comprising
(iii) separating butadiene from the gas stream G-2, thereby obtaining a purified gas stream G-3 comprising butadiene.
31. The process of any of claims 1 to 30, wherein the gas stream G-2 further comprises diethyl ether, and wherein the diethyl ether is separated from the gas stream G-2.
32. The process of claim 30 or 31, wherein the gas stream G-2 contains the diethyl ether in an amount of from 1 to 65 vol.-%, based on the total weight of the gas stream G-2.
33. The process of claim 31 or 32, further comprising hydrolyzing at least a portion of the separated diethyl ether to ethanol prior to its recycling to the gas-phase process for the preparation of butadiene.
34. The process of claim 33, wherein the separated diethyl ether is hydrolyzed under acidic conditions.
35. The process of any of claims 1 to 34, wherein the gas mixture G-2 further comprises crotonaldehyde.

36. The process of claim 35, wherein the gas stream G-2 contains crotonaldehyde in an amount of from 0.1 to 15 vol.-%, based on the total weight of the gas stream G-2.
37. The process of any of claims 1 to 36, further comprising regenerating the catalyst.
- 5 38. Use of a crystalline material supporting one or more catalytically active metals M, as a catalytically active material in a process for the preparation of butadiene.
- 10 39. The use of claim 38, wherein the crystalline material is a crystalline material supporting one or more catalytically active metals M as defined in any one of claims 5 to 19.
40. The use of claim 38 or 39, wherein the selectivity to butadiene is in the range of from 10 to 90 %.

Figure 1



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Figure 2

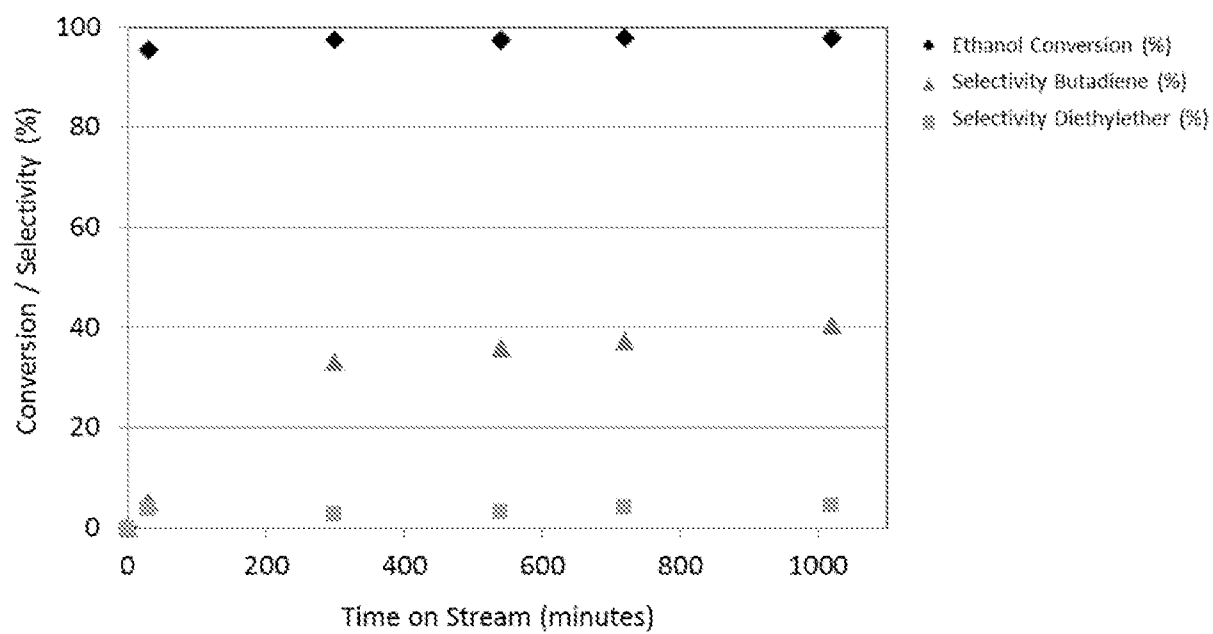


Figure 3

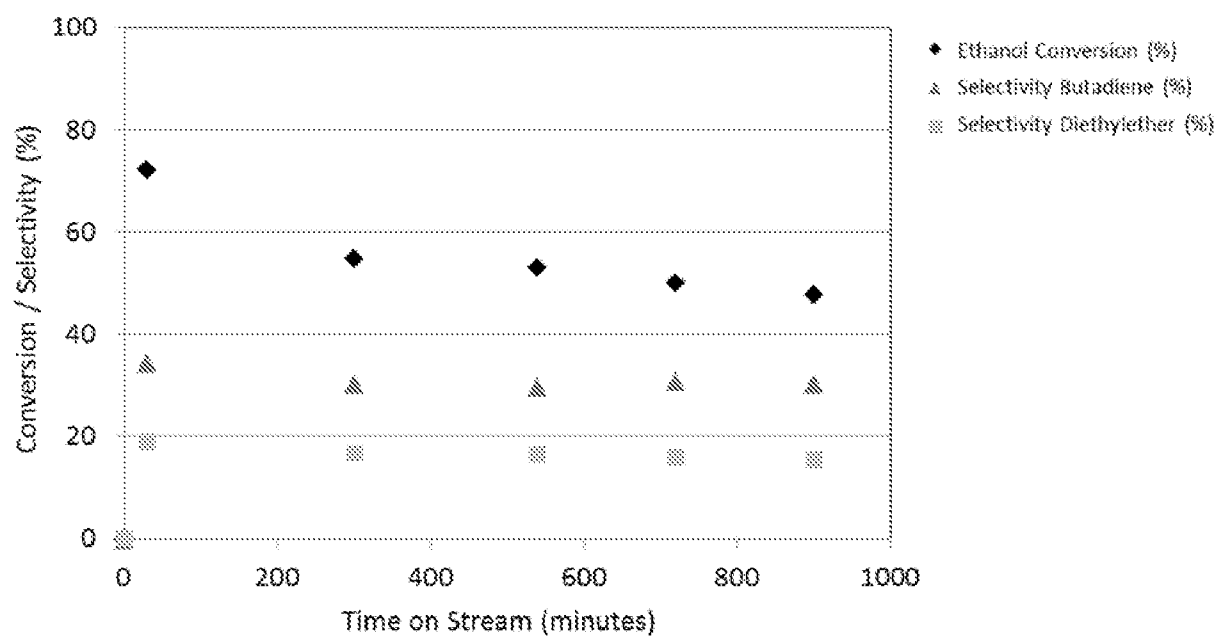


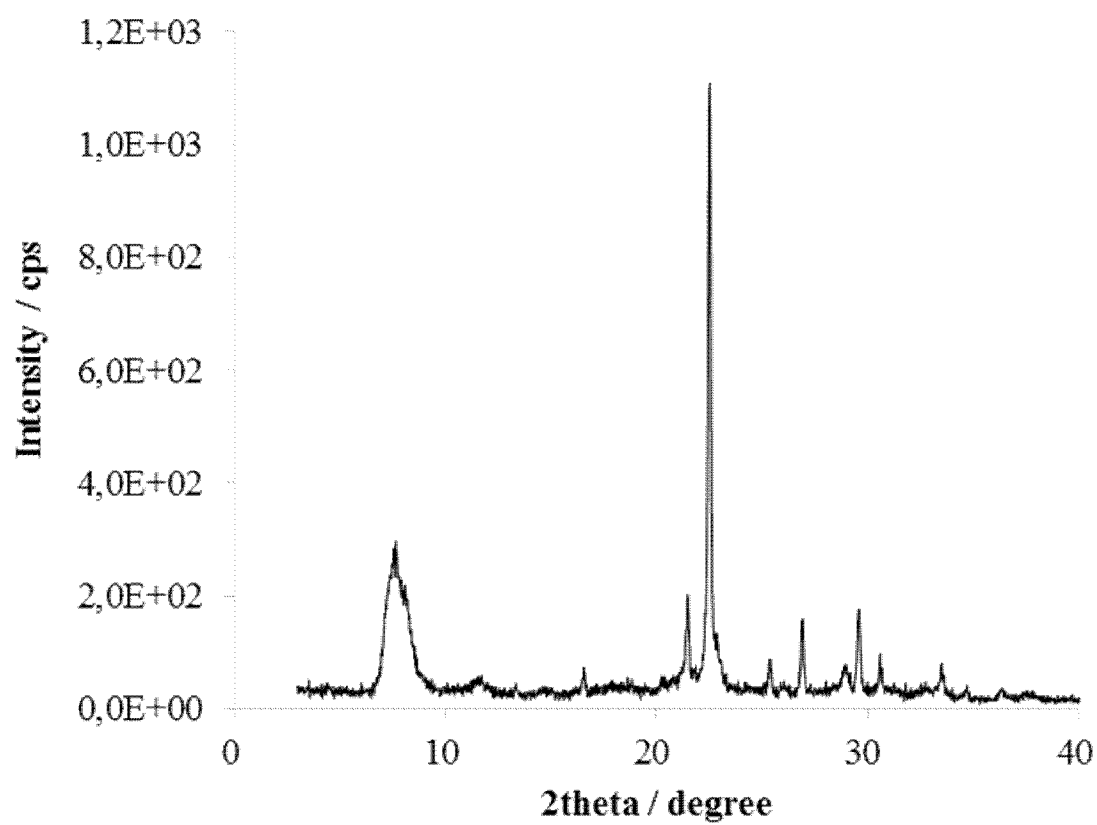
Figure 4

Figure 5

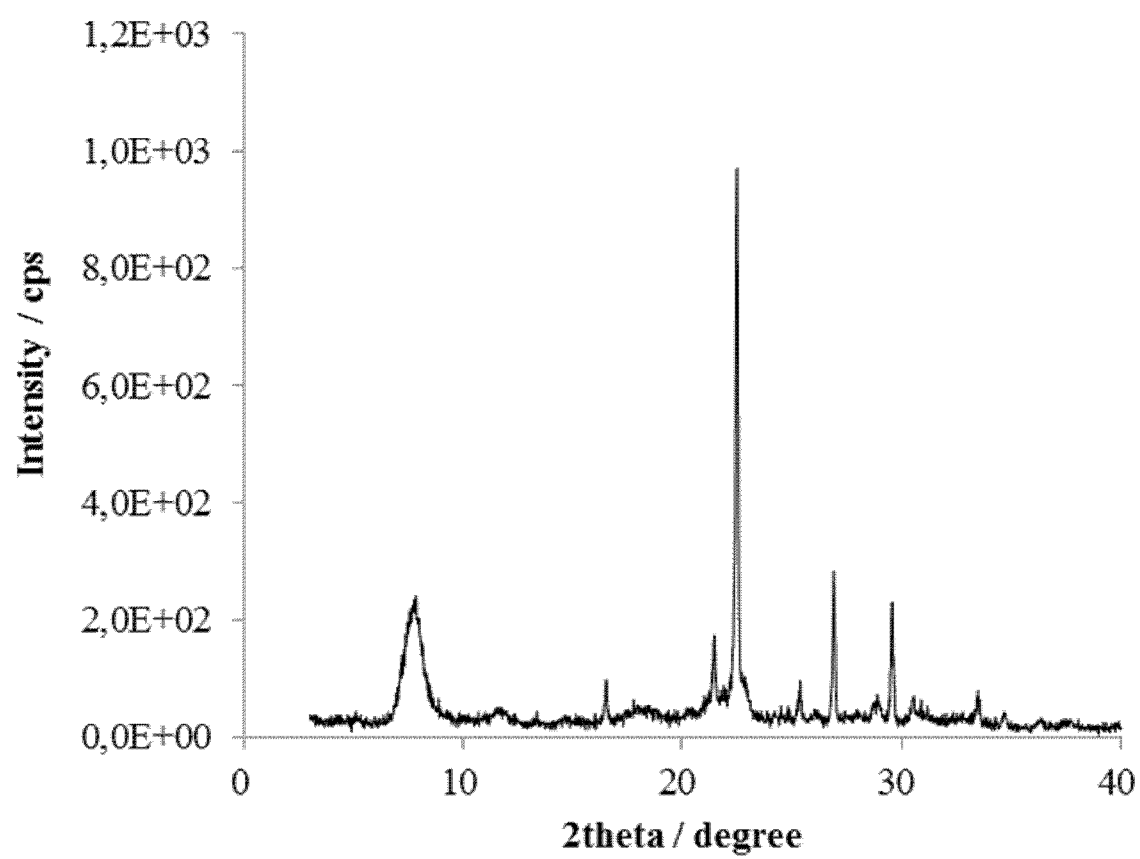


Figure 6

