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CATALYST PARTICLES, PROCESS FOR THE PREPARATION OF AN  
OLEFINIC PRODUCT, AND PROCESS FOR THE PREPARATION OF AN  
OXYGENATE CONVERSION CATALYST

Field of the Invention

This invention relates to catalyst particles, a  
process for the an olefinic product, and to a process for  
the preparation of an oxygenate conversion catalyst. The  
5 invention is useful for for the preparation of an olefin  
or olefinic product, especially lower olefins such as  
ethylene and/or propylene. In particular this invention  
relates to the conversion of an oxygenate feedstock into  
olefins.

Background of the invention

Processes for the preparation of olefins from  
oxygenates are known in the art. Of particular interest  
is often the production of light olefins, in particular  
ethylene and/or propylene. The oxygenate feedstock can  
15 for example comprise methanol and/or dimethylether, and  
an interesting route includes their production from  
synthesis gas derived from e.g. natural gas or via coal  
gasification.

For example, WO2007/135052 discloses a process  
20 wherein an alcohol and/or ether containing oxygenate  
feedstock and an olefinic co-feed are reacted in the  
presence of a zeolite having one-dimensional 10-membered  
ring channels to prepare an olefinic reaction mixture,  
and wherein part of the obtained olefinic reaction  
25 mixture is recycled as olefinic co-feed. With a methanol  
and/or dimethylether containing feedstock, and an  
olefinic co-feed comprising C4 and/or C5 olefins, an  
olefinic product rich in light olefins can be obtained.

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WO2004/056944 discloses a process for cracking C4-C8 hydrocarbons, to prepare olefins, especially propylene, wherein a catalyst with a combination of ZSM-12 with either ZSM-5 or ZSM-23 is used. No reference to oxygenates is made.

US 6 797 851 describes a process for making ethylene and propylene from an oxygenate feed. The process is conducted in two stages using two different zeolite catalysts, wherein in the first stage oxygenates are converted to a light olefin stream, and wherein in the second stage C4+ olefins produced in the first stage are converted to additional ethylene and propylene. The only zeolite that is disclosed for the first step is ZSM-5. For the second stage, zeolite ZSM-22 and ZSM-35 are disclosed in experiments. Various embodiments of reaction systems with first and second stage catalyst in separate reaction zones are discussed. Without disclosing an embodiment, it is generally mentioned that the two catalysts can be mixed.

#### Summary of the invention

It is desired to provide a process and suitable catalyst to maximise production of light olefins, and in a particular aspect maximise the production of ethylene, from an oxygenate feedstock.

According to a first aspect of the present invention, there is provided catalyst particles comprising a first molecular sieve having one-dimensional 10-membered ring channels, and a second molecular sieve having more-dimensional channels. Thus, the individual catalyst particles comprise both the first molecular sieve and the second molecular sieve. Typically the molecular sieves comprise or consist of crystals.

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According to a second aspect of the present invention, there is provided a process for the preparation of an olefinic product, which process comprises reacting an oxygenate feedstock in a reaction zone in the presence of oxygenate conversion catalyst particles to prepare an olefinic reaction product; wherein individual oxygenate conversion catalyst particles comprise both a first molecular sieve having one-dimensional 10-membered ring channels, and a second molecular sieve having more-dimensional channels, according to the first aspect of the invention. .

Thus the first and second molecular sieves are intimately mixed, that is crystals of the first and second molecular sieves are present in the same particle, as opposed to a mixture of catalyst particles where individual particles include one or other of the various molecular sieve types, not both.

Preferably therefore an average distance between a crystal of the first molecular sieve and a crystal of the second molecular sieve is less than an average particle size of the catalyst particles, preferably 40  $\mu\text{m}$  or less, more preferably 20  $\mu\text{m}$  or less, especially 10  $\mu\text{m}$  or less. For near-spherical particles the average particle size can be determined by the weight-averaged diameter of a statistically representative quantity of particles, such as of e.g. 10 mg, 100 mg, 250 mg, or 1 g of particles. Such a statistically representative quantity of particles is referred to herein as a bed of particles. For other shapes of catalyst particles the skilled person knows how to define a suitable average of a characteristic dimension as average particle size, preferably a weight-average is used.

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Preferably a bed of the catalyst particles comprises at least 1 wt% and less than 50 wt% of the second molecular sieve, based on the total weight of first and second molecular sieves in the bed; preferably at least 5 wt% and less than 40 wt%, more preferably at least 8 wt% and less than 25 wt%. For certain embodiments the second molecular sieve may be present at less than 18wt% and indeed may be less than 15 wt% based on the total weight of molecular sieves in the catalyst composition.

According to a further aspect of the present invention there is provided a process for the preparation of an oxygenate conversion catalyst, the process comprising preparing oxygenate conversion catalyst particles comprising a first molecular sieve having one-dimensional 10-membered ring channels, and a second molecular sieve having more-dimensional channels such that the resulting individual catalyst particles comprise both the first molecular sieve and second molecular sieve.

To form a catalyst the first and second molecular sieves are typically embedded in a matrix. For the purposes of this invention 'matrix' is herein referred to as including any filler and/or binder components.

For certain embodiments, a mixture comprising the first and second molecular sieves and matrix are spray dried to form the catalyst particles. Typically a mixture comprising the first and second molecular sieves are milled, either separately but preferably together, before the matrix is added to form a slurry that is spray dried.

Alternatively the first and second molecular sieves are co-crystallised or intergrown. For such embodiments a

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matrix is typically added after co-crystallisation and the resulting mixture is then spray dried.

Preferably the catalyst particles prepared in accordance with the further aspect of the present invention are used in a process in accordance with the  
5 second aspect of the present invention.

The process of the invention allows maximising of olefin production, in particular ethylene and/or propylene production, more in particular a high ethylene  
10 make, from an oxygenate feedstock comprising e.g. methanol and/or dimethylether. It has been found that an oxygenate conversion catalyst comprising or consisting of oxygenate conversion particles according to the present invention is particularly effective for this purpose. It  
15 has been found particularly advantageous to apply this catalyst for converting a reaction mixture comprising an olefinic co-feed in addition to the oxygenate, to an olefinic product comprising ethylene and/or propylene.

Examples of an oxygenate that can be used as  
20 feedstock in the present invention include alcohols, such as methanol, ethanol, isopropanol, ethylene glycol, propylene glycol; ketones, such as acetone and methylethylketone; aldehydes, such as formaldehyde, acetaldehyde and propionaldehyde; ethers, such as  
25 dimethylether, diethylether, methylethylether, tetrahydrofuran and dioxane; epoxides such as ethylene oxide and propylene oxide; and acids, such as acetic acid, propionic acid, formic acid and butyric acid. Further examples are dialkyl carbonates such as dimethyl  
30 carbonate or alkyl esters of carboxylic acids such as methyl formate. Of these examples, alcohols and ethers are preferred.

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Examples of preferred oxygenates include alcohols, such as methanol, ethanol, isopropanol, ethylene glycol, propylene glycol; and dialkyl ethers, such as dimethylether, diethylether, methylethylether. Cyclic ethers such as tetrahydrofuran and dioxane, are also suitable.

The oxygenate used in the process according to the invention is preferably an oxygenate which comprises at least one oxygen-bonded alkyl group. The alkyl group preferably is a C1-C4 alkyl group, i.e. comprises 1 to 4 carbon atoms; more preferably the alkyl group comprises 1 or 2 carbon atoms and most preferably one carbon atom. The oxygenate can comprise one or more of such oxygen-bonded C1-C4 alkyl groups. Preferably, the oxygenate comprises one or two oxygen-bonded C1-C4 alkyl groups.

More preferably an oxygenate is used having at least one C1 or C2 alkyl group, still more preferably at least one C1 alkyl group.

Preferably the oxygenate is chosen from the group of alkanols and dialkyl ethers consisting of dimethylether, diethylether, methylethylether, methanol, ethanol and isopropanol, and mixtures thereof.

Most preferably the oxygenate is methanol or dimethylether, or a mixture thereof.

Preferably the oxygenate feedstock comprises at least 50 wt% of methanol and/or dimethylether, more preferably at least 80 wt%, most preferably at least 90 wt%.

The oxygenate feedstock can be obtained from a prereactor, which converts methanol at least partially into dimethylether. In this way, water may be removed by distillation and so less water is present in the process of converting oxygenate to olefins, which has advantages

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for the process design and lowers the severity of hydrothermal conditions the catalyst is exposed to.

5 The oxygenate feedstock can comprise an amount of water, preferably less than 10 wt%, more preferably less than 5 wt%, based on the total weight of oxygenate feedstock. Preferably the oxygenate feedstock contains essentially no hydrocarbons other than oxygenates, i.e. less than 5 wt%, preferably less than 1 wt%, based on the total weight of oxygenate feedstock.

10 In one embodiment, the oxygenate is obtained as a reaction product of synthesis gas. Synthesis gas can for example be generated from fossil fuels, such as from natural gas or oil, or from the gasification of coal. Suitable processes for this purpose are for example  
15 discussed in Industrial Organic Chemistry, Klaus Weissermehl and Hans-Jürgen Arpe, 3rd edition, Wiley, 1997, pages 13-28. This book also describes the manufacture of methanol from synthesis gas on pages 28-30.

20 In another embodiment the oxygenate is obtained from biomaterials, such as through fermentation. For example by a process as described in DE-A-10043644.

In a particular embodiment the oxygenate feedstock is reacted to produce the olefinic product in the presence  
25 of an olefinic co-feed. By an olefinic composition or stream, such as an olefinic product, product fraction, fraction, effluent, reaction product or the like is understood a composition or stream comprising one or more olefins, unless specifically indicated otherwise. Other  
30 species can be present as well. Apart from olefins, the olefinic co-feed may contain other hydrocarbon compounds, such as for example paraffinic compounds. Preferably the olefinic co-feed comprises an olefinic portion of more

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than 50 wt%, more preferably more than 60 wt%, still more preferably more than 70 wt%, which olefinic portion consists of olefin(s). The olefinic co-feed can also consist essentially of olefin(s).

5           Any non-olefinic compounds in the olefinic co-feed are preferably paraffinic compounds. Such paraffinic compounds are preferably present in an amount in the range from 0 to 50 wt%, more preferably in the range from 0 to 40 wt%, still more preferably in the range from 0 to  
10       30 wt%.

          By an olefin is understood an organic compound containing at least two carbon atoms connected by a double bond. The olefin can be a mono-olefin, having one double bond, or a poly-olefin, having two or more double  
15       bonds. Preferably olefins present in the olefinic co-feed are mono-olefins. C4 olefins, also referred to as butenes (1-butene, 2-butene, iso-butene, and/or butadiene), in particular C4 mono-olefins, are preferred components in the olefinic co-feed.

20           Preferably, when an olefinic co-feed is used, it is at least partially obtained by a recycle stream formed by recycling a suitable fraction of the reaction product comprising C4 olefin. The skilled artisan knows how to obtain such a fraction from the olefinic reaction product  
25       such as by distillation.

          In one embodiment at least 70 wt% of the olefinic co-feed, during normal operation, is formed by the recycle stream, preferably at least 90 wt%, more preferably at least 99 wt%. Most preferably the olefinic co-feed is  
30       during normal operation formed by the recycle stream, so that the process converts oxygenate feedstock to predominantly light olefins without the need for an external olefins stream. During normal operation means

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for example in the course of a continuous operation of the process, for at least 70% of the time on stream. The olefinic co-feed may need to be obtained from an external source, such as from a catalytic cracking unit or from a naphtha cracker, during start-up of the process, when the reaction product comprises no or insufficient C4+ olefins.

The C4 fraction contains C4 olefin(s), but can also contain a significant amount of other C4 hydrocarbon species, in particular C4 paraffins, because it is difficult to economically separate C4 olefins and paraffins, such as by distillation.

In a preferred embodiment the olefinic co-feed and preferably also the recycle stream comprises C4 olefins and less than 10 wt% of C5+ hydrocarbon species, more preferably at least 50 wt% of C4 olefins, and at least a total of 70 wt% of C4 hydrocarbon species.

The olefinic co-feed and preferably also the recycle stream, can in particular contain at least a total of 90 wt% of C4 hydrocarbon species. In a preferred embodiment, the olefinic co-feed comprises less than 5 wt% of C5+ olefins, preferably less than 2 wt% of C5+ olefins, even more preferably less than 1 wt% of C5+ olefins, and likewise the recycle stream. In another preferred embodiment, the olefinic co-feed, comprises less than 5 wt% of C5+ hydrocarbon species, preferably less than 2 wt% of C5+ hydrocarbon species even more preferably less than 1 wt% of C5+ hydrocarbon species, and likewise the recycle stream.

Thus in certain preferred embodiments, the olefinic portion of the olefinic co-feed, and of the recycle stream, comprises at least 90 wt% of C4 olefins, more preferably at least 99 wt%. Butenes as co-feed have been

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found to be particularly beneficial for high ethylene selectivity. Therefore one particularly suitable recycle stream consists essentially, i.e. for at least 99 wt%, of 1-butene, 2-butene (cis and trans), isobutene, n-butane, isobutene, butadiene.

In certain embodiments, the recycle stream can also comprise propylene. This may be preferred when a particularly high production of ethylene is desired, so that part or all of the propylene produced, such as at least 5 wt% thereof, is recycled together with C4 olefins.

The preferred molar ratio of oxygenate in the oxygenate feedstock to olefin in the olefinic co-feed depends on the specific oxygenate used and the number of reactive oxygen-bonded alkyl groups therein. Preferably the molar ratio of oxygenate to olefin in the total feed lies in the range of 10:1 to 1:10, more preferably in the range of 5:1 to 1:5 and still more preferably in the range of 3:1 to 1:3.

In a preferred embodiment wherein the oxygenate comprises only one oxygen-bonded methyl group, such as methanol, the molar ratio preferably lies in the range from 5:1 to 1:5 and more preferably in the range of 2.5:1 to 1:2.5.

In another preferred embodiment wherein the oxygenate comprises two oxygen-bonded methyl groups, such as for example dimethylether, the molar ratio preferably lies in the range from 5:2 to 1:10 and more preferably in the range of 2:1 to 1:4. Most preferably the molar ratio in such a case is in the range of 1.5:1 to 1:3.

The expression 'molecular sieve' is used in the description and claims for a material containing small regular pores and/or channels and exhibiting catalytic

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activity in the conversion of oxygenate to olefin. The first molecular sieve having one-dimensional 10-membered ring channels and/or the second molecular sieve having more-dimensional channels ("more-dimensional molecular sieve") can in particular be a zeolite or zeolites. A zeolite is understood to be an aluminosilicate molecular sieve. Where reference is made in the description and in the claims to a molecular sieve, this can in particular be a zeolite. The first molecular sieve having one-dimensional 10-membered ring channels and/or the second molecular sieve having more-dimensional channels can be a mixture of different types of molecular sieves having the respective channel structures. So, for example, a mixture of ZSM-22 and ZSM-23 zeolites, both having one-dimensional 10-membered ring channels, can be used as first molecular sieve. Similarly, different more-dimensional molecular sieves can be mixed to form the second molecular sieve.

The process to prepare an olefin is carried out in presence of the first molecular sieve having one-dimensional 10-membered ring channels. These are understood to be molecular sieves having only 10-membered ring channels in one direction, which are not intersected by other channels, in particular other 8, 10 or 12-membered ring channels, from another direction.

Preferably, the first molecular sieve is a zeolite especially one selected from the group of TON-type (for example zeolite ZSM-22), MTT-type (for example zeolite ZSM-23), STF-type (for example SSZ-35), SFF-type (for example SSZ-44), EUO-type (for example ZSM-50), and EU-2-type molecular sieves or mixtures thereof.

MTT-type catalysts are more particularly described in e.g. US-A-4,076,842. For purposes of the present

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invention, MTT is considered to include its isotypes, e.g., ZSM-23, EU-13, ISI-4 and KZ-1.

TON-type molecular sieves are more particularly described in e.g. US-A-4,556,477. For purposes of the present invention, TON is considered to include its isotypes, e.g., ZSM-22, Theta-1, ISI-1, KZ-2 and NU-10.

EU-2-type molecular sieves are more particularly described in e.g. US-A-4,397,827. For purposes of the present invention, EU-2 is considered to include its isotypes, e.g., ZSM-48.

In a further preferred embodiment a first molecular sieve of the MTT-type, such as ZSM-23, and/or a TON-type, such as ZSM-22 is used.

Molecular sieve and zeolite types are for example defined in Ch. Baerlocher and L.B. McCusker, Database of Zeolite Structures: <http://www.iza-structure.org/databases/>, which database was designed and implemented on behalf of the Structure Commission of the International Zeolite Association (IZA-SC), and based on the data of the 4th edition of the Atlas of Zeolite Structure Types (W.M. Meier, D.H. Olson and Ch. Baerlocher).

The second molecular sieve having more-dimensional channels is understood to have intersecting channels in at least two directions. So, for example, the channel structure is formed of substantially parallel channels in a first direction, and substantially parallel channels in a second direction, wherein channels in the first and second directions intersect. Intersections with a further channel type are also possible. Preferably the channels in at least one of the directions are 10-membered ring channels. The second molecular sieve can be for example a FER type zeolite which is a two-dimensional structure and

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has 8- and 10-membered rings intersecting each other. Preferably however the intersecting channels in the second molecular sieve are each 10-membered ring channels. Thus the second molecular sieve may be a zeolite, or a SAPO-type (silicoaluminophosphate) molecular sieve. More preferably however the second molecular sieve is a zeolite. A preferred second molecular sieve is an MFI-type zeolite, in particular zeolite ZSM-5.

The presence of the second molecular sieve in the oxygenate conversion catalyst particles was found to improve stability (slower deactivation during extended runs) and hydrothermal stability compared to a catalyst with only the one-dimensional molecular sieve and without the more-dimensional molecular sieve. Without wishing to be bound by a particular hypothesis or theory, it is presently believed that this is due to the possibility for converting larger molecules by the second molecular sieve having more-dimensional channels, that were produced by the first molecular sieve having one-dimensional 10-membered ring channels, and which would otherwise form coke. Moreover the intimate mix of the first with the second molecular sieve, such that both are present in the individual catalyst particles, was found to improve the selectivity towards ethylene and propylene, more in particular towards ethylene.

The weight ratio between the first molecular sieve having one-dimensional 10-membered ring channels, and the second molecular sieve having more-dimensional channels can be in the range of from 1:100 to 100:1. Preferably, the first molecular sieve is present in a weight majority. The weight ratio of first to second molecular

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sieve can be of from 1:1 to 100:1, more preferably in the range of from 9:1 to 2:1.

In preferred embodiments the second molecular sieve is an MFI-type molecular sieve, in particular zeolite ZSM-5, having a Silica-to-Alumina ratio SAR of at least 60, more preferably at least 80, even more preferably at least 100, yet more preferably at least 150. At higher SAR the percentage of C4 saturates in the C4 totals produced is minimized. In special embodiments the oxygenate conversion catalyst particles can comprise less than 35 wt% of the second molecular sieve, based on the total molecular sieve in the oxygenate conversion catalyst, in particular less than 20 wt%, more in particular less than 18 wt%, still more in particular less than 15 wt%. Suitably at least 1 wt% of the second molecular sieve, based on the total molecular sieve, is present in the particles.

In one embodiment the oxygenate conversion catalyst can comprise more than 50 wt%, preferably at least 65 wt%, based on total molecular sieve in the oxygenate conversion catalyst, of the molecular sieve having one-dimensional 10-membered ring channels. The presence of a majority of such molecular sieve strongly determines the predominant reaction pathway.

Without wishing to be bound by a particular hypothesis or theory, it is currently believed that the reaction is dominated by a majority portion of the molecular sieve having one-dimensional 10-membered ring channels. In such molecular sieve an alcohol or ether oxygenate can be converted to an olefinic product by an initial alkylation step with an olefin from the olefinic co-feed, followed by cracking. The presence of a minority portion of a more-dimensional molecular sieve in the

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oxygenate conversion catalyst particles was found sufficient to significantly improve stability and hydrothermal stability compared to a catalyst with only the one-dimensional molecular sieve and without the more-  
5 dimensional molecular sieve.

In one embodiment, the first and second molecular sieves are used in their hydrogen form in the oxygenate conversion catalyst, e.g., HZSM-22, HZSM-23, and HZSM-48, HZSM-5. Preferably at least 50% w/w, more preferably at  
10 least 90% w/w, still more preferably at least 95% w/w and most preferably 100% of the total amount of molecular sieve used is in the hydrogen form. When the molecular sieves are prepared in the presence of organic cations the molecular sieve may be activated by heating in an  
15 inert or oxidative atmosphere to remove organic cations, for example, by heating at a temperature over 500 °C for 1 hour or more. The sieves are typically obtained in the sodium or potassium form. The hydrogen form can then be obtained by an ion exchange procedure with ammonium salts  
20 followed by another heat treatment, for example in an inert or oxidative atmosphere at a temperature over 300 °C. The molecular sieves obtained after ion-exchange are also referred to as being in the ammonium form.

In a preferred embodiment the first molecular sieve  
25 having one-dimensional 10-membered ring channels comprises at least one of a molecular sieve of the MTT-type and/or of the TON-type. Examples are ZSM-23 for MTT, and ZSM-22 for TON.

Suitably the molecular sieve having one-dimensional  
30 10-membered ring channels has a Silica-to-Alumina ratio (SAR) in the range from 1 to 500. A particularly suitable SAR is less than 200, in particular 150 or less. A preferred range is from 10 to 200 or from 10-150. The SAR

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is defined as the molar ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  corresponding to the composition of the molecular sieve.

For ZSM-22, a SAR in the range of 40-150 is preferred, in particular in the range of 70-120. Good performance in terms of activity and selectivity has been observed with a SAR of about 100.

For ZSM-23, a SAR in the range of 20-120 is preferred, in particular in the range of 30-80. Good performance in terms of activity and selectivity has been observed with a SAR of about 50.

Preferably the second molecular sieve having more-dimensional channels has a silica-to-alumina ratio (SAR) in the range from 1 to 1000. For ZSM-5, a SAR of 60 or higher is preferred, in particular 80 or higher, more preferably 100 or higher, still more preferably 150 or higher, such as 200 or higher.

The catalyst particles are typically formulated from the molecular sieves, such as in a mixture or in combination within a matrix component such as a so-called binder material and/or a filler material. Other components can also be present in the formulation.

It is desirable to provide a catalyst having good mechanical or crush strength, because in an industrial environment the catalyst is often subjected to rough handling, which tends to break down the catalyst into powder-like material. The latter causes problems in the processing. Preferably the molecular sieve is therefore incorporated within a matrix such as a binder material. Examples of suitable materials in a formulation include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica, alumina, silica-alumina, titania, zirconia and aluminosilicate or mixtures thereof. For present

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purposes, inert materials, such as silica, are preferred because they may prevent unwanted side reactions which may take place in case a more acidic material, such as alumina or silica-alumina is used.

5            Preferably the matrix and therefore the formulated catalyst particles (i.e. the combination of the first and second molecular sieves and the matrix) comprise non-zeolitic components. Typically at least 5wt% of the formulated catalyst comprises non-zeolitic components,  
10           preferably at least 20wt%.

            Preferably the total molecular sieve content, especially where the molecular sieves are both zeolites, is at most 60wt% of the formulated catalyst particles, especially at most 50wt%; typically at least 10wt%.

15           Silica binder is especially preferred where the molecular sieve comprises ZSM-22.

            Now the aspect of the present invention relating to the process for the preparation of an olefinic product will be discussed in more detail, which process comprises  
20           reacting an oxygenate feedstock in a reaction zone in the presence of catalyst particles according to the invention.

            The process for the preparation of an olefinic product of the present invention can be carried out in a  
25           batch, continuous, semi-batch or semi-continuous manner. Preferably the process of the present invention is carried out in a continuous manner.

            Since a second molecular sieve having more-dimensional channels such as ZSM-5 is present in the  
30           oxygenate conversion catalyst particles, start up is possible without an olefinic co-feed from an external source. ZSM-5 for example is able to convert an oxygenate to an olefin-containing product, so that a recycle can be

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established. Molecular sieves with one-dimensional 10-membered ring channels such as ZSM-22 or ZSM-23 are typically not able to convert an oxygenate feed to an olefinic product stream with any useful conversion,  
5 unless an olefinic co-feed is provided.

In a particular embodiment an olefinic co-feed obtained from an external source may be used at start-up, and/or after start-up. Such olefins may for example be obtained from a steam cracker, a catalytic cracker,  
10 alkane dehydrogenation (e.g. propane or butane dehydrogenation). Further, such olefins can be bought from the market. In a special embodiment the olefins for such start-up are obtained from a previous process that converted oxygenates, with or without olefinic co-feed,  
15 to olefins. Such a previous process may have been located at a different location or it may have been carried out at an earlier point in time.

Typically the oxygenate conversion catalyst deactivates in the course of the process. Conventional  
20 catalyst regeneration techniques can be employed. The catalyst particles used in the process of the present invention can have any shape known to the skilled person to be suitable for this purpose, for it can be present in the form of spray dried catalyst particles, spheres,  
25 tablets, rings, extrudates, etc. Extruded catalysts can be applied in various shapes, such as, cylinders and trilobes. If desired, spent oxygenate conversion catalyst can be regenerated and recycled to the process of the invention.

30 Spherical particles are normally obtained by spray drying. Preferably the average particle size is in the range of 1 - 200  $\mu\text{m}$ , preferably 50 - 100  $\mu\text{m}$ .

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The reaction zone for the oxugenate conversion reaction is typically in a reactor system, which may comprise any suitable reactor known to the skilled person and may for example contain a fixed bed, moving bed, fluidized bed, riser reactor and the like. A riser reactor system is preferred, in particular a riser reactor system comprising a plurality of serially arranged riser reactor stages.

In processes where a riser reactor system is preferred, a catalyst is required which has high attrition resistance to limit the catalyst losses by attrition. Such catalyst is typically formed of spray-dried catalyst particles. The composition of the catalyst particles strongly influence their resistance to attrition.

The reaction to convert oxygenates and optionally the olefinic co-feed to an olefinic product can be carried out over a wide range of temperatures and pressures. Suitably, however, the oxugenate feed and optional olefinic co-feed are contacted with the molecular sieve at a temperature in the range from 200 °C to 650 °C. In a further preferred embodiment the temperature is in the range from 250 °C to 600 °C, more preferably in the range from 300 °C to 550 °C, most preferably in the range from 450 °C to 550 °C. Preferably the reaction to produce the olefins is conducted at a temperature of more than 450 °C, preferably at a temperature of 460 °C or higher, more preferably at a temperature of 490 °C or higher. At higher temperatures a higher activity and ethylene selectivity is observed. Molecular sieves having one-dimensional 10-membered ring channels can be operated under oxugenate conversion conditions at such high temperatures with acceptable deactivation due to coking,

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contrary to molecular sieves with smaller pores or channels, such as 8-membered ring channels. Temperatures referred to hereinabove represent reaction temperatures, and it will be understood that a reaction temperature can be an average of temperatures of various feed streams and the catalyst in the reaction zone.

In addition to the oxygenate, and the olefinic co-feed, a diluent may be fed into the reactor system. It is preferred to operate without a diluent, or with a minimum amount of diluent, such as less than 200 wt% of diluent based on the total amount of oxygenate feed, in particular less than 100 wt%, more in particular less than 20 wt%. Any diluent known by the skilled person to be suitable for such purpose can be used. Such diluent can for example be a paraffinic compound or mixture of compounds. Preferably, however, the diluent is an inert gas. The diluent can be argon, nitrogen, and/or steam. Of these, steam is the most preferred diluent. For example, the oxygenate feed and optionally olefinic co-feed can be diluted with steam, for example in the range from 0.01 to 10 kg steam per kg oxygenate feed.

In one embodiment small amounts of water are added in order to improve the stability of the catalyst by reducing coke formation.

The olefinic reaction product is typically fractionated. The skilled artisan knows how to separate a mixture of hydrocarbons into various fractions, and how to work up fractions further for desired properties and composition for further use. The separations can be carried out by any method known to the skilled person in the art to be suitable for this purpose, for example by vapour-liquid separation (e.g. flashing), distillation, extraction, membrane separation or a combination of such

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methods. Preferably the separations are carried out by means of distillation. It is within the skill of the artisan to determine the correct conditions in a fractionation column to arrive at such a separation. He  
5 may choose the correct conditions based on, inter alia, fractionation temperature, pressure, trays, reflux and reboiler ratios.

At least a light olefinic fraction comprising ethylene and/or propylene and a heavier olefinic fraction  
10 comprising C4 olefins are normally obtained. The heavier olefinic fraction preferably contains less than 10 wt% of C5+ hydrocarbon species. Preferably also a water-rich fraction is obtained. Also a lighter fraction comprising methane, carbon monoxide, and/or carbon dioxide can be  
15 obtained, as well as one or more heavy fractions comprising C5+ hydrocarbons. Such heavy fraction can for example be used as gasoline blending component.

In a particular aspect the present invention provides a process for the preparation of an olefinic product,  
20 which process comprises the step a) of reacting an oxygenate feedstock and an olefinic co-feed in a reactor in the presence of oxygenate conversion catalyst particles comprising both a first molecular sieve having one-dimensional 10-membered ring channels, and a second  
25 molecular sieve having more-dimensional channels, to prepare an olefinic reaction effluent. Preferably the weight ratio between the one-dimensional molecular sieve and the further molecular sieve is in the range of from 1:1 to 100:1. In a preferred embodiment, this process  
30 comprises the further steps of b) separating the olefinic reaction effluent into at least a first olefinic fraction and a second olefinic fraction; and c) recycling at least part of the second olefinic fraction obtained in step b)

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to step a) as olefinic co-feed; and d) recovering at least part of the first olefinic fraction obtained in step b) as olefinic product.

5 In step b) of this process according to the invention the olefinic reaction effluent of step a) is separated (fractionated). At least a first olefinic fraction and a second olefinic fraction, preferably containing C<sub>4</sub> olefins, are obtained. The first olefinic fraction typically is a light olefinic fraction comprising  
10 ethylene, and the second olefinic fraction is typically a heavier olefinic fraction comprising C<sub>4</sub> olefins.

Preferably also a water-rich fraction is obtained. Also a lighter fraction comprising contaminants such as methane, carbon monoxide, and/or carbon dioxide can be  
15 obtained and withdrawn from the process, as well as one or more heavy fractions comprising C<sub>5</sub>+ hydrocarbons, including C<sub>5</sub>+ olefins. Such heavy fraction can for example be used as gasoline blending component. For example, the first olefinic fraction can comprise at  
20 least 50 wt%, preferably at least 80 wt%, of C<sub>1</sub>-C<sub>3</sub> species, the recycled part of the second olefinic fraction can comprise at least 50 wt% of C<sub>4</sub> species, a heavier carbonaceous fraction that is withdrawn from the process can comprise at least 50 wt% of C<sub>5</sub>+ species.

25 In step c) at least part of the second olefinic fraction, preferably containing C<sub>4</sub> olefins, obtained in step b) is recycled to step a) as olefinic co-feed.

Only part of the second olefinic fraction or the complete second olefinic fraction may be recycled to  
30 step a).

In the process also a significant amount of propylene is normally produced. The propylene can form part of the light olefinic fraction comprising ethene, and which can

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suitably be further fractionated into various product components. Propylene can also form part of the heavier olefinic fraction comprising C4 olefins.

5 The various fractions and streams referred to herein, in particular the recycle stream, can be obtained by fractionating in various stages, and also by blending streams obtained during the fractionation. Typically, an ethylene- and a propylene-rich stream of predetermined purity such as export quality will be obtained from the process, e.g. from a C2 or C3 splitter, and also a stream  
10 rich in C4 comprising C4 olefins and optionally C4 paraffins, such as an overhead stream from a debutaniser column receiving the bottom stream from a depropanizer column at their inlet. It shall be clear that the heavier olefinic fraction comprising C4 olefins, forming the  
15 recycle stream, can be composed from quantities of various fractionation streams. So, for example, some amount of a propylene-rich stream can be blended into a C4 olefin-rich stream. In a particular embodiment at least 90 wt% of the heavier olefinic fraction comprising  
20 C4 olefins can be formed by the overhead stream from a debutaniser column receiving the bottom stream from a depropanizer column at their inlet, more in particular at least 99 wt% or substantially all.

25 Suitably the olefinic reaction product comprises less than 10 wt%, preferably less than 5 wt%, more preferably less than 1 wt%, of C6-C8 aromatics. Producing low amounts of aromatics is desired since any production of aromatics consumes oxygenate which is therefore not  
30 converted to lower olefins.

The present invention will now be discussed in more detail and by way of example at the hand of several embodiments.

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In these examples dimethyl ether (DME) and 1-butene were reacted over oxygenate conversion catalysts comprising particles, the catalysts containing 40 wt% of total zeolite (molecular sieve) and a matrix of 36 wt% kaolin clay (as filler) and 24 wt% of silica binder. The catalysts were prepared by spray drying wherein the weight-based average particle size is between 70-90  $\mu\text{m}$ .

Example 1:

This catalyst with particles in accordance with the invention was spray dried, wherein the zeolite component was obtained by mixing MTT (ZSM-23 SAR 46) and the MFI (ZSM-5 SAR 280) zeolites, so that the final catalyst was intimately mixed, meaning that crystals of both zeolites are present in individual catalyst particles. The MTT / MFI weight ratio is 80/20, based on total zeolite present in the catalyst.

Example 2:

This catalyst in accordance with the invention was prepared as detailed in example 1 but with an MTT / MFI weight ratio of 62.5/37.5 based on total zeolite present in the catalyst.

Comparative Example 3

This catalyst comprises 40 wt% of MTT zeolite (ZSM-23 SAR 46) and no other molecular sieves, and catalyst particles were otherwise prepared by spray drying as in Example 1.

Comparative Example 4

The catalyst comprises 40 wt% of MFI zeolite (ZSM-5 SAR 280) and no other molecular sieves, and catalyst particles were otherwise prepared by spray drying as in Example 1.

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Comparative Example 5

This catalyst consists of a physical mixture of catalyst particles of the two catalysts of examples 3 and 4 above which were spray dried separately and then mixed to produce a physical mixture of catalyst particles. Thus, for physical mixtures each particle consists of either the first or the second zeolite, not both. In contrast, the intimately mixed examples 1 and 2 in accordance with the present invention have particles comprising both the first and second zeolites. The catalyst powders catalyst 3/catalyst 4 were mixed in an 80/20 weight ratio.

Comparative Example 6

This catalyst was prepared as detailed in example 5 (i.e. a physical mixture of the catalysts in examples 3 and 4) but mixed with a 62.5/37.5 weight ratio of catalyst 3/catalyst 4.

For performance evaluation a sample of the respective catalyst powder was pressed into tablets and the tablets were broken into pieces and sieved.

The various catalysts were tested to determine the selectivity towards ethylene and propylene from oxygenates and stability under such reaction conditions. For the catalytic testing, the sieve fraction of 40-60 mesh was used. Prior to reaction, the fresh catalyst in its ammonium-form was treated ex-situ in air at 600 °C for 2 hours.

The reaction was performed using a quartz reactor tube of 3.6 mm internal diameter. The catalyst was heated in argon to 525 °C and a mixture consisting of 3 vol% dimethyl ether, 3 vol% 1-butene, 1 vol% steam balanced in N<sub>2</sub> was passed over the catalyst at atmospheric pressure (1 bar). The Gas Hourly Space Velocity (GHSV) is

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determined by the total gas flow over the catalyst weight per unit time ( $\text{ml.g}_{\text{catalyst}}^{-1}.\text{h}^{-1}$ ). The effluent from the reactor was analyzed by gas chromatography (GC) to determine the product composition. The composition has  
5 been calculated on a weight basis of all hydrocarbons analyzed. The selectivity has been defined by the division of the mass of product by the sum of the masses of all products.

Results from the catalytic testing are shown in  
10 table 1.

|                                                                | Catalyst 1      |      |      | Catalyst 2      |                 |      | Catalyst 3<br>(Comparative) |                 |      | Catalyst 4<br>(Comparative) |      |      | Catalyst 5<br>(Comparative) |      |      | Catalyst 6<br>(Comparative) |                 |                 |
|----------------------------------------------------------------|-----------------|------|------|-----------------|-----------------|------|-----------------------------|-----------------|------|-----------------------------|------|------|-----------------------------|------|------|-----------------------------|-----------------|-----------------|
| Time-on-stream (h)                                             | ~0.5            | ~10  | ~40  | ~0.5            | ~0.5            | ~0.5 | ~0.5                        | ~10             | ~40  | ~0.5                        | ~10  | ~40  | ~0.5                        | ~10  | ~40  | ~0.5                        | ~0.5            | ~0.5            |
| DYE conversion (%)                                             | 100             | 100  | 100  | 100             | 100             | 100  | 99.5                        | 37.2            | 100  | 100                         | 100  | 100  | 100                         | 100  | 100  | 100                         | 100             | 100             |
| C2 <sup>+</sup> /C3 <sup>+</sup> wt-ratio                      | 0.40            | 0.28 | 0.19 | 0.34            | 0.36            | 0.36 | 0.15                        | 0.37            | 0.30 | 0.27                        | 0.24 | 0.33 | 0.23                        | 0.15 | 0.15 | 0.29                        | 0.29            | 0.29            |
| Methane (wt%)                                                  | 0.7             | 0.5  | 0.5  | 0.6             | 1.1             | 1.1  | 1.6                         | 0.5             | 0.5  | 0.4                         | 0.5  | 0.8  | 0.4                         | 0.5  | 0.5  | 0.5                         | 0.5             | 0.5             |
| C2 <sup>+</sup> + C3 <sup>+</sup> totals<br>wt% <sup>(1)</sup> | 64.0            | 58.4 | 47.4 | 61.5            | 59.2            | 28.8 | 0.5                         | 62.5            | 61.4 | 58.0                        | 55.5 | 51.1 | 41.9                        | 57.2 | 57.2 | 57.2                        | 57.2            | 57.2            |
| C2 - C5 totals<br>wt% <sup>(1)</sup>                           | 94.3            | 94.1 | 92.2 | 93.7            | 93.8            | 85.8 | 55                          | 93.6            | 94.5 | 93.9                        | 90.9 | 94.6 | 92.4                        | 92.5 | 92.5 | 92.5                        | 92.5            | 92.5            |
| wt% C4 <sub>base</sub> of C4 <sub>tot</sub>                    | 5.3             | 5.9  | 7.3  | 8.2             | 4.7             | 3.4  | n.a.                        | 12.4            | 10.9 | 10.5                        | 13.3 | 6.4  | 7.5                         | 11.0 | 11.0 | 11.0                        | 11.0            | 11.0            |
| C6+ totals <sup>(1)</sup>                                      | 5.0             | 5.4  | 7.3  | 5.6             | 5.1             | 12.3 | 2.9                         | 6.1             | 5.1  | 5.6                         | 8.3  | 5.0  | 7.1                         | 7.0  | 7.0  | 7.0                         | 7.0             | 7.0             |
| GHSV (ml/g/h) <sup>(11)</sup>                                  | 6,000           |      |      | 6,000           | 6,000           |      |                             | 6,000           |      |                             |      |      |                             |      |      | 6,000                       | 6,000           | 6,000           |
| Catalyst intake (mg)                                           | 250             |      |      | 250             | 250             |      |                             | 250             |      |                             |      |      |                             |      |      | 250                         | 250             | 250             |
| DYE breakthrough (h)                                           | >58 h on stream |      |      | >58 h on stream | >58 h on stream |      |                             | >58 h on stream |      |                             |      |      |                             |      |      | >58 h on stream             | >58 h on stream | >58 h on stream |

<sup>(1)</sup> wt% in product stream on carbon basis <sup>(11)</sup> Gas hourly space velocity is based on total flow per weight of catalyst per hour (ml.g<sup>-1</sup>.h<sup>-1</sup>). n.a.= not accurate

Table 1

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In Table 1 C<sub>n</sub> refers to hydrocarbon species having n carbon atoms, C<sub>n+</sub> refers to hydrocarbon species having n or more carbon atoms (n being an integer) figures include all; C<sub>n=</sub> refers to olefinic hydrocarbon species having n carbon atoms. The index sat refers to saturated carbon species, and tot or totals refer to all respective hydrocarbon species.

Thus it can be observed from table 1 that the intimately mixed catalysts in accordance with the present invention, i.e. catalysts 1 and 2, produce better results than the comparative catalysts 3 - 6. A particular advantage is that the amount of ethylene and propylene after 0.5 hours is highest for catalyst 1. At the same time the ethylene/propylene ratio C<sub>2=</sub>/C<sub>3=</sub> is highest for catalysts 1 and 2. Performance at short times on stream is very relevant for continuous processes such as fluidized bed with continuous regeneration of part or all of the catalyst.

Moreover, the stability with respect to catalyst 3 is much improved by the addition of more-dimensional zeolite to the catalyst, as can be seen from the increase of the DME breakthrough time well above the 13h for catalyst 3.

With respect to catalyst 4, the catalyst according to the present invention provides a significantly higher amount of ethylene in the product, also a higher ethylene/propylene ratio, in particular at short time on stream. Moreover, the MFI based catalyst 4 produces a much higher amount of saturates, in particular C<sub>4</sub> saturates. A high amount of saturates is a particular disadvantage, not only as it lowers the overall conversion to olefins, but also when (part of) the C<sub>4</sub> fraction of the product is to be recycled as olefinic co-

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feed. C4 saturates would build up in the reaction system much more.

Further experiments have shown that catalyst 4 also produces more aromatics. In the experiments using a diluted feed presented in Table 1, this effect is not very pronounced; aromatics contribute to the C6+ fraction in Table 1. However, it was found that in fluid bed experiments using catalyst 4 and a non-diluted feed of DME/butene (1:1 mol/mol) at 525 C and a weight hourly space velocity of  $8 \text{ gfeed} \cdot \text{gcat}^{-1} \cdot \text{h}^{-1}$ , 17 wt% of aromatics were formed, whereas catalyst 1 only produced 9.8 wt% of aromatics under the same conditions.

The strength of the catalyst particles is measured by their attrition resistance using a test procedure described by Weeks et al. in Oil & Gas Journal 88 (16) 1990. Catalysts 1 - 4 were first subjected to a calcination at 600 °C for 2 hours. Each test was run with 6 grams of humidified catalyst. The samples were subjected to abrasion for 36 minutes by putting the catalyst in a jet-cup using high velocity air. In this process, wear on the particles occurs as the particles collide with the jet-cup wall and each other with high velocity. The fines formed (less than 16 micrometer) are removed from the cup and collected. The formation of fines is determined over time at 5, 12, 24 and 36 minutes. An attrition index of the sample was determined by using the slope of the accumulated catalyst fines recorded at the given times. An index of less than 20 is indicated as a catalyst with good resistance for attrition. The attrition rate indicated in Table 1 is determined by taking the fines formed after 24 minutes minus the fines formed after 5 minutes divided by the total catalyst sample and divided by 0.317 hour. The

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attrition index and the attrition rate for catalyst 1-4 are given in Table 2.

| Catalyst                  | 1    | 2    | 3<br>(Comparative) | 4<br>(Comparative) |
|---------------------------|------|------|--------------------|--------------------|
| Attrition index           | 17   | 17   | 13                 | 29                 |
| Attrition rate<br>(wt%/h) | 16.1 | 15.9 | 11.2               | 26.9               |

Table 2. Results from attrition tests

From table 2 it can be observed that all catalysts containing the MTT zeolite with or without the MFI zeolite have good attrition resistance. Catalyst 4 having only the MFI zeolite shows poor attrition resistance. It is therefore desirable to have at least the MTT zeolite present to obtain a catalyst with sufficient attrition resistance to be applied in a riser reactor.

C L A I M S

1. Catalyst particles comprising both a first molecular sieve in the hydrogen form having one-dimensional 10-membered ring channels, and a second molecular sieve in the hydrogen form having more-dimensional channels.
2. Catalyst particles according to claim 1, wherein the Silica-to-Alumina ratio of the first molecular sieve is less than 200.
3. Catalyst particles according to claim 1, wherein an average distance between a crystal of the first molecular sieve and a nearest crystal of the second molecular sieve is less than an average particle size of the catalyst particles.
4. Catalyst particles according to claim 1, wherein the molecular sieve having one-dimensional 10-membered ring channels comprises at least one of a molecular sieve of the MTT-type and the TON-type.
5. Catalyst particles according to claim 1, wherein the second molecular sieve is an MFI-type molecular sieve.
6. Catalyst particles according to claim 5, wherein the second molecular sieve has a Silica-to-Alumina ratio (SAR) of at least 60.
7. Catalyst particles according to claim 1, wherein a bed of catalyst particles

comprises at least 1 wt% and less than 50 wt% of the second molecular sieve, based on the total weight of first and second molecular sieves in the catalyst composition.

8. Catalyst particles according to claim 1, further comprising a matrix and a total of 60 wt% or less of the first and second molecular sieves, based on the total catalyst particles.

9. A process for the preparation of an olefinic product, which process comprises reacting an oxygenate feedstock in a reaction zone in the presence of catalyst particles as claimed in claim 1, to prepare an olefinic reaction product.

10. A process according to claim 9, wherein the reaction of the oxygenate feedstock is performed in the presence of an olefinic co-feed.

11. A process for the preparation of an oxygenate conversion catalyst, the process comprising preparing oxygenate conversion catalyst particles comprising both a first molecular sieve in the hydrogen form having one-dimensional 10-membered ring channels, and a second molecular sieve in the hydrogen form having more-dimensional channels.

12. A process according to claim 11, wherein the first and second molecular sieves are embedded in a matrix.

13. A process according to claim 12, wherein a slurry comprising the first and second molecular sieves and the matrix is spray dried to form the catalyst particles.

14. A process according to claim 11, wherein crystals of the first and second molecular sieves are grown together.