

- 1 -

PROCESS FOR PRODUCING OLEFINS

The invention relates to a process for producing olefins, an integrated system for producing olefins.

In recent years increasing attention is given to the exploration and utilisation of natural gas resources around the globe. A disadvantage of natural gas with respect to oil is the difficulty to transport large volumes of natural gas from the source to the market. One way of efficiently transporting natural gas is by liquefying the natural gas and to transport the liquefied natural gas (LNG). Another way is to convert the methane in the natural gas to liquid hydrocarbons using a Gas-to-Liquid process (GtL). The GtL products are typically liquid and can be transported in a similar way as traditional oil and oil products.

Besides methane, the natural gas typically comprises other hydrocarbons such as ethane, propane, and butanes. Such a natural gas is referred to as wet gas. The latter two can be added to the LPG pool, however, ethane cannot. Moreover, for various reasons the ethane content in the natural gas supplied to an LNG or GtL process is restricted and therefore a significant part of the ethane must be removed from the natural gas prior to providing the natural gas to either a LNG or GtL process.

Although, the application of ethane is limited, typically ethane is combusted in a furnace to provide heat; its corresponding olefin ethylene is a base chemical with a wide application and is of great commercial interest. Ethane can be converted into ethylene, e.g. using a thermal cracking process. Subsequently, the ethylene can be used to produce e.g. polyethylene, styrene, ethylene oxide or mono-ethyl-

produced, while coproducing valuable propylene. A disadvantage mentioned by C.Eng et al. is the fluctuating price of methanol, which is the primary feed to the MTO reaction.

5 In WO 2009/039948 A2, a combined steam cracking and MTP process is suggested for preparing ethylene and propylene. According to WO 2009/039948 A2, in this process, a particular advantage is obtained by combining the back-end of both processes. The methanol feedstock is
10 produced from methane, requiring a sufficient supply of methane.

 In US2005/0038304, an integrated system for producing ethylene and propylene from an OTO system and a steam cracking system is disclosed. According to
15 US2005/0038304, in this process, a particular advantage is obtained by combining the back-end of both processes. The methanol feedstock to the OTO process is produced from synthesis gas. However, according to US2005/0038304 the production of methanol from synthesis gas has high
20 energy requirements due to the endothermic nature of the synthesis gas production process, such an endothermic synthesis gas production process is normally steam methane reforming.

 Methanol can be produced from hydrogen and carbon
25 monoxide or carbon dioxide. Typically, methanol is produced from a mixture of hydrogen, carbon monoxide and carbon dioxide. In order to synthesize methanol, hydrogen, carbon monoxide and carbon dioxide should be provided in a molar ratio of at least 2, which ratio is
30 calculated by:

$$\text{molar ratio} = (\# \text{ mol H}_2 - \# \text{ mol CO}_2) / (\# \text{ mol CO} + \# \text{ mol CO}_2).$$

There is a need in the art for an improved integrated ethane cracking and OTO process.

It has now been found that it is possible to produce olefins by thermally cracking ethane to an olefin and hydrogen while at the same time producing further olefins using a OTO process, wherein hydrogen obtained from the cracking process and the OTO process is used to produce at least part of the oxygenate feed to the OTO process.

Accordingly, the present invention provides process for producing olefins, comprising:

- a. cracking an ethane-comprising feed in a cracking zone under cracking conditions to obtain a cracking zone effluent comprising at least olefins and hydrogen;
- b. converting an oxygenate feedstock in an oxygenate-to-olefin zone to obtain an OTO zone effluent at least olefins and hydrogen;
- c. combining at least part of the cracking zone effluent and part of the OTO zone effluent to a combined effluent; and
- d. separating hydrogen from the combined effluent, wherein at least part of the oxygenate feedstock is obtained by providing hydrogen obtained in step d) and a feed containing carbon monoxide and/or carbon dioxide to an oxygenate synthesis zone and synthesizing oxygenates.

The process according to the present invention is directed at producing olefins, in particular lower olefins (C2-C4), more in particular ethylene and propylene. Several processes, such as ethane cracking or Oxygenate-to-Olefin (OTO) processes can produce olefins. The ethane cracking and the OTO processes typically produce ethylene from different starting materials. In case of the ethane cracking step, the feed is preferably

OTO zone effluent. The amount of hydrogen in the OTO zone effluent, however, is relatively small, making separating of the hydrogen from the remainder of the OTO zone effluent not worthwhile. In the process according to the invention at least part of the cracking zone effluent and at least part of the OTO zone effluent are combined into a combined effluent in as step (c) and subsequently in step (d) hydrogen is separated from that combined effluent. The hydrogen obtained from the combined effluent is referred to as hydrogen ex. combined effluent. In this way not only part or all of the hydrogen in the cracking zone effluent, but also at least part of the hydrogen in the OTO zone effluent is retrieved and is used to synthesise oxygenates.

These oxygenates are subsequently fed to the OTO reaction to form further olefins. By using hydrogen ex. cracker and the hydrogen ex. OTO, the need to provide hydrogen rich synthesis gas obtained from an endothermic reforming process is reduced if not omitted. Thereby, carbon dioxide penalty for producing oxygenates is reduced as at least part of the hydrogen required for producing the oxygenate is obtained as co-product and does not add additional carbon dioxide on top what is required for the main reaction product ethylene.

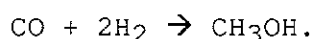
By providing at least part of the hydrogen ex. cracker and hydrogen ex. OTO to the oxygenate synthesis zone the amount of synthesis gas needed to synthesise the oxygenates may be reduced, at least compared to providing only hydrogen ex. cracker. The synthesis gas is typically produced by partial oxidation of hydrocarbons using essentially pure oxygen or at least oxygen enriched air. The production of pure oxygen is highly energy consuming, therefore a reduction in the synthesis gas demand also

subsequently methanol and/or DME. The methanol and/or DME can be converted to ethylene using an OTO process. As a result the ethylene production is less vulnerable to variation in the feed supply of either methane or ethane.

5 As mentioned herein above, hydrogen obtained in step (d) is used to produce at least part of the oxygenate feedstock provided to the OTO zone in step (b). Any suitable oxygenate or mixture of oxygenates may be produced, in particular alkylalcohols and alkylethers,
10 preferably methanol and/or DME.

 In the process according to the invention, hydrogen and a feed containing carbon monoxide and/or carbon dioxide are provided to the oxygenate synthesis zone.

 Methanol may be produced directly from hydrogen and
15 at least one of carbon monoxide and carbon dioxide in the oxygenate synthesis zone. Hydrogen can react with carbon monoxide to produce methanol following:



 Alternatively hydrogen may react with carbon dioxide to also form methanol following:



20 It is also possible to use a mixture of carbon monoxide and carbon dioxide. Preferably, the hydrogen and carbon monoxide and/or carbon dioxide are provided to the oxygenate synthesis zone in a molar ratio of in the range of from 2.0 to 3.0, preferably 2.0 to 2.2. The molar
25 ratio herein is defined as:

$$\text{molar ratio} = (\# \text{ mol H}_2 - \# \text{ mol CO}_2) / (\# \text{ mol CO} + \# \text{ mol CO}_2).$$

 In the above definition at least one of the number of moles carbon monoxide or the number of moles carbon dioxide is higher than zero.

Preferably, the catalyst is a copper and zinc based catalyst, more preferably in the form of copper, copper oxide, and zinc oxide.

- A copper based catalyst, which includes an oxide of at least one element selected from the group consisting of silver, zinc, boron, magnesium, aluminium, vanadium, chromium, manganese, gallium, palladium, osmium and zirconium.

Preferably, the catalyst contains copper oxide and an oxide of at least one element selected from the group consisting of zinc, magnesium, aluminium, chromium, and zirconium.

- A catalyst selected from the group consisting of: copper oxides, zinc oxides and aluminium oxides.

More preferably, the catalyst contains oxides of copper and zinc.

- A catalyst comprising copper oxide, zinc oxide, and at least one other oxide.

Preferably, the at least one other oxide is selected from the group consisting of zirconium oxide, chromium oxide, vanadium oxide, magnesium oxide, aluminum oxide, titanium oxide, hafnium oxide, molybdenum oxide, tungsten oxide, and manganese oxide.

Particular suitable catalysts include catalysts comprising in the range of from 10 to 70 wt % copper oxide, based on total weight of the catalyst. Preferably, comprising in the range of from 15 to 68 wt % copper oxide, and more preferably of from 20 to 65 wt % copper oxide, based on total weight of the catalyst.

Such catalyst may preferably also contain in the range of from 3 to 30 wt % zinc oxide, based on total weight of the catalyst. Preferably, contain in the range of from 4 to 27 wt % zinc oxide, more preferably of from

of carbon monoxide and carbon dioxide with the catalyst in the oxygenate synthesis zone at a pressure of in the range of from 15 to 125 atmospheres, more preferably of from 20 to 100 atmospheres, more preferably of from 25 to 75 atmospheres.

For methanol synthesis, gas hourly space velocities in the oxygenate synthesis zone vary depending upon the type of continuous process that is used. Preferably, gas hourly space velocity of flow of gas through the catalyst bed is in the range of from 50 hr^{-1} to $50,000 \text{ hr}^{-1}$. Preferably, gas hourly space velocity of flow of gas through the catalyst bed is in the range of from about 250 hr^{-1} to $25,000 \text{ hr}^{-1}$, more preferably from about 500 hr^{-1} to $10,000 \text{ hr}^{-1}$.

A methanol synthesis process as described herein above may produce several oxygenates as by-products, including aldehydes and other alcohols. Such by-products are also suitable reactants in the OTO reaction. Other less desirable by-products may be removed from the effluent of the oxygenate synthesis zone effluent if required prior to providing the oxygenate synthesis zone effluent to the OTO zone as to form at least part of the oxygenate feed.

Another suitable and preferred oxygenate, which may be synthesised in the oxygenate synthesis zone is dimethylether (DME). DME can be directly synthesized from hydrogen obtained in step (d) and at least one of carbon monoxide and carbon dioxide, but is preferably synthesized from methanol, which was at least in part produced from hydrogen obtained in step (d) as described herein above. Optionally, DME is obtained from methanol and hydrogen and at least one of carbon monoxide and carbon dioxide. The conversion of methanol to DME is

equilibrium by applying different reaction conditions and/or by adding or withdrawing any of the reactants.

In the process according to the invention at least part of the oxygenate feed is methanol and/or DME
5 produced by reacting hydrogen obtained from step (d) with at least one of carbon monoxide and carbon dioxide.

The feed containing carbon monoxide and/or carbon dioxide may be any feed containing carbon monoxide and/or carbon dioxide available. A particularly suitable feed
10 containing carbon monoxide and/or carbon dioxide is source comprising a synthesis gas obtained from a process for preparing synthesis gas. Such processes for preparing synthesis gas preferably include non-catalytic partial oxidation processes, catalytic partial oxidation
15 processes, steam methane reforming processes, auto-thermal reforming processes, and water-gas-shift processes. Although a water-gas-shift process is in principle not a process for preparing a synthesis gas, the effluent of a water-gas-shift process typically
20 comprises hydrogen carbon monoxide, carbon dioxide and hydrogen. The source may also comprise synthesis gas obtained from several processes for preparing synthesis gas.

Preferred sources of carbon monoxide and/or carbon dioxide are those that comprise synthesis gas having a
25 hydrogen and carbon monoxide and/or carbon dioxide molar ratio, as defined herein above, which is below the ratio preferred for synthesising methanol, i.e. sources that are hydrogen deficient. Such synthesis gases are
30 typically obtained from synthesis gas producing processes, in which natural gas or another methane-comprising gas is partially oxidised to provide synthesis gas feed for a Fischer-Tropsch process. Such processes

directed towards the oxygenate synthesis process rather than to the Fischer-Tropsch process in which carbon dioxide is regarded as an undesired inert.

Another suitable feed containing carbon monoxide
5 and/or carbon dioxide is a source comprising carbon dioxide obtained from a subsurface natural gas or oil reservoir. Such carbon dioxide is also referred to as field carbon dioxide. Some subsurface natural gas or oil reservoir comprise substantial concentration of carbon
10 dioxide, up to 70 mol% based on the total gas volume extracted from the reservoir. By using this carbon dioxide to synthesise oxygenates and subsequently olefins, this carbon dioxide is captured, reducing the carbon dioxide penalty for exploiting the subsurface
15 natural gas or oil reservoir.

Another suitable feed containing carbon monoxide and/or carbon dioxide is a source comprising carbon dioxide obtained from a carbon dioxide-comprising flue gas stream, in particular a flue gas obtained from the
20 integrated process according to the invention or optionally an oxygen purification unit or synthesis gas production process. Preferably, the flue gas is first concentrated to increase the carbon dioxide concentration.

25 A particularly suitable feed containing carbon monoxide and/or carbon dioxide may be a source comprising the flue gas obtained from an oxidative de-coking of an ethane cracking furnace, typically one of the ethane cracking furnaces used in for producing olefins in step
30 (a). In case the oxidative de-coking of the furnace is done using pure oxygen or pure oxygen diluted in carbon dioxide instead of air, an essentially pure stream of carbon dioxide can be produced, which is especially

hydrogen, carbon monoxide and carbon dioxide in the mixture.

Preferably, a synthesis gas is used comprising little or no carbon dioxide. The carbon dioxide from e.g. a MEG process comprises little or no inerts like Ar, N₂ or CH₄. When using a synthesis gas with little or no carbon dioxide, more carbon dioxide from for instance a MEG process can be added and less inerts are introduced to the oxygenate synthesis zone. Less waste carbon dioxide is thus produced, which would otherwise need to be sequestered or captured and stored.

By combining at least part of the cracking zone effluent and at least part of the OTO zone effluent to a combined effluent, at least part of the olefins obtained in step (a) and step (b) are also combined in one stream.

Based on a feed that comprises predominantly ethane, the cracker zone effluent obtained from the cracking zone of step (a) comprises predominantly ethylene, but may also comprise up to 2 wt% propylene, based on the total weight of the ethylene in the cracking zone effluent. This amount of propylene is not economically recoverable, however by combining the olefins obtained from the cracking zone in step (a) and the olefins obtained from the OTO zone in step (b), i.e. combining at least part of the cracking zone effluent and at least part of the OTO zone effluent to a combined effluent, a combined effluent is obtained that comprises in the range of 10 to 40 % of propylene, based on the total hydrocarbon content in the combined effluent. The high propylene content in the combined effluent is caused by the high propylene content in the OTO zone effluent. OTO processes produce a mix of olefins, comprising in the range of from 5 to 80 wt% of ethylene and in the range of from 10 to 80wt% of

providing at least part of the ethylene with a source of oxygen to an ethylene oxidation zone, further referred to as EO zone.

5 Preferably, the ethylene oxide is further converted to mono-ethylene-glycol (MEG). MEG is a liquid and therefore can be transported and stored more conveniently than ethylene oxide. Preferably, the EO zone is part of a larger Mono-ethylene-glycol synthesis zone, i.e. a second oxygenate synthesis zone, further referred to as MEG
10 zone. Preferably, the MEG zone then comprises a first section comprising the EO zone and a second ethylene oxide hydrolyses section. The MEG is synthesised by providing the ethylene oxide with a source of water to the ethylene oxide hydrolyse zone and converting the
15 ethylene oxide to MEG. Optionally, the ethylene oxide is first reacted with carbon dioxide to form ethylene carbonate, which is subsequently hydrolysed to obtain MEG and carbon dioxide, reference herein is made to for instance US2008139853, incorporated by reference.

20 Ethylene is typically converted to ethylene oxide by oxidising ethylene to form ethylene oxide.

The conversion of ethylene to ethylene oxide may be done by any ethylene oxidation process that produces at least ethylene oxide and carbon dioxide. In the EO zone,
25 at least a part of the ethylene is partly oxidised to form ethylene oxide. Preferably, the oxidation of ethylene takes place in the EO zone to which the ethylene and a source of oxygen are provided. Preferably, the source of oxygen is oxygen-enriched air or, more
30 preferably pure oxygen. The oxidation of ethylene may be performed over a catalyst present in the first section, preferably a silver based catalyst. Reference is for example made to Kniel et al., Ethylene, Keystone

Preferably, the carbon dioxide is separated from the OE zone effluent to obtain a separate carbon dioxide comprising stream. Preferably, the EO zone effluent is further treated to convert the ethylene oxide into MEG in a MEG zone. From the MEG zone a MEG zone effluent is obtained, comprising MEG and carbon dioxide. Suitably, the carbon dioxide can be separated from the MEG zone effluent by cooling the MEG zone effluent to a temperature below the boiling point of MEG, this carbon dioxide is also referred to as carbon dioxide ex. MEG. As no additional carbon dioxide is produced by converting ethylene oxide into MEG the carbon dioxide ex. MEG is the same as the carbon dioxide ex. EO. By reusing the carbon dioxide to synthesize oxygenates, the carbon dioxide penalty for producing EO is reduced. A further advantage is that the stream comprising carbon dioxide obtained from the EO or MEG zone comprises predominantly carbon dioxide and, depending on the temperature of the stream, steam. Preferably the stream comprises in the range of 80 to 100 mol% of carbon dioxide and steam, based on the total amount of moles in the stream. More preferably, the stream comprising carbon dioxide comprises essentially only carbon dioxide and, optionally, steam. Such a stream is particularly suitable to be used in an oxygenate synthesis process as it does not introduce significant amounts of inert, e.g. CH₄, N₂ and Ar, to the oxygenate synthesis zone. Should, however, the stream comprising carbon dioxide comprise significant amounts of other, undesired, compounds, e.g. ethylene oxide, the stream is preferably treated to remove such compounds prior to being introduced into the oxygenate synthesis zone. Typically, small amounts of chlorinated compounds are present during the oxidation of ethylene to EO. As a

Reference is for example made to made to Kniel et al.,
Ethylene, Keystone to the petrochemical industry, Marcel
Dekker, Inc, New York, 1980, in particular section 3.4.1,
page 24 to 25. While the styrene is produced by the
5 catalytic dehydrogenation of ethyl benzene in the
presence suitable catalyst, examples of suitable catalyst
include but are not limited to dehydrogenation catalysts
based on iron(III) oxide.

By integrating the process according to the
10 invention with the production of styrene monomer, as
described above, further hydrogen is produced next to the
desired products. Preferably, this hydrogen is separated
from the other reaction products, and subsequently
provided to the oxygenate synthesis zone to prepare at
15 least part of the oxygenate feed to step (b) of the
process.

By using hydrogen obtained from the conversion of
ethylene, via ethylbenzene, into styrene to synthesise
oxygenates, the carbon dioxide penalty for producing
20 oxygenates is reduced as at least part of the hydrogen
required for producing the oxygenate is obtained as co-
product and does not add additional carbon dioxide on top
what is required for the main reaction product styrene.

The produced styrene monomer may be used to produce
25 polystyrene.

In one embodiment the invention includes:

- i) providing a feed comprising methane and ethane;
- ii) separating the feed into at least a methane-
comprising feed and an ethane-comprising feed;
- 30 iii) providing at least part the methane-comprising feed
to a process for preparing synthesis gas to obtain a
synthesis gas; and

lower olefins. In the OTO zone, at least part of the feed is converted into a product containing one or more olefins, preferably including light olefins, in particular ethylene and/or propylene.

5 Examples of oxygenates that can be used in the oxygenate feedstock of step b) of the process include alcohols, such as methanol, ethanol, isopropanol, ethylene glycol, propylene glycol; ketones, such as acetone and methylethylketone; aldehydes, such as
10 formaldehyde, acetaldehyde and propionaldehyde; ethers, such as 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.
15 Further examples are dialkyl carbonates such as dimethyl carbonate or alkyl esters of carboxylic acids such as methyl formate. Of these examples, alcohols and ethers are preferred.

 Examples of preferred oxygenates include alcohols,
20 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.

25 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
30 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.

Catalysts as described in WO A 2006/020083 are suitable for converting the oxygenate feedstock in step (b) of the present invention. Such catalysts preferably include molecular sieve catalyst compositions. Suitable molecular sieves are silicoaluminophosphates (SAPO), such as SAPO-17, -18, -34, -35, -44, but also SAPO-5, -8, -11, -20, -31, -36, -37, -40, -41, -42, -47 and -56.

Alternatively, the conversion of the oxygenate feedstock may be accomplished by the use of an aluminosilicate catalyst, in particular a zeolite. Suitable catalysts include those containing a zeolite of the ZSM group, in particular of the MFI type, such as ZSM-5, the MTT type, such as ZSM-23, the TON type, such as ZSM-22, the MEL type, such as ZSM-11, the FER type. Other suitable zeolites are for example zeolites of the STF-type, such as SSZ-35, the SFF type, such as SSZ-44 and the EU-2 type, such as ZSM-48. Aluminosilicate catalysts are preferred when an olefinic co-feed is fed to the oxygenate conversion zone together with oxygenate, for increased production of ethylene and propylene.

The reaction conditions of the oxygenate conversion include those that are mentioned in WO-A 2006/020083. Hence, a reaction temperature of 200 to 1000 °C, preferably from 250 to 750 °C, and a pressure from 0.1 kPa (1 mbar) to 5 MPa (50 bar), preferably from 100 kPa (1 bar) to 1.5 MPa (15 bar), are suitable reaction conditions.

A specially preferred OTO process for use in step (b) of the present invention will now be described. This process provides particularly high conversion of oxygenate feed and a recycle co-feed to ethylene and propylene. Reference is made in this regard also to WO2007/135052, WO2009/065848, WO2009/065875,

conversion catalyst, of the second molecular sieve having more-dimensional channels, preferably at least 5 wt%, more preferably at least 8 wt%, and furthermore can comprise less than 35 wt% of the further molecular sieve, in certain embodiments less than 20 wt%, or less than 18 wt%, such as less than 15 wt%.

Especially when the oxygenate conversion is carried out over a catalyst containing MTT or TON type aluminosilicates, it may be advantageous to add an olefin-containing co-feed together with the oxygenate feed (such as dimethylether-rich or methanol-rich) feed to the OTO zone when the latter feed is introduced into this zone. It has been found that the catalytic conversion of the oxygenates, in particular methanol and DME, to ethylene and propylene is enhanced when an olefin is present in the contact between methanol and/or dimethylether and the catalyst. Therefore, suitably, an olefinic co-feed is added to the reaction zone together with the oxygenate feedstock.

In special embodiments, at least 70 wt% of the olefinic co-feed, during normal operation, is formed by a recycle stream of a C3+ or C4+ olefinic fraction from the OTO conversion effluent, preferably at least 90 wt%, more preferably at least 99 wt%, and most preferably the olefinic co-feed is during normal operation formed by such recycle stream. In one embodiment the olefinic co-feed can comprise at least 50 wt% of C4 olefins, and at least a total of 70 wt% of C4 hydrocarbon species. It can also comprise propylene. The OTO conversion effluent can comprise 10 wt% or less, preferably 5 wt% or less, more preferably 1 wt% or less, of C6-C8 aromatics, based on total hydrocarbons in the effluent. At least one of the olefinic co-feed, and the recycle stream, can in

hydrogen form. When the molecular sieves are prepared in the presence of organic cations the molecular sieve may be activated by heating in an inert or oxidative atmosphere to remove organic cations, for example, by
5 heating at a temperature over 500 °C for 1 hour or more. The zeolite is typically obtained in the sodium or potassium form. The hydrogen form can then be obtained by an ion exchange procedure with ammonium salts followed by another heat treatment, for example in an inert or
10 oxidative atmosphere at a temperature over 500 °C for 1 hour or more. The molecular sieves obtained after ion-exchange are also referred to as being in the ammonium form.

The molecular sieve can be used as such or in a
15 formulation, such as in a mixture or combination with a so-called binder material and/or a filler material, and optionally also with an active matrix component. Other components can also be present in the formulation. If one or more molecular sieves are used as such, in particular
20 when no binder, filler, or active matrix material is used, the molecular sieve itself is/are referred to as oxygenate conversion catalyst. In a formulation, the molecular sieve in combination with the other components of the mixture such as binder and/or filler material
25 is/are referred to as oxygenate conversion catalyst.

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
30 powder-like material. The latter causes problems in the processing. Preferably the molecular sieve is therefore incorporated in a binder material. Examples of suitable materials in a formulation include active and inactive

be added to at least two of the sequential reaction sections.

When multiple reaction zones are employed, an olefinic co-feed is advantageously added to the part of the dimethylether-rich feed that is passed to the first reaction zone.

The preferred molar ratio of oxygenate in the oxygenate feedstock to olefin in the olefinic co-feed provided to the OTO conversion zone 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 20:1 to 1:10, more preferably in the range of 18:1 to 1:5 and still more preferably in the range of 15:1 to 1:3.

A diluent can also be fed to the OTO zone, mixed with the oxygenate and/or co-feed if present, or separately. A preferred diluents is steam, although other inert diluents can be used as well. In one embodiment, the molar ratio of oxygenate to diluent is between 10:1 and 1:10, preferably between 4:1 and 1:2, most preferably between 3:1 and 1:1, such as or 1.5:1, in particular when the oxygenate is methanol and the diluent is water (steam).

The ethane-comprising feed to step (a) of the first process for producing olefins according to the invention may be any ethane-comprising feed. Reference herein to the ethane-comprising feed to the fresh feed supplied to the process, prior to entering the cracking zone the ethane-comprising feed may be combined with one or more recycled process steams originating from either the cracking zone, OTO zone, or any other origin in the process. Besides ethane, the ethane-comprising feed may

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

5 The oxygenate feedstock may provided directly from one or more oxygenate synthesis zones, however, it may also be provided from a central oxygenate storage facility.

10 The olefinic co-feed optionally provided together with the oxygenate feedstock to the OTO conversion zone may contain one olefin or a mixture of olefins. Apart from olefins, the olefinic co-feed may contain other hydrocarbon compounds, such as for example paraffinic, alkylaromatic, aromatic compounds or a mixture thereof. Preferably the olefinic co-feed comprises an olefinic
15 fraction of more than 20 wt%, more preferably more than 25 wt%, still more preferably more than 50 wt%, which olefinic fraction consists of olefin(s). The olefinic co-feed can consist essentially of olefin(s).

20 Any non-olefinic compounds in the olefinic co-feed are preferably paraffinic compounds. If the olefinic co-feed contains any non-olefinic hydrocarbon, these are preferably paraffinic compounds. Such paraffinic compounds are preferably present in an amount in the range from 0 to 80 wt%, more preferably in the range from
25 0 to 75 wt%, still more preferably in the range from 0 to 50 wt%.

By an unsaturate is understood an organic compound containing at least two carbon atoms connected by a double or triple bond. By an olefin is understood an
30 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 bonds. Preferably olefins present in

proving the synthesis gas to a oxygenate synthesis zone to synthesise oxygenates. The methane is preferably obtained from natural gas or associated gas, more preferably the same natural gas or associated gas, from which the ethane-comprising feed was obtained.

The benzene used to convert ethylene into ethyl benzene may be any benzene available. The benzene may be benzene produced by in step (a) of the process according to the invention. As disclosed in US 6677496, an ethane cracking processes typically produce up to 0.6wt% of benzene, based on the total ethane feed. However, the benzene may also be obtained from any other source.

Preferably, the benzene is produced from higher hydrocarbons such as propane and butane, more preferably propane and butane obtained as condensate or LPG from natural gas or associated gas, even more preferably the same natural gas or associated gas, from which the ethane-comprising feed was obtained.

The feed comprising methane and ethane provided to the second process for producing olefins according to the invention may be any feed comprising methane and ethane. Preferably, the feed comprising methane and ethane is natural gas or associated gas.

Preferably, the feed comprising methane and ethane comprises in the range of from 1 to 20 mol% of ethane, based on the total feed.

In a further aspect, the invention provides an integrated system for producing olefins, which system comprises:

a) a steam cracking system having one or more inlets for an ethane-comprising feedstock and steam, and an outlet for a cracker effluent comprising olefins and hydrogen;

1 and 3 respectively to steam cracking system 5, comprising a cracking zone for steam cracking ethane to ethylene. From steam cracking system 5, a cracking zone effluent is retrieved via conduit 7.

5 In Figure 1, also a feed containing carbon monoxide and/or carbon dioxide, e.g. a synthesis gas is provided via conduit 9 to oxygenate synthesis system 11, comprising an oxygenate synthesis zone for synthesizing oxygenates from hydrogen and at least one of carbon
10 monoxide and carbon dioxide. From oxygenate synthesis system 11, an oxygenate feedstock is retrieved via conduit 13. The oxygenate feedstock is provided to oxygenate-to-olefins conversion system 15, comprising an
15 OTO zone from converting oxygenates to lower olefins, e.g. ethylene and propylene. Optionally, an olefinic co-feed (not shown) is provided to oxygenate-to-olefins conversion system 15 together with the oxygenate
 feedstock. From oxygenate-to-olefins conversion system 15, an OTO zone effluent is retrieved via conduit 17.

20 The cracking zone effluent and the OTO zone effluent are combined to combined effluent in conduit 19 and provided to work-up section 21. Work-up section 21 comprises at least a separation system to separate
25 hydrogen from the combined effluent and to separate ethylene from the combined effluent. The hydrogen is retrieved from workup section 21 and provided via conduit 23 to conduit 9 and mixed with the synthesis gas. The
 ethylene is retrieved separately from workup section 21 and provided via conduit 25 to ethylene oxidation system
30 27, which comprises an oxygenation zone for oxidising ethylene to ethylene oxide. Oxygen is provided to ethylene oxidation system 27 via conduit 29. From ethylene oxide system 27, ethylene oxide is retrieved via

distributions for single-pass OTO conversions. Therein, all components that were fed to the OTO reactor have been evaporated and heated such that the temperature in the reactor is controlled between 550 - 600 °C. The pressure in the reactor is 2 bar absolute. The OTO catalyst is fluidized in the reaction medium under the condition that the weight hourly space velocity (WHSV) is 4-10 h⁻¹, whereby WHSV is defined as the total weight of the feed flow over the catalyst weight per hour. The following catalyst was used: Composition and preparation: 32 wt% ZSM-23 SAR 46, 8 wt% ZSM-5 SAR 280, 36 wt% kaolin, 24 wt% silica sol, and, after calcination of the ammonium form of the spray dried particle, 1.5 wt% P was introduced by H₃PO₄ impregnation. The catalyst was again calcined at 550 C. The steam and C4 recycle streams are excluded from the product composition tables.

The methanol provided to the OTO process (approximately 5000 t/d, see Table 1) is synthesised using at least part of the hydrogen ex. combined effluent.

The feed containing carbon monoxide and/or carbon dioxide is prepared by combining synthesis gas obtained from one or more synthesis gas producing processes and optionally a carbon dioxide stream obtained from a MEG synthesis. The yields of methanol are calculated by an Aspen model. To keep the inert concentration of about 40wt% in the synthesis gas recycle, the amount of purge stream from the recycle is adjusted.

The hydrogen ex. combined effluent and carbon dioxide ex. MEG synthesis are taken as 99.9+% pure.

Natural gas composition is 94.3 mol% CH₄, 0.6 mol% C₂H₆, 4.6 mol% N₂, 0.4 mol% CO₂, and 0.1 mol% Ar, based on the total number of moles in the natural gas stream.

Experiment 1b:

The methanol feed to the OTO process is synthesised from a mixture of part of the hydrogen ex. combined effluent and SGP synthesis gas. By providing hydrogen ex. combined effluent to the methanol synthesis, the natural gas consumption for producing the methanol has decreased by 8 wt% based on the natural gas required for producing the methanol in Experiment 1a. There is no longer the need to add additional SMR synthesis gas. Moreover, by not using a SMR synthesis gas the water consumption decreases significantly, in principle no water is used for the synthesis gas production.

Furthermore, inert (N_2 , Ar and CH_4) concentration in the feed to the methanol synthesis are reduced, compared to the levels seen in experiment 1a, due to dilution of the SGP synthesis gas with hydrogen obtained from the ethane cracker.

Experiment 1c:

The methanol feed to the OTO process is synthesised from a mixture of hydrogen ex. combined effluent and SGP synthesis gas. In addition, pure carbon dioxide is added from a MEG production unit to increase the carbon dioxide content to 3.3 mol%, based on the total feed to the methanol synthesis. The natural gas consumption for producing the methanol has decreased by 12 wt% based on the natural gas required for producing the methanol in Experiment 1a. In addition, 255 ton/day of methanol is produced based on waste carbon dioxide, i.e. carbon dioxide not produced as part of the process to prepare synthesis gas, which would need to be sequestered or otherwise captured and stored. As a result, the carbon dioxide penalty of the process is reduced.

Experiment 1f:

The methanol feed to the OTO process is synthesised from a mixture of part of the hydrogen ex. combined effluent and ATR synthesis gas. In addition, pure carbon dioxide is added from a MEG production unit to increase the carbon dioxide content to 7.1 mol%, based on the total feed to the methanol synthesis. The natural gas consumption for producing the methanol has decreased by 6 wt% based on the natural gas required for producing the methanol in Experiment 1a. In addition 273 ton/day of methanol is produced based on waste carbon dioxide. As a result, the carbon dioxide penalty of the process is reduced.

Again, inert (N_2 , Ar and CH_4) concentrations are further lowered.

Experiment 1g:

The methanol feed to the OTO process is synthesised from a mixture of almost all of the hydrogen ex. combined effluent and ATR synthesis gas. In addition, pure carbon dioxide is added from a MEG production unit added to increase the carbon dioxide content to 7.9 mol%, based on the total feed to the methanol synthesis. The natural gas consumption for producing the methanol has decreased by 9 wt% based on the natural gas required for producing the methanol in Experiment 1a. In addition 443 ton/day of methanol is produced based on waste carbon dioxide. As a result, the carbon dioxide penalty of the process is reduced.

Again, inert (N_2 , Ar and CH_4) concentrations are further lowered.

Table 2a

	Feed 10 ³ kg/day			Product 10 ³ kg/day
Exp.	H ₂ ex. combined effluent	Synthesis gas	CO ₂ ex. MEG	Methanol
1a	–	2236 (ex.SMR) 3883 (ex.SGP)	–	5000
1b	129	5488 (ex.SGP)	–	5000
1c	173	5208 (ex.SGP)	365	5000
1d	321	4322 (ex.SGP)	1584	5000
1e	82	5837 (ex.ATR)	–	5000
1f	134	5518 (ex.ATR)	398	5000
1g	165	5320 (ex.ATR)	635	5000

Table 2b

	Composition mol%*					Molar ratio
Exp.	H ₂	CO	CO ₂	N ₂ , AR, CH ₄	H ₂ O	
1a	65.8	25.6	4.4	3.8	0.2	2.05
1b	66.1	29.7	1.8	2.2	0.2	2.04
1c	66.7	27.8	3.3	2.0	0.2	2.04
1d	68.5	21.8	8.0	1.6	0.1	2.03
1e	68.1	24.6	5.9	1.4	>0.1	2.04
1f	68.6	22.9	7.2	1.3	>0.1	2.04
1g	69.0	21.9	7.9	1.2	>0.1	2.05

*Based on the total number of moles in the feed

** molar ratio = (#mol H₂ - #mol CO₂) / (#mol CO + #mol CO₂)

products derived thereof. In addition, by using a
synthesis gas which is produced by a process in which in
principle no or only little water is used, such as a non-
catalytic partial oxidation process, water consumption is
5 significantly lowered.

C L A I M S

1. A process for producing olefins, comprising:
 - a. cracking an ethane-comprising feed in a cracking zone under cracking conditions to obtain an cracking zone effluent comprising at least olefins and hydrogen;
 - 5 b. converting an oxygenate feedstock in an oxygenate-to-olefin zone to obtain an OTO zone effluent at least olefins and hydrogen;
 - c. combining at least part of the cracking zone effluent and part of the OTO zone effluent to a combined effluent;
 - 10 and
 - d. separating hydrogen from the combined effluent, wherein at least part of the oxygenate feedstock is obtained by providing hydrogen obtained in step d) and a feed containing carbon monoxide and/or carbon dioxide to
 - 15 an oxygenate synthesis zone and synthesizing oxygenates.
2. A process according to claim 1, wherein the olefins obtained in step a) and/or b) include ethylene and propylene.
3. A process according to claim 1 or 2, comprising
- 20 providing hydrogen and at least one of carbon monoxide and carbon dioxide to the oxygenate synthesis zone in a molar ratio of in the range of from 2.0 to 3.0, preferably 2.0 to 2.2.
4. A process according to any one of the preceding
- 25 claims, wherein the feed containing carbon monoxide and/or carbon dioxide comprises a synthesis, preferably synthesis gas with a molar ratio of hydrogen to carbon monoxide and/or carbon dioxide of in the range of from 1.0 to 1.9, more preferably of from 1.3 to 1.8.

5. A process according to any one of the preceding claims, wherein the feed containing carbon monoxide and/or carbon dioxide comprises carbon dioxide obtained from a subsurface natural gas or oil reservoir.
- 5 6. A process according to any one of the preceding claims, wherein the feed containing carbon monoxide and/or carbon dioxide comprises carbon dioxide obtained from a process for preparing ethylene oxide and/or Mono-ethylene-glycol.
- 10 7. A process according to according to any one of the preceding claims, wherein the olefins obtained in step a) and/or b) include ethylene and comprising:
- providing at least part of the ethylene to an ethylene oxidation zone together with a source of
- 15 oxygen and performing a process for preparing ethylene oxide to obtain ethylene oxide and carbon dioxide.
8. A process according to any one of the preceding claims, wherein the olefins obtained in step a) and/or b) include ethylene and comprising:
- converting at least part of the ethylene with benzene to obtain styrene monomer and hydrogen; and
 - providing at least part of the obtained hydrogen to the oxygenate synthesis zone.
- 20
9. A process according to any of the preceding claims, comprising:
- 25
- i) providing a feed comprising methane and ethane;
 - ii) separating the feed into at least a methane-comprising feed and an ethane-comprising feed;
 - iii) providing at least part the methane-comprising
- 30 feed to a process for preparing synthesis gas to obtain a synthesis gas; and

iv) providing at least part of the ethane to the cracking zone and at least part of the synthesis gas to the oxygenate synthesis zone.

5 10. A process according to claim 10, wherein the feed comprising methane and ethane is natural gas or associated gas.

11. A process according to claim 10, wherein the feed comprising methane and ethane comprises in the range of 1 to 20 mol% of ethane, based on the total feed.

10 12. An integrated system for producing olefins, which system comprises:

a) a steam cracking system having one or more inlets for an ethane-comprising feedstock and steam, and an outlet for a cracker effluent comprising olefins and hydrogen;

15 b) an oxygenate-to-olefins conversion system, having one or more inlets for receiving an oxygenate feedstock, and comprising a reaction zone for contacting the oxygenate feedstock with an oxygenate conversion catalyst under oxygenate conversion conditions, and an outlet for a
20 oxygenate-to-olefins effluent comprising olefins;

c) a work-up system arranged to receive at least part of the cracker effluent and at least part of the oxygenate-to-olefins effluent to obtain a combined effluent, the work-up section comprising a separation system, an outlet
25 for a olefin product stream and an outlet for hydrogen;

d) an oxygenate synthesis system having one or more inlets for a feed containing carbon monoxide and/or carbon dioxide and an inlet for hydrogen, and an outlet for an oxygenate feedstock; and means for providing
30 hydrogen from the outlet for hydrogen of the workup section to the hydrogen inlet of the oxygenate synthesis system.