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(54) Title: PROCESS FOR OBTAINING A CATALYST COMPOSITE

(57) Abstract: A process for obtaining a catalyst composite comprising the following steps: a) selecting a molecular sieve having pores of 10-or more-membered rings b) contacting the molecular sieve with a metal silicate different from said molecular sieve comprising at least one alkaline earth metal and one or more of the following metals: Ga, Al, Ce, In, Cs, Sc, Sn, Li, Zn, Co, Mo, Mn, Ni, Fe, Cu, Cr, Ti and V, such that the composite comprises at least 0.1 wt% of silicate.

Process for obtaining a catalyst composite

FIELD OF THE INVENTION

The present invention relates to a catalyst composite comprising a molecular sieve and a catalyst promoter as well as their use in conversion of organics to light olefins. More precisely the molecular sieves of the invention are obtained from crystalline aluminosilicates having pores of 10-or more-membered rings. The invention is useful as a catalyst in a variety of processes including cracking, hydrocracking, isomerisation, reforming, dewaxing, alkylation, transalkylation, and conversion of oxygenates (or halogenide-containing or sulphur-containing organic compounds) to light olefins.

BACKGROUND OF THE INVENTION

The limited supply and increasing cost of crude oil has prompted the search for alternative processes for producing hydrocarbon products. One such process is the conversion of oxygen-containing (for example methanol), halogenide-containing or sulphur-containing organic compounds to hydrocarbons, in particular, to light olefins, i.e. C_2 to C_4 olefins, or gasoline and aromatics. In the present application the conversion of said oxygen-containing (also referred to as oxygenates), halogenide-containing or sulphur-containing organic compounds to hydrocarbons, especially light olefins, is referred to as the XTO process. The interest in the XTO process is based on the fact that feedstocks, especially methanol can be obtained from coal, biomass, hydrocarbon residues, petcoke, organic waste or natural gas by the production of synthesis gas, which is then further processed to produce methanol. The XTO process can be combined with an OCP (olefin cracking process) process to increase production of olefins. The XTO process produces light olefins such as ethylene and propylene, as well as heavy hydrocarbons such as butenes and above. These heavy hydrocarbons are cracked in an OCP process to give mainly ethylene and propylene.

In accordance with US 5573990 methanol and/or dimethylether is converted to light olefins in the presence of a catalyst, which contains at least 0.7% by weight of phosphorus and at least 0.97% by weight of rare earth elements, which are incorporated within the structure of the catalyst and allegedly enhance the hydrothermal stability of the zeolite. The rare earth elements are preferably rich in lanthanum, the content of lanthanum in the catalyst being preferably comprised between 2.5 and 3.5% by weight of the catalyst. The rare earth elements are introduced via impregnation onto the crystals in an aqueous solution of a

lanthanum salt, for example $La(NO_3)_3$, or of mixed rare earth salts rich in lanthanum. The zeolite ZSM-5 based catalyst presents a mole ratio SiO_2/Al_2O_3 comprised between 40 and 80, a crystal size comprised between 1 and 10 µm and adsorption capacities of n-hexane and water of from 10 to 11% by weight and of from 6 to 7% by weight respectively. Said ZSM-5 is synthesized in the presence of a template, then extruded with colloidal silica and converted to the hydrogen form by ion exchange using hydrochloric acid.

US 20060144759 A1 is related to the production of ethylene and propylene from the catalytic cracking of hydrocarbons, which may include an unsaturated bond, but no mention is made of oxygen-containing feedstocks. The aim was to find a catalyst, which could be used in a reactor permitting continuous regeneration of the catalyst. The zeolite thus cited as suitable is a high silica zeolite, preferably a ZSM-5 and/or a ZSM-11, having a SiO_2/Al_2O_3 molar ratio ranging from 25 to 800 and carrying a rare earth element preferably chosen from lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium and dysprosium. It is stated that mere physical mixing of the zeolite with the rare earth compound is not sufficient. The zeolite may also contain other components such as an alkali metal, an alkaline earth metal, a transition metal, a noble metal, a halogen and phosphorus.

In accordance with US 2007/0032379 A1, an alkaline earth metal-containing MFI zeolite is disclosed, having a Si/Al atomic ratio of from 30 to 400, an alkaline earth metal/Al atomic ratio ranging from 0.75 to 15, and an average particle diameter ranging from 0.05 to 2 µm. This zeolite is selective for the production of lower hydrocarbons, e.g. ethylene and propylene, from dimethyl ether and/or methanol and is stated to have an extended catalyst life. The zeolite is obtained by synthesising a zeolite raw material solution, which contains a SiO_2 source, a metal oxide source, an alkali source and a structure-directing agent, i.e. a template, in the presence of an alkaline earth metal salt, such as calcium acetate, and a zeolite seed crystal. This implies that the metal salt is present within the zeolite crystal structure.

According to US 4049573, a catalytic process is provided for converting lower monohydric alcohols to a hydrocarbon mixture rich in ethylene and propylene and mononuclear aromatics with a high selectivity for para-xylene, using a catalyst comprising a crystalline aluminosilicate zeolite having a silica to alumina ratio of at least about 12, a constraint index in the range of 1 to 12, said catalyst having been modified by the addition thereto of a minor proportion of an oxide of boron or magnesium either alone or in combination, optionally with an oxide of phosphorus. The zeolite can be ion-exchanged to form metal-modified zeolites

for example with nickel, zinc, calcium or rare earth metals. There is no mention of adding metal silicates to the zeolite.

In accordance with US 3911041, methanol or dimethyl ether is subjected to conversion, at a temperature of at least about 300°C, with a catalyst comprising a crystalline aluminosilicate zeolite having a silica to alumina ratio of at least about 12, a constraint index of about 1 to 12, and containing phosphorus incorporated within the crystal structure thereof in an amount of at least about 0.78 percent by weight, preferably not higher than about 4.5 percent by weight. The zeolite, preferably, also has a dried crystal density of not less than about 1.6 grams per cubic centimetre. The crystalline aluminosilicate zeolite is first converted to the hydrogen form, then phosphorus is introduced by reaction with a phosphorus-containing compound having a covalent or ionic constituent capable of reacting or exchanging with a hydrogen ion. Thereafter, the phosphorus-modified zeolite is heated. There is no steaming of the zeolite prior to introduction of phosphorus. Preferably, prior to reacting the zeolite with the phosphorus-containing compound, the zeolite is dried, preferably in the presence of air and at an elevated temperature. The phosphorus-containing zeolite thus obtained may be further modified by impregnating the zeolite with zinc. This can be carried out by contacting the zeolite with a solution of a zinc salt, so that the zinc salt can fill the pore volume of the phosphorus-containing zeolite. Zinc-impregnated phosphorus-containing zeolites are claimed to have higher levels of conversion than those zeolites not impregnated with zinc.

Sano *et. al.* (*Applied Catalysis*, 33 (1987) 209-217) discusses the differences of Ca-H-ZSM-5, $CaCO_3$/Ca-H-ZSM-5 and CaO/Ca-H-ZSM-5. The Ca-H-ZSM-5 zeolite was obtained by mixing aluminium nitrate, colloidal silica and calcium acetate, template and sodium hydroxide in solution. Thus, the calcium is contained within the crystal structure of the zeolite. After crystallisation of the zeolite from the hydrogel, the crystals were filtered off and then washed, dried, calcined at 500°C for 16 hours, protonated and calcined again at 500°C for 6 hours to obtain $CaCO_3$/Ca-H-ZSM-5. To obtain CaO/Ca-H-ZSM-5, the $CaCO_3$-containing catalyst was calcined once more for a further 24 hours at 600°C. The catalyst stabilities and long-term aging of Ca-H-ZSM-5, $CaCO_3$/Ca-H-ZSM-5 and CaO/Ca-H-ZSM-5 were then compared in methanol conversions. Very slow decays of conversion and selectivity were observed for the $CaCO_3$/Ca-H-ZSM-5 and the CaO/Ca-H-ZSM-5 zeolites. However Ca-H-ZSM-5 decayed rapidly, which is claimed to be due to the increased coke deposition on the catalyst surface. The amount of coke deposited on the $CaCO_3$/Ca-H-ZSM-5 and the CaO/Ca-H-ZSM-5 zeolites was far less. On the other hand, the modification of the calcium-containing catalyst to a $CaCO_3$- or CaO-containing catalyst did not seem to affect resistance to steaming. Thus,

the extended catalyst life was attributed to the improved resistance to coking and not to the improved resistance to hydrothermal treatment.

EP448000 relates to a process for the conversion of methanol or dimethylether into light olefins in the presence of water vapour over a silicoaluminate of the pentasil structure having a Si/Al ratio of at least 10, thereby producing at least 5 wt% of ethylene, at least 35 wt% of propylene and at most 30 wt% butenes by (1) using a total pressure of 10 to 90 kPa, (2) a weight ratio of water to methanol of 0.1 to 1.5, (3) a reactor temperature of 280 to 570°C and (4) a proton-containing catalyst of the pentasil-type, having an alkali-content of at most 380 ppm, less than 0.1 wt% of ZnO and less than 0.1 wt% of CdO and a BET surface area of 300 to 600 m2/gram and a pore volume of 0.3 to 0.8 cm^3/gram.

WO2007/043741 discloses a catalyst for producing light olefins from a hydrocarbon feedstock wherein the catalyst consists of a product obtained by the evaporation of water from a raw material mixture comprising 100 parts by weight of a molecular sieve with a framework of Si-OH-Al groups, 0.01-5.0 parts by weight of a water-insoluble metal salt, and 0.05-17.0 parts by weight of a phosphate compound. The water-insoluble metal salt is a metal salt with a solubility product (Ksp) of less than 10^{-4}, i.e. a pKsp of more than 4. This includes oxides, hydroxides, carbonates or oxalates of metals with an oxidation state of more than +2, preferably alkaline earth metals (Mg, Ca, Sr, and Ba), transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) and heavy metals (B, Al, Ga, In, Ti, Sn, Pb, Sb and Bi). Metal silicates are however not disclosed. There is also no indication that this catalyst can be used in XTO processes.

Molecular sieves in combination with matrix and binder components for XTO and OCP processes are known in the arts. Usually, the binder and matrix are chemically neutral materials, typically serving only to provide desired physical characteristics to the catalyst composition. Usually, they have very little effect on catalytic performance. These molecular sieve catalyst compositions are formed by combining the molecular sieve and the matrix e.g. an inorganic oxide such as alumina, titania, zirconia, silica or silica-alumina with a binder, e. g. clay, to form a coherent, stable, attrition-resistant composite of the sieve, matrix material and binder. In particular, the use of silica (SiO_2) as a binder/matrix material is well known in the art. This solid is neutral and is selected when catalytic effects of the binder/matrix are undesired. Metal modified zeolites, particularly, P-zeolites and their use as XTO catalysts are known in the art. Typically, rare earth elements, which are very expensive, are used in such catalyst composites.

Metal is introduced typically in the form of water-soluble metal salts, mainly oxides/oxide-precursor salts, by ion-exchanged/impregnation. However, ion-exchange/impregnation potentially leads to the modification of the acidity of catalytic sites throughout the whole microporous structure of the molecular sieve. This could lead to decreased catalytic activity. Metal oxides are chemically active compounds. Without taking special precautions during pre-treatment and catalyst formulation these compounds may partially damage the molecular sieve pore structure. The proposed current invention is very different from the prior art. The combination of molecular sieves with chemically inert metal silicates allows selectively modifying only the sites located on the external surface and in the pore mouths of the molecular sieve. As a result, the formation of side products is avoided and coke formation is decreased without losses in the catalyst's activity by minimising reactions outside the microporous space.

A huge variety of naturally occurring and synthetically produced silicates are known in the art.

For example, US 3729429 discloses layered complex metal silicate compositions, in particular chrysotiles, and their preparation.

US 3806585 discloses the production of a hydrous calcium silicate composed preponderantly of xonotlite in the shape of rod crystals, which is described as having outstanding refractory properties, whereby moulded bodies comprised primarily of xonotlite provide strength unattained by other inorganic materials. The specification discloses that hydrous calcium silicate of the xonotlite type has use in construction as a fire proof coating material, as a fire proof moisture retaining material and as a potential filler for plastics and rubber products.

US 3804652 discloses a method of producing calcium silicate-based products, such as drain pipes and insulating material.

US 3928539 discloses a method of producing hydrous calcium silicates such as xonotlite, tobermorite and the like.

US 3915725 discloses a process for producing hollow spherical aggregates of xonotlite, which are employed to form shaped articles.

US 4298386 discloses the production of globular secondary particles of the woolastonite group of calcium silicate crystals, including woolastonite and xonotlite.

US 7294604 discloses the use of calcium silicate as a catalyst support for metal supported hydrogenation and dehydrogenation catalysts.

Thus, the current invention proposes an improved catalyst for XTO and/or OCP processes.

It is thus an aim of the invention is to find a catalyst for XTO and/or OCP processes with an increased yield of light olefins.

It is another aim of the invention to find a catalyst for XTO and/or OCP processes with a higher stability.

In addition, it is another aim of the invention to find a catalyst for XTO and/or OCP processes with reduced selectivity for paraffins.

It is an aim of this invention to avoid the use of heavy and expensive rare earth metals.

The invention fulfils at least one of the above aims.

SUMMARY OF THE INVENTION

The present invention covers a process for obtaining a catalyst composite comprising the following steps:

a). selecting a molecular sieve having pores of 10-or more-membered rings

b). contacting the molecular sieve with a metal silicate comprising at least one alkaline earth metal, such that the composite comprises at least 0.1 wt% of silicate.

The molecular sieve is preferably brought into contact with the metal silicate by one of the following two methods:

- During the formulation step of the catalyst by mechanically blending the molecular sieve with the metal silicate forming a precursor to be used in the formulation step;
- Physical blending of the previously formulated molecular sieve and the previously formulated metal silicate *in situ* in the XTO and/or OCP reaction medium.

The molecular sieve could be selected from the list of MFI, MOR, MEL, clinoptilolite, FER, FAU, MWW, BETA, ZSM-21, ZSM-22, ZSM-23, ZSM-42, ZSM-57, LTL, or a mixture of thereof. Preferably, the MFI is a ZSM-5 zeolite. More preferably, the molecular sieve is selected from the group of MFI, MOR, MEL, clinoptilolite, FER or a mixture thereof. In another embodiment, the molecular sieve is preferably obtained without direct addition of template

Said molecular sieve and/or said catalyst composite containing the molecular sieve and the metal silicate can be post-treated by calcinations, reductions or steaming. In the case of using zeolites as molecular sieve components, phosphorus can be introduced before, simultaneously or after blending with the metal silicate.

A catalyst composite obtainable by the process described above is covered by the present invention.

The invention also covers the catalyst composite comprising:

a). at least 10 wt % of a molecular sieve having pores of 10-or more-membered rings

b). at least one metal silicate comprising at least one alkaline earth metal, such that the catalyst composite comprises at least 0.1 wt % of silicate

c). optionally metal phosphates

d). optionally matrix material

e). optionally binder

This catalyst composite can be made according to the process described above.

The present invention also relates to a process (hereunder referred as "XTO process") for making an olefin product from an oxygen-containing, halogenide-containing or sulphur-containing organic feedstock, wherein said oxygen-containing, halogenide-containing or sulphur-containing organic feedstock is contacted with the above catalyst composite (in the XTO reactor) under conditions effective to convert at least a portion of the oxygen-containing, halogenide-containing or sulphur-containing organic feedstock to olefin products (the XTO reactor effluent). It is desirable to have a substantially 100% conversion of the organic compound in the XTO reactor. This conversion rate is adjusted by optimisation of the contact time and the frequency of regeneration of the catalyst.

According to a specific embodiment the XTO reactor effluent comprising light olefins and a heavy hydrocarbon fraction is sent to a fractionation section to separate said light olefins from said heavy hydrocarbon fraction; said heavy hydrocarbon fraction is recycled in the XTO reactor at conditions effective to convert at least a portion of said heavy hydrocarbon fraction to olefin products.

With regards to said effluent of the XTO process, "light olefins" means ethylene and propylene and the "heavy hydrocarbon fraction" is defined herein as the fraction containing hydrocarbons having a molecular weight greater than propane, which means hydrocarbons having 4 carbon atoms or more and written as C_4^+.

According to another embodiment of the invention said olefin products (the effluent of the XTO) are fractionated to form a stream comprising essentially ethylene and at least a part of said stream is recycled in the XTO reactor to increase the propylene production.
According to another embodiment of the invention both ethylene and the C_4^+ can be recycled in the XTO reactor.

The present invention also relates to a process (hereunder referred to as the "combined XTO and OCP process") to make light olefins from an oxygen-containing, halogenide-containing or sulphur-containing organic feedstock comprising:

- contacting said oxygen-containing, halogenide-containing or sulphur-containing organic feedstock in the XTO reactor with the above catalyst at conditions effective to convert at least a portion of the feedstock to form an XTO reactor effluent comprising light olefins and a heavy hydrocarbon fraction;
- separating said light olefins from said heavy hydrocarbon fraction;
- contacting said heavy hydrocarbon fraction in the OCP reactor at conditions effective to convert at least a portion of said heavy hydrocarbon fraction to light olefins. It is desirable to have a substantially 100% conversion of the organic compound in the XTO reactor. This conversion rate is adjusted by optimization of contact time and the frequency of regeneration of the catalyst.

The catalyst composite of the invention can also be used only in the OCP process i.e. the process for the catalytic cracking of an olefin-rich feedstock which is selective towards light olefins in the effluent, the process comprising contacting a hydrocarbon feedstock containing one or more olefins, with a catalyst composite according to the invention, to produce an effluent with an olefin content of lower molecular weight than that of the feedstock.

The catalyst composites according to the invention show high propylene yield, high propylene/ethylene ratio, high stability, high propylene purity and reduced selectivity to paraffin's and to aromatics in the XTO process. These catalysts also provide the additional flexibility for ethylene and C_4^+ recycling to increase propylene production. The average propylene yield can be substantially enhanced by using the catalyst composite of the invention in a combination of XTO and OCP process.

DETAILED DESCRIPTION OF THE INVENTION

The molecular sieves that can be used in the invention are preferably zeolites, for example crystalline silicates, more precisely aluminosilicates. Crystalline silicates are microporous crystalline inorganic polymers based on a framework of XO_4 tetrahydra linked to each other by sharing oxygen ions, where X may be trivalent (e.g. Al, B, . . .) or tetravalent (e.g. Ge, Si, . . .). The crystal structure of a crystalline silicate is defined by the specific order in which a network of tetrahedral units are linked together. The size of the crystalline silicate pore openings is determined by the number of tetrahedral units, or, alternatively, oxygen atoms, required to form the pores and the nature of the cations that are present in the pores. They possess a unique combination of the following properties: high surface area; uniform pores with one or more discrete sizes; ion exchangeability; good thermal stability; and ability to adsorb organic compounds. Since the pores of these crystalline aluminosilicates are similar in size to many organic molecules of practical interest, they control the ingress and egress of reactants and products, resulting in particular selectivity in catalytic reactions.

The selected molecular sieve can be made with the help of the seeding technique, but advantageously they are made without template. However, the seeds themselves may have been made with a template, which means in this case that the molecular sieve is made without direct addition of a template. It is preferred that the molecular sieve used in the invention is made without direct addition of template.

The molecular sieves selected for the purposes of this invention have pores the size of 10 or more-membered rings. It can be envisaged to use molecular sieves, which have ring pores consisting of 10, 12 or more members.

The selected molecular sieve according to the present invention has an average pore size of at least 0.5, preferably from 0.5 to 10, more preferably from 0.5 to 5 and most preferably at least from 0.5 to 0.9 nm. The average pore size is determined according to the procedure of the International Zeolite Association.

The selected molecular sieve has an initial atomic ratio Si/Al of at least 4 and not greater than 500. The Si/Al atomic ratio is measured by chemical analysis, for example using XRF and/or NMR. It includes only those Al that are part of the framework structure of the molecular sieve.

As regards to the selected molecular sieve, advantageously it is selected from the group of MFI, MOR, MEL, clinoptilolite, FER, FAU, MWW, BETA, ZSM-21, ZSM-22, ZSM-23, ZSM-42, ZSM-57, LTL, or mixtures thereof, according to the International Zeolite Association (*Atlas of Zeolite Structure Types,* 1987, Butterworths). Preferably it is selected from group of the MFI, MOR, MEL, clinoptilolite, FER or a mixture of thereof. More preferably, the MFI is a ZSM-5 zeolite.

In another embodiment, the molecular sieve selected from the group of MFI, MOR, MEL, clinoptilolite, FER or a mixture of, is preferably obtained without direct addition of template.

The molecular sieve may be used as synthesised to form the catalyst composite. Prior to formulation of the catalyst composite the molecular sieve may undergo further treatments including steaming, leaching (e.g. acid leaching), washing, drying, calcination, impregnation and ion exchanging steps. In addition or alternatively, these steps can also be carried out after formulation of the catalyst composite.

In a particular embodiment of the invention, the molecular sieve can be modified either prior to or after introduction of the metal silicate. Preferably, the molecular sieve has undergone some form of modification prior to the metal silicate introduction. By modification, it is meant herein that the molecular sieve may have undergone steaming, leaching (e.g. acid leaching), washing, drying, calcination, impregnation or some form of ion-exchange. This means that at least a portion of the cations originally comprised in the crystal structure can be replaced with a wide variety of other cations according to techniques well known in the art. The replacing cations can be hydrogen, ammonium or other metal cations, including mixtures of such cations.

The selected molecular sieve is then formulated into a catalyst composite to comprise at least 10 % by weight of a molecular sieve as described herein and at least one metal silicate comprising at least one alkaline earth metal, such that the composite comprises at least 0.1 % by weight of silicate.

At least one of the metal silicates comprised in the catalyst composite includes at least one alkaline earth metal, preferably Ca. Metal silicates are insoluble in water and alkaline earth metal ions, particularly calcium, are polyvalent and possess a large radius in the hydrated state. Thus, without wishing to be bound by theory, it is thought that the ion exchange reaction with the molecular sieve occurs very slowly, as the alkaline earth metal ion must

lose many of its strongly coordinated water molecules in order to penetrate into the micropores of the molecular sieve structure. As a result, the alkaline earth metal ions expose only the acid sites located on the external surface of the molecular sieve, and thus increasing the selectivity of the catalyst.

Furthermore, without wishing to be bound by theory, it is thought that the presence of silicate anions further improve the catalytic properties of the catalyst composite. The silicate anions, for example, can supply silicon atoms to heal defects in the molecular sieve. This can thus lead to additional stabilisation of the catalyst under severe hydrothermal conditions.

As a result the metal silicate acts as a catalyst promoter.

The metal silicate can comprise more than one alkaline earth metal selected from Ca, Mg, Sr and Ba.

The metal silicates may also comprise other metals selected from one or more of the following: Ga, Al, Ce, In, Cs, Sc, Sn, Li, Zn, Co, Mo, Mn, Ni, Fe, Cu, Cr, Ti and V. Preferably, the other metal is selected from one or more of Al, Mg, Ce, Co and Zn or mixtures thereof.

These bi-, tri- or polymetal silicates can be synthesised according to any method known in the art. This can be for example by ion exchange in the solution or solid state (Labhsetwar et al., Reactivity of Solids, Vol. 7, Issue 3, 1989, 225-233).

The silicate anion can be present in any form in the solid metal silicate. Examples include SiO_3^{2-}, SiO_4^{4-}, $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$ and the like.

The preferred catalyst promoter is a calcium silicate with a very open and accessible pore structure. An even more preferred catalyst promoter comprises a synthetic crystalline hydrated calcium silicate having a chemical composition of $Ca_6Si_6O_{17}(OH)_2$ which corresponds to the known mineral xonotlite (having a molecular formula $6CaO.6SiO_2.H_2O$).

Generally, a synthetic hydrated calcium silicate is synthesised hydrothermally under autogeneous pressure. A particularly preferred synthetic hydrated calcium silicate is available in commerce from the company Promat of Ratingen in Germany under the trade name Promaxon.

In order to demonstrate the thermal stability of xonotlite, and therefore the applicability of xonotlite as a catalyst promoter in MTO and OCP, commercial xonotlite sold under the trade name Promaxon D was calcined in ambient air at a relative humidity of about 50% at 650° C for a period of 24 hours. The initial xonotlite had a crystalline phase $Ca_6Si_6O_{17}(OH)_2$ with a BET surface area of 51 m^2/gram and a pore volume (of less than 100 nanometres) of 0.35 ml/gram. After calcination at 650° C, the carrier retained its crystallinity, which corresponds to that of xonotlite. Thus after a 24 hour calcination at 650° C, the crystalline phase still comprised xonotlite ($Ca_6Si_6O_{17}(OH)_2$) with a BET surface area of 47.4 m^2/gram and a pore volume (less than 100 nanometres) of 0.30 ml/gram.

Other examples of metal silicates comprising alkaline earth metals include $CaAl_2Si_2O_8$, $Ca_2Al_2SiO_7$, $CaMg(Si_2O_6)_x$, as well as mixtures thereof.

Before mixing with the molecular sieve said metal silicate compounds may be modified by calcination, steaming, ion-exchange, impregnation, or phosphatation. Said metal silicates may be an individual compound or may be a part of mixed compounds.

The metal silicate can be brought into contact with the molecular sieve by a simultaneous formulation step of a blend of the metal silicate with the molecular sieve or *in situ* blending of separately formulated materials in the reaction medium prior to the XTO or OCP process. Said contact can be realised by mechanically blending of the molecular sieve with the alkaline earth metal-comprising metal silicate. This can be carried out via any known blending method. Blending can last for a period of time starting from 1 minute up to 24 hours, preferably from 1 min to 10 hours. If not carried out in the XTO or OCP reactor *in situ*, it can be carried out in a batchwise Mixer or in a continuous process, such as in an extruder e.g. a single or twin screw extruder at a temperature of from 20 to 300°C under vacuum or elevated pressure. Said contact may be performed in an aqueous or non-aqueous medium. Prior to the formulation step, other compounds that aid the formulation may be added, like thickening agents or polyelectrolytes that improve the cohesion, dispersion and flow properties of the precursor. In case of extrusion, rotating granulation or pelletising a paste-like precursor with low water content is prepared. In case of oil-drop or spray-drying a rather liquid (high water content) is prepared. In another embodiment, the contact is carried out in the presence of phosphorus containing compounds. In a particular embodiment, the contact is carried out in the aqueous medium at pH lower than 5, more preferably lower than 3.

Either prior to, after or simultaneously with the formulation step to form the composite, other components may be optionally blended with the molecular sieve. In a particular embodiment, the molecular sieve can be combined with other materials that provide additional hardness or catalytic activity to the finished catalyst product. Materials, which can be blended with the molecular sieve, can be various inert or catalytically active matrix materials and/or various binder materials. Such materials include clays, silica and/or metal oxides such as alumina. The latter is either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. In an embodiment, some binder materials can also serve as diluents in order to control the rate of conversion from feed to products and consequently improve selectivity. The occurrence of hot spots in the catalyst composites can

also be reduced when binder is included. According to one embodiment, the binders also improve the crush strength of the catalyst under industrial operating conditions.

Naturally occurring clays, which can be used as binder, are for example clays from the kaolin family or montmorillonite family. Such clays can be used in the raw state as mined or they can be subjected to various treatments before use, such as calcination, acid treatment or chemical modification.

In addition to the foregoing, other materials which can be included in the catalyst composite of the invention include various forms of metals, phosphates (for instance metal phosphates, wherein the metal is chosen from one or more of Ca, Ga, Al, Ca, Ce, In, Cs, Sr, Mg, Ba, Sc, Sn, Li, Zn, Co, Mo, Mn, Ni, Fe, Cu, Cr, Ti and V), alumina or alumina sol, titania, zirconia, quartz, silica or silica sol, and mixtures thereof. Examples of possible phospates include amorphous calcium phosphate monocalcium phosphate, dicalcium phosphate, dicalcium phosphate dehydrate, α- or β- tricalcium phosphate, octacalcium phosphate, hydroxyapatite etc.

Examples of possibly binary oxide binder compositions include, silica-alumina, silica magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, calcium-alumina. Examples of ternary binder compositions include for instance calcium-silica-alumina or silica-alumina-zirconia.

These components are effective in increasing the density of the catalyst and increasing the strength of the formulated catalyst. The catalyst may be formulated into pellets, spheres, extruded into other shapes, or formed into spray-dried particles. Generally, the size of the catalyst particles can vary from about 20 to 50,000 μm. In general pellets, spheres and extrudates are employed in fixed bed reactors and exhibit a particle size of from about 0.5 mm to 5 mm. In general spray-dried particles are used in fluidised bed reactors and exhibit a particle size of from about 20 to 200 μm. In particular spheres are employed in moving bed reactors and exhibit a size from about 0.5 to 5 mm. Spheres can be made in rotating granulator or by oil-drop methods. The crystal size of the molecular sieve contained in the catalyst composite, is preferably less than about 10 μm, more preferably less than about 5 μm and most preferably less than about 2 μm. The amount of molecular sieve, which is contained in the final catalyst composite ranges from 10 to 90 % by weight of the total catalyst composite, preferably 20 to 70 % by weight.

According to another embodiment, non-modified molecular sieves were first formulated with a binder and matrix materials and then modified with phosphorous and alkaline earth metal silicates.

According to a further particular embodiment, molecular sieves were optionally dealuminated and then modified with phosphorous during the formulation step. Introduction of the alkaline earth metal silicate can be performed during the formulation step or on the formulated solid.

According to a preferred embodiment, molecular sieves were first optionally dealuminated and modified with phosphorous and then formulated. Introduction of the metal is performed simultaneously with the phosphorous modification step and/or on the already formulated catalyst.

After formulation, the catalyst composite may undergo further treatments including further steaming, leaching, washing, drying, calcination, impregnations and ion exchanging steps. If the molecular sieve was not modified with phosphorus prior to the formulation step of the blend i.e. the step introducing the metal silicate to the molecular sieve, it may be carried out after such a step.

According to another embodiment of the invention, the molecular sieve is a phosphorus-modified (P-modified) zeolite. The zeolite can be dealuminated and/or modified with phosphorus. Phosphorus can be introduced before, simultaneously or after contact of the zeolite with the metal silicate, preferably before or simultaneously, most preferably before. Preferably, the P-modification is carried out with a steaming step followed by leaching using any acid solution containing a source of P, preferably a solution of phosphoric acid.

According to one embodiment of the invention, the zeolite can be modified with phosphorus according to the process comprising the following steps, in the order given:

- steaming of the zeolite at a temperature ranging from 400 to 870°C for 0.01-200h;
- leaching with an aqueous acid solution containing the source of P at conditions effective to remove a substantial part of Al from the zeolite and to introduce at least 0.3 % of phosphorus by weight of the zeolite;
- separation of the solid from the liquid;
- an optional washing step or an optional drying step or an optional drying step followed by a washing step;
- a calcination step.

In the steam treatment step, the temperature is preferably from 420 to 870°C, more preferably from 480 to 760°C. The pressure is preferably atmospheric pressure and the water partial pressure may range from 13 to 100 kPa. The steam atmosphere preferably contains from 5 to 100 vol % steam with from 0 to 95 vol % of an inert gas, preferably nitrogen. The steam treatment is preferably carried out for a period of from 0.05 to 200 hours, more preferably from 0.05 to 50 hours. It is generally known by the persons in the art that

steam treatment of zeolites results in aluminium that leaves the zeolite framework and resides as aluminiumoxides in and outside the pores of the zeolite. This transformation is known as dealumination of zeolites and this term will be used throughout the text.

The treatment of the steamed zeolite with an acid solution results in dissolution of the extra-framework aluminiumoxides. This transformation is known as leaching and this term will be used throughout the text. The leaching with an aqueous acid solution containing the source of phosphorus is advantageously made under reflux conditions, meaning boiling temperature of the solution.

Amount of said acid solution is advantageously between 2 and 10 litres per kg of zeolite. A typical leaching period is around 0.5 to 24 hours. Advantageously the aqueous acid solution containing the source of P in the leaching step has a pH of 3, advantageously 2, or lower. Advantageously said aqueous acid solution is phosphorus acids, a mixture of phosphorus acids and organic or inorganic acid or mixtures of salts of phosphorus acids and organic or inorganic acids. The phosphorus acids or the corresponding salts can be of the phosphate ($[PO_4]^{3-}$, being tribasic), phosphite ($[HPO_3]^{2-}$, being dibasic), or hypophosphite ($[H_2PO_2]^{1-}$, being monobasic), type. Of the phosphate type also di- or polyphosphates ($[P_nO_{3n+1}]^{(n+2)-}$) can be used. The other organic acids may comprise an organic acid such as citric acid, formic acid, oxalic acid, tartaric acid, malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, phthalic acid, isophthalic acid, fumaric acid, nitrilotriacetic acid, hydroxyethylenediaminetriacetic acid, ethylenediaminetetracetic acid, trichloroacetic acid trifluoroacetic acid or a salt of such an acid (*e.g.* the sodium salt) or a mixture of two or more of such acids or salts. The other inorganic acids may comprise an inorganic acid such as nitric acid, hydrochloric acid, methansulfuric acid, sulfuric acid or a salt of such an acid (*e.g.* the sodium or ammonium salts) or a mixture of two or more of such acids or salts.

It has been found that phosphorus acid is very efficient in complexing the extra-framework aluminiumoxides and hence removing them from the zeolite solid material. Unexpectedly, a larger quantity of phosphorus than what could be expected from the typical pore volume of the zeolite and assuming that the pores of the zeolites are filled with the used phosphorus acid solution, stays in the solid zeolite material. Both factors dealumination and the retention of P stabilize the lattice aluminium in the zeolitic lattice, thus avoiding further dealumination. This leads to higher hydrothermal stability, tuning of molecular sieves properties and adjustment of acid properties and thus increasing the zeolite's selectivity. The degree of dealumination can be adjusted by the steaming and leaching conditions.

Advantageously, the final P-content of the zeolite is at least 0.3 wt% and preferably between 0.3 and 7 w%. Advantageously at least 10% of Al have been extracted and removed from the zeolite by the leaching. The residual P-content is adjusted by P-concentration in the leaching

solution, drying conditions and a washing procedure if any. A drying step can be envisaged between filtering and washing steps.

Then the zeolite either is separated from the washing solution or is dried without separation from the washing solution. Said separation is advantageously made by filtration. Then the zeolite is calcined, by way of example, at 400°C for 2-10 hours.

With regards to the XTO process, the catalyst composite of the invention is particularly suited for the catalytic conversion of oxygen-containing, halogenide-containing or sulphur-containing organic compounds to hydrocarbons. Accordingly, the present invention also relates to a method for making an olefin product from an oxygen-containing, halogenide-containing or sulphur-containing organic feedstock wherein said oxygen-containing, halogenide-containing or sulphur-containing organic feedstock is contacted with the above catalyst under conditions effective to convert the oxygen-containing, halogenide-containing or sulphur-containing organic feedstock to olefin products (the effluent of the XTO). Said effluent comprises light olefins and a heavy hydrocarbon fraction.

In this process a feedstock containing an oxygen-containing, halogenide-containing or sulphur-containing organic compound contacts the above described catalyst composite in a reaction zone of a reactor at conditions effective to produce light olefins, particularly ethylene and propylene. Typically, the oxygen-containing, halogenide-containing or sulphur-containing organic feedstock is contacted with the catalyst composite when the oxygen-containing, halogenide-containing or sulphur-containing organic compounds are in the vapour phase. Alternately, the process may be carried out in a liquid or a mixed vapour/liquid phase. In this process, converting oxygen-containing, halogenide-containing or sulphur-containing organic compounds, olefins can generally be produced at a wide range of temperatures. An effective operating temperature range can be from about 200°C to 700°C. At the lower end of the temperature range, the formation of the desired olefin products may become markedly slow. At the upper end of the temperature range, the process may not form an optimum amount of product. An operating temperature of at least 300° C, and up to 600°C is preferred.

The pressure also may vary over a wide range. Preferred pressures are in the range of about 0.005 bars to about 50 bars, with the most preferred range being of from about 0.05 bars to about 5 bars. The foregoing pressures refer to the partial pressure of the oxygen-containing, halogenide-containing, sulphur-containing organic compounds and/or mixtures thereof.

The process can be carried out in any system using a variety of transport beds, particularly a fixed bed or moving bed system could be used. Advantageously a fluidized bed is used. It is particularly desirable to operate the reaction process at high space velocities. The process can be conducted in a single reaction zone or a number of reaction zones arranged in series or in parallel. Any standard commercial scale reactor system can be used, for example fixed

bed, fluidised or moving bed systems. After a certain time on-stream the catalyst needs to be regenerated. This regeneration can be carried out in a separate reactor or in the same reactor. In case of a moving bed or fluidised bed reactor, a part of the catalyst is continuously or intermittently withdrawn from the conversion reactor and sent to a second reactor for regeneration. After the regeneration, the regenerated catalyst is continuously or intermittently sent back to the conversion reactor. In case of fixed bed reactor the reactor is taken off-line for regeneration. Generally this requires a second spare reactor that can take over the conversion into light olefins. After regeneration the fixed bed reactor is in stand-by until the spare reactor needs regeneration and the regenerated reactor takes over the conversion. Regeneration is carried out by injecting an oxygen-containing stream over the catalyst composite at a sufficiently high temperature to burn the deposited coke on the catalyst composite. The commercial scale reactor systems can be operated at a weight hourly space velocity (WHSV) of from 0.1 hr^{-1} to 1000 hr^{-1}.

One or more inert diluents may be present in the feedstock, for example, in an amount of from 1 to 95 molar percent, based on the total number of moles of all feed and diluent components fed to the reaction zone. Typical diluents include, but are not necessarily limited to helium, argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, paraffins, alkanes (especially methane, ethane, and propane), aromatic compounds, and mixtures thereof. The preferred diluents are water and nitrogen. Water can be injected in either liquid or vapour form.

According to a specific embodiment essentially no water (or steam) is injected as a diluent of the feedstock sent to the XTO reactor. However it means that the feedstock can contain the water already contained in the fresh oxygen-containing, halogenide-containing or sulphur-containing organic feedstock or the steam used to engage proper flowing of catalyst in fluidised bed or moving bed reactors of the XTO reactor.

The oxygenate feedstock is any feedstock containing a molecule or any chemical having at least an oxygen atom and capable, in the presence of the above catalyst composite, to be converted to olefin products. The oxygenate feedstock comprises at least one organic compound which contains at least one oxygen atom, such as aliphatic alcohols, ethers, carbonyl compounds (aldehydes, ketones, carboxylic acids, carbonates, esters and the like). Representative oxygenates include but are not necessarily limited to lower straight and branched chain aliphatic alcohols and their unsaturated counterparts. Examples of suitable oxygenate compounds include, but are not limited to: methanol; ethanol; n-propanol; isopropanol; C_4-C_{20} alcohols; methyl ethyl ether; dimethyl ether; diethyl ether; di-*iso*propyl ether; formaldehyde; dimethyl carbonate; dimethyl ketone; acetic acid; and mixtures thereof. Representative oxygenates include lower straight chain or branched aliphatic alcohols, their unsaturated counterparts. Analogously to these oxygenates, compounds containing sulphur

or halides may be used. Examples of suitable compounds include methyl mercaptan; dimethyl sulfide; ethyl mercaptan; diethyl sulfide; ethyl monochloride; methyl monochloride, methyl dichloride, n-alkyl halides, n-alkyl sulfides having n-alkyl groups of comprising the range of from about 1 to about 10 carbon atoms; and mixtures thereof. Preferred oxygenate compounds are methanol, dimethyl ether, or a mixture thereof.

In the XTO effluent among the olefins having 4 or more carbon atoms, more than 50 % by weight are butenes. More than 80% by weight and advantageously more than 85% of the hydrocarbons having 4 carbon atoms or more are C4 to C8 olefins.

According to a specific embodiment the XTO reactor effluent comprising light olefins and a heavy hydrocarbon fraction is sent to a fractionation section to separate said light olefins from said heavy hydrocarbon fraction; said heavy hydrocarbon fraction is recycled in the XTO reactor at conditions effective to convert at least a portion of said heavy hydrocarbon fraction to olefin products.

With regards to said effluent of the XTO process, "light olefins" means ethylene and propylene and the "heavy hydrocarbon fraction" is defined herein as the fraction containing hydrocarbons having a molecular weight greater than propane, which means hydrocarbons having 4 carbon atoms or more and written as C_4^+.

According to another embodiment of the invention said olefin products (the effluent of the XTO) are fractionated to form a stream comprising essentially ethylene and at least a part of said stream is recycled in the XTO reactor to increase the propylene production and hence the flexibility of ethylene vs propylene production. Advantageously the ratio of ethylene to the oxygen-containing, halogenide-containing or sulphur-containing organic feedstock is 1.8 or less.

According to another embodiment of the invention both ethylene and the C_4^+ can be recycled in the XTO reactor.

The present invention also relates to a process (hereunder referred to as a "combined XTO and OCP process") to make light olefins from an oxygen-containing, halogenide-containing or sulphur-containing organic feedstock comprising :

- contacting said oxygen-containing, halogenide-containing or sulphur-containing organic feedstock in the XTO reactor with the above catalyst at conditions effective to convert at least a portion of the feedstock to form an XTO reactor effluent comprising light olefins and a heavy hydrocarbon fraction;
- separating said light olefins from said heavy hydrocarbon fraction;
- contacting said heavy hydrocarbon fraction in the OCP reactor at conditions effective to convert at least a portion of said heavy hydrocarbon fraction to light olefins.

The effluent of the XTO reactor comprising light olefins and a heavy hydrocarbon fraction is sent to a fractionation section to separate said light olefins from said heavy hydrocarbon fraction. With regards to said effluent of the XTO process, "light olefins" means ethylene and propylene and the "heavy hydrocarbon fraction" is defined herein as the fraction containing hydrocarbons having a molecular weight greater than propane, which means hydrocarbons having 4 carbon atoms or more and written as C_4^+. It is desirable to have a substantially 100% conversion of the organic compound in the primary reactor. This conversion rate is adjusted by optimisation of the contact time and the frequency of the regeneration of the catalyst.

With regards to the OCP process, said process is known per se. It has been described in EP 1036133, EP 1035915, EP 1036134, EP 1036135, EP 1036136, EP 1036138, EP 1036137, EP 1036139, EP 1194502, EP 1190015, EP 1194500 and EP 1363983 the content of which are incorporated in the present invention. The heavy hydrocarbon fraction produced in the XTO reactor is converted in the OCP reactor, also called an "olefin cracking reactor" herein, to produce additional amounts of ethylene and propylene.

According to a specific embodiment the catalysts found to produce this conversion comprise a crystalline aluminosilicate of the MFI family or the MEL family. These aluminosilicates have been described above in the description of the molecular sieve.

The MFI or MEL catalyst having a high Si/Al atomic ratio for use in the OCP reactor of the present invention may be manufactured by removing aluminum from a commercially available crystalline silicate. A typical commercially available silicalite has a silicon/aluminum atomic ratio of around 120. The commercially available MFI crystalline silicate may be modified by a steaming process, which reduces the tetrahedral aluminum in the crystalline silicate framework and converts the aluminum atoms into octahedral aluminum in the form of amorphous alumina. Although in the steaming step aluminum atoms are chemically removed from the crystalline silicate framework structure to form alumina particles, those particles cause partial obstruction of the pores or channels in the framework. This inhibits the olefinic cracking processes of the present invention. Accordingly, following the steaming step, the crystalline silicate is subjected to an extraction step wherein amorphous alumina is removed from the pores and the micropore volume is, at least partially, recovered. The physical removal, by a leaching step, of the amorphous alumina from the pores by the formation of a water-soluble aluminum complex yields the overall effect of de-alumination of the MFI crystalline silicate. In this way by removing aluminum from the MFI crystalline silicate framework and then removing alumina formed there from the pores, the process aims at achieving a substantially homogeneous dealumination throughout the whole pore surface of the catalyst. This reduces the acidity of the catalyst and thereby reduces the occurrence of

hydrogen transfer reactions in the cracking process. The reduction of acidity ideally occurs substantially homogeneously throughout the pores defined in the crystalline silicate framework. This is because in the olefin-cracking process hydrocarbon species can enter deeply into the pores. Accordingly, the reduction of acidity and thus the reduction in hydrogen transfer reactions, which would reduce the stability of the MFI catalyst are pursued throughout the whole pore structure in the framework. The framework silicon/aluminum ratio may be increased by this process to a value of at least about 180, preferably from about 180 to 500, more preferably at least 200, yet more preferably at least 300 and most preferably around 480.

The MEL or MFI crystalline silicate catalyst may be mixed with a binder, preferably an inorganic binder. The binder is selected so as to be resistant to the temperature and other conditions employed in the catalyst manufacturing process and in the subsequent catalytic cracking process for the olefins. The binder is an inorganic material selected from clays, silica, metal oxides such as ZrO_2 and/or metals, or gels including mixtures of silica and metal oxides. The binder is preferably alumina-free, although aluminum in certain chemical compounds as in aluminium phosphate's may be used as the latter are quite inert and not acidic in nature. If the binder, which is used in conjunction with the crystalline silicate, is itself catalytically active, this may alter the conversion and/or the selectivity of the catalyst. Inactive materials for the binder may suitably serve as diluents to control the amount of conversion so that products can be obtained economically and orderly without employing other means for controlling the reaction rate. It is desirable to provide a catalyst having a good crush strength. This is because in commercial use, it is desirable to prevent the catalyst from breaking down into powder-like materials. Such clay or oxide binders have been employed normally only for the purpose of improving the crush strength of the catalyst. A particularly preferred binder for the catalyst composite for use in an OCP reactor are silica or aluminium phosphates.

The relative proportions of the finely divided crystalline silicate material and the inorganic oxide matrix of the binder can vary widely. Typically, the binder content ranges from 5 to 95% by weight, more typically from 20 to 50% by weight, based on the weight of the composite catalyst. Such a mixture of crystalline silicate and an inorganic oxide binder is referred to as a formulated crystalline silicate. In mixing the catalyst with a binder, the catalyst may be formulated into extended pellets, spheres, extruded into other shapes, or formed into a spray-dried powder.

According to another specific embodiment the catalyst composite for the OCP process comprises a P-modified zeolite selected from a group of zeolites with a low Si/Al ratio (advantageously lower than 30) being in the H^+ or NH_4^+-form of MFI, MEL, FER, MOR, clinoptilolite, which have been made preferably without direct addition of organic template.

According to another specific embodiment of the invention, the P-zeolite can be modified with phosphorus according to the same process as described above.

The catalyst composites of the invention can thus be used both in the XTO and in the OCP processes. The catalyst composite in the OCP reactor can be the same as the catalysts of the XTO reactor or they can be different, due to differences in the starting zeolite, the P content and so on. The catalyst composite of the invention can also be used only in the OCP process i.e. the process for the catalytic cracking of an olefin-rich feedstock which is selective towards light olefins in the effluent, the process comprising contacting a hydrocarbon feedstock containing one or more olefins, with a catalyst composite according to the invention, to produce an effluent with an olefin content of lower molecular weight than that of the feedstock.

The crystalline aluminosilicate catalyst has structural and chemical properties and is employed under particular reaction conditions during the OCP process whereby the catalytic cracking of the C_4^+ olefins readily proceeds. Different reaction pathways can occur on the catalyst. The cracking of the olefins is preferably performed at an inlet temperature of the feedstock of from 400° to 650°C, more preferably from 450° to 600°C, yet more preferably from 540°C to 590°C, typically around 560° to 585°C and under an olefin partial pressure of from 0.1 to 2 bars, most preferably around atmospheric pressure. Olefin catalytic cracking may be understood to comprise a process yielding shorter molecules via bond breakage.

In the catalytic cracking process of the OCP reactor, the process conditions are selected in order to provide high selectivity towards propylene or ethylene, as desired, a stable olefin conversion over time, and a stable olefinic product distribution in the effluent. Such objectives are favoured by the use of a low acid density in the catalyst (i.e. a high Si/Al framework atomic ratio) in conjunction with a low pressure, a high inlet temperature and a short contact time, all of which process parameters are interrelated and provide an overall cumulative effect.

The process conditions are selected to disfavour hydrogen transfer reactions leading to the formation of paraffins, aromatics and coke precursors. The process operating conditions thus employ a high space velocity, a low pressure and a high reaction temperature. The LHSV ranges from 0.5 to 30 hr^{-1}, preferably from 1 to 30 hr^{-1}. The olefin partial pressure ranges from 0.1 to 2 bars, preferably from 0.5 to 1.5 bars (absolute pressures referred to herein). A particularly preferred olefin partial pressure is atmospheric pressure (i.e. 1 bar). The heavy hydrocarbon fraction feedstock is preferably fed at a total inlet pressure sufficient to convey the feedstocks through the reactor. Said feedstock may be fed undiluted or diluted in an inert gas, e.g. nitrogen or steam. Preferably, the total absolute pressure in the second reactor ranges from 0.5 to 10 bars. The use of a low olefin partial pressure, for example atmospheric

pressure, tends to lower the incidence of hydrogen transfer reactions in the cracking process, which in turn reduces the potential for coke formation, which tends to reduce catalyst stability. The cracking of the olefins is preferably performed at an inlet temperature of the feedstock of from 400° to 650°C, more preferably from 450° to 600°C, yet more preferably from 540°C to 590°C, typically around 560° to 585°C.

In order to maximize the amount of ethylene and propylene and to minimize the production of methane, aromatics and coke, it is desired to minimize the presence of diolefins in the feed. Diolefin conversion to monoolefin hydrocarbons may be accomplished with a conventional selective hydrogenation process such as disclosed in US 4695560 hereby incorporated by reference.

The OCP reactor can be a fixed bed reactor, a moving bed reactor or a fluidized bed reactor. A typical fluid bed reactor is one of the fluid catalytic cracking (FCC) type used for fluidized-bed catalytic cracking in the oil refinery. A typical moving bed reactor is of the continuous catalytic reforming type. As described above, the process may be performed continuously using a pair of parallel "swing" reactors. The heavy hydrocarbon fraction cracking process is endothermic; therefore, the reactor should be adapted to supply heat as necessary to maintain a suitable reaction temperature. Online or periodic regeneration of the catalyst may be provided by any suitable means known in the art.

The various preferred catalysts of the OCP reactor have been found to exhibit high stability, in particular being capable of giving a stable propylene yield over several days, *e.g.* up to ten days. This enables the olefin cracking process to be performed continuously in two parallel "swing" reactors wherein when one reactor is operating, the other reactor is undergoing catalyst regeneration. The catalyst can be regenerated several times.

The OCP reactor effluent comprises methane, light olefins and hydrocarbons having 4 carbon atoms or more. Advantageously said OCP reactor effluent is sent to a fractionator and the light olefins are recovered. Advantageously the hydrocarbons having 4 carbon atoms or more are recycled at the inlet of the OCP reactor, optionally mixed with the heavy hydrocarbon recovered from the effluent of the XTO reactor. Advantageously, before recycling said hydrocarbons having 4 carbon atoms or more at the inlet of the OCP reactor, said hydrocarbons having 4 carbon atoms or more are sent to a second fractionator to purge the heavies. In a preferred embodiment the light olefins recovered from the effluent of the XTO reactor and the light olefins recovered from the fractionator following the OCP reactor are treated in a common recovery section.

Optionally, in order to adjust the propylene to ethylene ratio of the whole process (XTO+OCP), ethylene in whole or in part can be recycled over the OCP reactor and advantageously converted into more propylene. This ethylene can either come from the fractionation section of the XTO reactor or from the fractionation section of the OCP reactor

or from both the fractionation section of the XTO reactor and the fractionation section of the OCP reactor or even from the optional common recovery section.

Optionally, in order to adjust the propylene to ethylene ratio of the whole process (XTO+OCP), ethylene in whole or in part can be recycled over the XTO reactor where it combines with the oxygen-containing, halogenide-containing or sulphur-containing organic feedstock to form more propylene. This ethylene can either come from the fractionation section of the XTO reactor or from the fractionation section of the OCP reactor or from both the fractionation section of the XTO reactor and the fractionation section of the OCP reactor or even from the optional common recovery section.

These ways of operation allow to respond with the same equipment and catalyst to market propylene to ethylene demand.

Fig 1 illustrates a specific embodiment of the invention. The effluent of the XTO reactor is passed to a fractionator 11. The overhead, a C1-C3 fraction including the light olefins is sent via line 2 to a common recovery section (not shown). The bottoms (the heavy hydrocarbon fraction) are sent via line 3 to the OCP reactor. The effluent of the OCP reactor is sent via line 10 to a fractionator 8. The overhead, a C1-C3 fraction including the light olefins, is sent via line 9 to a common recovery section (not shown). The bottoms, hydrocarbons having 4 carbon atoms or more, are sent to a fractionator 5. The overhead, hydrocarbons having 4 to substantially 5 carbon atoms are recycled via line 4 at the inlet of the OCP reactor. The bottoms, hydrocarbons having substantially 6 carbon atoms or more, are purged via line 6.

The method of making the olefin products from an oxygenate feedstock can include the additional step of making the oxygenate feedstock from hydrocarbons such as oil, coal, tar sand, shale, biomass and natural gas. Methods for making oxygenate feedstocks are known in the art. These methods include fermentation to alcohol or ether, making synthesis gas, then converting the synthesis gas to alcohol or ether. Synthesis gas can be produced by known processes such as steam reforming, autothermal reforming and partial oxidization in case of gas feedstocks or by reforming or gasification using oxygen and steam in case of solid (coal, organic waste) or liquid feedstocks. Methanol, methylsulfide and methylhalides can be produced by oxidation of methane with the help of dioxygen, sulphur or halides in the corresponding oxygen-containing, halogenide-containing or sulphur-containing organic compound.

One skilled in the art will also appreciate that the olefin products made by the oxygenate-to-olefin conversion reaction using the molecular sieve of the present invention can be polymerized optionally with one or more comonomers to form polyolefins, particularly

polyethylenes and polypropylenes. The present invention relates also to said polyethylenes and polypropylenes.

The following non-limiting examples are provided to illustrate the invention.

EXAMPLES

Example 1

A sample of zeolite ZSM-5 with Si/Al=12 (CBV2314) from Zeolyst International was first calcined for 6 hours at 550°C (60°/min heating rate). It was then was steamed at 680°C for 2 hours in 100% steam. The steamed solid was treated with a 3.14-M solution of H_3PO_4 for 18h under reflux conditions (4,2liter/1kg of zeolite). The solid was then separated by filtration from the solution. The obtained solid was dried first at 110°C for 16h and then at 400°C for 3h.

Example 2

The sample obtained from example 1 was blended with 10wt% of xonotlite ($Ca_6Si_6O_{17}(OH)_2$) and subjected under reflux conditions in contact with hot water for 2 hours. Then the solid was separated by filtering from the solution, dried immediately at 110°C for 16 hours and steamed at 600°C for 2 hours in 100% steam (Atomic ratio Si/Al 15, P-content 2.5 wt%).
The sample is hereinafter identified as SAMPLE A.

Example 3

The sample described in example 1 was subjected to reflux conditions for 2 hours in contact with hot water under. Then the solid was separated by filtering from the solution and dried immediately at 110°C for 16 hours and steamed at 600°C for 2 hours in 100% steam. (Atomic ratio Si/Al 15, P-content 2.0 wt%). Contrary to example 2, no calcium compound is added.

The sample is hereinafter identified as Comparative I.

Example 4

The sample obtained in example 1 was impregnated with an aqueous solution of calcium acetate (0.5-M solution) (1ml/1g of zeolite) with a target of 2 wt% Ca. Then the

sample was dried at 110°C and subjected in a contact with hot water under reflux condition for 2 hours. Then the solid was separated by filtering from the solution and dried right away at 110°C for 16h and steamed at 600°C for 2 hours in 100% steam. (Atomic ratio Si/Al 15, P-content 2.1 wt%). Contrary to example 2, the calcium is added in the form of calcium acetate.

The sample is hereinafter identified as Comparative II.

Example 5

Contrary to example 2, in this example SiO_2 and calcium compound were added separately. Calcium compound was introduced as calcium acetate and SiO_2 was added as in the form of Ludox LS-40™.

A sample of zeolite ZSM-5 with Si/Al=12 (CBV2314) from Zeolyst International was first calcined for 6 hours at 550°C (60°/min heating rate) and then was steamed at 680°C for 2h in 100% steam. The steamed solid was blended with 10 wt% of SiO_2 in the form of Ludox LS-40™ treated with a 3.14-M solution of H_3PO_4 for 18 hours under reflux conditions (4.2 liter/1 kg of zeolite). Then the solid was separated by filtering from the solution. The obtained solid was dried first at 110°C for 16 hours and then at 400°C for 3 hours. The dried solid was subjected to reflux conditions for 2h in contact with a hot 0.1-M calcium acetate aqueous solution. Then the solid was separated by filtering from the solution and dried immediately at 110°C for 16 hours and steamed at 600°C for 2 hours in 100%. (Atomic ratio Si/Al 15, P-content 2.0 wt%).

The sample is hereinafter identified as Comparative III.

Example 6

A sample of zeolite ZSM-5 with Si/Al=13 synthesized without template has been obtained from TRICAT (TZP-302). This sample was steamed at 550°C for 48h in 100% steam. Then the steamed solid was treated with 3,14M solution of H_3PO4 for 18h under reflux condition (4,2liter/1kg of zeolite). Then the solid was separated by filtering from the solution, dried at 110°C for 16h and calcined at 400°C for 10h.

The sample is hereinafter identified as Comparative IV.

Example 7

A sample identified hereinafter as SAMPLE B was prepared by mechanically blending 90 wt% of the solid described in example 6 and 10 wt% of xonotlite ($Ca_6Si_6O_{17}(OH)_2$).

Example 8

XTO process

Catalyst tests were performed on 2g catalyst samples with a pure methanol feed in a fixed-bed, down flow stainless-steel reactor. Catalyst powders was pressed into wafers and crushed to 35–45 mesh particles. Prior to the catalytic runs all catalysts were heated in flowing N_2 (5 Nl/h) up to the reaction temperature. Analysis of the products was performed on-line by a gas chromatograph equipped with a capillary column. The table below presents the average catalytic performance during the cycle (from 2 to 6 h on TOS) at substantially full methanol conversion. The results are displayed on a carbon, water-free basis. The values in Table I are the weight percent on a carbon basis. Conditions: WHSV=1.6h^{-1}, P=1.5 bara, T=550°C.

Table I

	Comparative I	Comparative II	Comparative III	Sample A
Methane	2.0	1.3	1.8	1.3
Paraffins (non cyclic)	5.1	5.2	6.9	3.9
Olefins	86.9	86.2	81.6	89.8
Aromatics	5.4	6.2	9.2	3.9
Ethylene	8.6	12.2	14.6	7.6
Propylene	42.5	42.2	39.4	44.3

Example 9

Catalyst tests were performed under the same conditions as described in example 8 for catalyst composites Comparative IV and SAMPLE B. The results are shown in table II on a carbon, water-free basis.

Table II

	Comparative IV	SAMPLE B
Methane	2.0	2.0
Paraffins (non cyclic)	6.0	5.0
Olefins	86.0	87.0
Ethylene	6.8	9.4
Propylene	37.8	42.2

CLAIMS

1. A process for obtaining a catalyst composite comprising the following steps:

   a). selecting a molecular sieve having pores of 10-or more-membered rings

   b). contacting the molecular sieve with a metal silicate, different from said molecular sieve, comprising at least one alkaline earth metal and one or more of the following metals: Ga, Al, Ce, In, Cs, Sc, Sn, Li, Zn, Co, Mo, Mn, Ni, Fe, Cu, Cr, Ti and V, such that the composite comprises at least 0.1 wt% of silicate.

2. A process according to claim 1 wherein the molecular sieve is brought into contact with the metal silicate by one of the following two methods:
   - During the formulation step of the catalyst by mechanically blending the molecular sieve with the metal silicate forming a precursor;
   - Physical blending of the previously formulated molecular sieve and the previously formulated metal silicate *in situ* in the XTO and/or OCP reaction medium.

3. The process according to claim 1 or claim 2 wherein the metal silicate comprises one or more of the following metals: Mg, Ca, Sr and Ba.

4. The process according to any one of the preceding claims wherein the metal silicate comprises calcium.

5. The process according to any one of the preceding claims wherein the metal silicate is selected from xonotlite ($Ca_6Si_6O_{17}(OH)_2$), $CaAl_2Si_2O_8$, $Ca_2Al_2SiO_7$, $CaMg(Si_2O_6)_x$ and mixtures thereof.

6. The process according to any one of the preceding claims wherein the metal silicate is xonotlite ($Ca_6Si_6O_{17}(OH)_2$).

7. The process according to any one of the preceding claims wherein the molecular sieve is selected from one or more of MFI, MOR, MEL, clinoptilolite, FER, FAU, MWW, BETA, ZSM-21, ZSM-22, ZSM-23, ZSM-42, ZSM-57, LTL or a mixture thereof, wherein preferably the molecular sieve is obtained without direction addition of template.

8. The process according to any one of the preceding claims wherein prior to and/or after introducing said metal silicate the molecular sieve is treated according to one or more of the following steps:
   - steaming
   - leaching
   - washing
   - drying
   - calcination
   - impregnation
   - ion exchanging

9. The process according to any one of the preceding claims wherein the selected initial molecular sieve is a P-modified zeolite.

10. The process according to any one of claims 1 to 8 wherein the selected initial molecular sieve is a non-modified zeolite and is modified with P after contacting the molecular sieve with the metal silicate.

11. The process according to claim 9 or 10 wherein the zeolite is modified with P by undergoing a steam treatment step, whereby the zeolite is dealuminated, followed by a leaching step using an acid solution containing a source of P.

12. The process according to any one of claims 9 to 11 wherein the zeolite is modified with P according to the following steps in the order provided:
   a). steaming at a temperature ranging from 400 to 870°C for 0.01-200 hours
   b). leaching with an aqueous acid solution containing the source of P at conditions effective to remove a substantial part of Al from the zeolite and to introduce at least 0.3 wt % of P
   c). separation of the solid from the liquid
   d). an optional washing step or an optional drying step or an optional washing step followed by a drying step
   e). a calcination step

13. The catalyst composite obtainable according to any one of the preceding claims.

14. A catalyst composite comprising
   - at least 10 wt % of a molecular sieve having pores of 10-or more-membered rings

- at least one metal silicate, different from said molecular sieve, comprising at least one alkaline earth metal and one or more metals selected from Ga, Al, Ce, In, Cs, Sc, Sn, Li, Zn, Co, Mo, Mn, Ni, Fe, Cu, Cr, Ti and V, such that the catalyst composite comprises at least 0.1 wt % of silicate
- optionally metal phosphate
- optionally matrix material
- optionally binder

15. The catalyst composite according to claim 14 wherein the metal silicate comprises one or more of the following metals: Mg, Ca, Sr and Ba.

16. The catalyst composite according to claim 14 or 15 wherein the metal silicate comprises Ca.

17. The catalyst composite according to any one of claims 14 to 16 wherein the metal silicate is selected from xonotlite ($Ca_6Si_6O_{17}(OH)_2$), $CaAl_2Si_2O_8$, $Ca_2Al_2SiO_7$, $CaMg(Si_2O_6)_x$ and mixtures thereof.

18. The catalyst composite according to any one of claims 14 to 17 wherein the metal silicate is xonotlite ($Ca_6Si_6O_{17}(OH)_2$).

19. The catalyst composite according to any one of claims 14 to 18 wherein the metal phosphate comprises one or more metals selected from Ca, Ga, Al, Ce, In, Cs, Sr, Mg, Ca, Ba, Sc, Sn, Li, Zn, Co, Mo, Mn, Ni, Fe, Cu, Cr, Ti and V.

20. The catalyst composite according to any one of claims 14 to 19 wherein the molecular sieve is selected from one or more of MFI, MOR, MEL, clinoptilolite, FER, FAU, MWW, BETA, ZSM-21, ZSM-22, ZSM-23, ZSM-42, ZSM-57, LTL, or a mixture thereof.

21. The catalyst composite according to claim 20 wherein the molecular sieve is selected from one or more of MFI, MOR, MEL, clinoptilolite and FER synthesized without direct addition of template.

22. The catalyst composite according to any one of claims 14 to 21 wherein the molecular sieve is a P-modified zeolite.

23. The catalyst composite according to claim 22 wherein the zeolite is modified with P by undergoing a steam treatment step, whereby the zeolite is dealuminated, followed by a leaching step using an acid solution containing a source of P.

24. Process for making an olefin product from an oxygen-containing, halogenide-containing or sulphur-containing organic feedstock wherein said oxygen-containing, halogenide-containing or sulphur-containing organic feedstock is contacted in the XTO reactor with a catalyst composite comprising
- at least 10 wt % of a molecular sieve having pores of 10-or more-membered rings
- at least one metal silicate, different from said molecular sieve, comprising at least one alkaline earth metal, such that the catalyst composite comprises at least 0.1 wt % of silicate
- optionally metal phosphate
- optionally matrix material
-optionally binder
under conditions effective to convert the oxygen-containing, halogenide-containing or sulphur-containing organic feedstock to olefin products (the XTO reactor effluent).

25. Process according to claim 24 wherein the XTO reactor effluent comprising light olefins and a heavy hydrocarbon fraction is sent to a fractionation section to separate said light olefins from said heavy hydrocarbon fraction; said heavy hydrocarbon fraction is recycled in the XTO reactor at conditions effective to convert at least a portion of said heavy hydrocarbon fraction to olefin products.

26. Process according to claim 24 or claim 25 wherein the olefin products (the effluent of the XTO) are fractionated to form a stream comprising essentially ethylene and at least a part of said stream is recycled in the XTO reactor to increase the propylene production.

27. Process according to claim 24 wherein the XTO reactor effluent comprising light olefins and a heavy hydrocarbon fraction is sent to a fractionation section to separate said light olefins from said heavy hydrocarbon fraction; said heavy hydrocarbon fraction is sent in an OCP reactor at conditions effective to convert at least a portion of said heavy hydrocarbon fraction to light olefins.

28. Process according to claim 27 wherein the catalyst in the OCP reactor is a catalyst composite comprising
- at least 10 wt % of a molecular sieve having pores of 10-or more-membered rings

- at least one metal silicate, different from said molecular sieve, comprising at least one alkaline earth metal, such that the catalyst composite comprises at least 0.1 wt % of silicate
- optionally metal phosphate
- optionally matrix material
- optionally binder

29. Process according to claim 27 or 28 wherein said OCP reactor effluent is sent to a fractionator and the light olefins are recovered; the hydrocarbons having 4 carbon atoms or more are recycled at the inlet of the OCP reactor, optionally mixed with the heavy hydrocarbon recovered from the effluent of the XTO reactor.

30. Process according to claim 29 wherein, before recycling said hydrocarbons having 4 carbon atoms or more at the inlet of the OCP reactor, said hydrocarbons having 4 carbon atoms or more are sent to a second fractionator to purge the heavies.

31. Process according to any one of claims 27 to 30 wherein, in order to adjust the propylene to ethylene ratio of the whole process (XTO+OCP), ethylene in whole or in part is recycled over the OCP reactor; said ethylene can either come from the fractionation section of the XTO reactor or from the fractionation section of the OCP reactor or from both the fractionation section of the XTO reactor and the fractionation section of the OCP reactor or even from an optional common recovery section.

32. Process according to any one of claims 27 to 31 wherein, in order to adjust the propylene to ethylene ratio of the whole process (XTO+OCP), ethylene in whole or in part is recycled over the XTO reactor; said ethylene can either come from the fractionation section of the XTO reactor or from the fractionation section of the OCP reactor or from both the fractionation section of the XTO reactor and the fractionation section of the OCP reactor or even from an optional common recovery section.

33. Process according to any one of claims 24 to 32 wherein ethylene is further polymerized optionally with one or more comonomers.

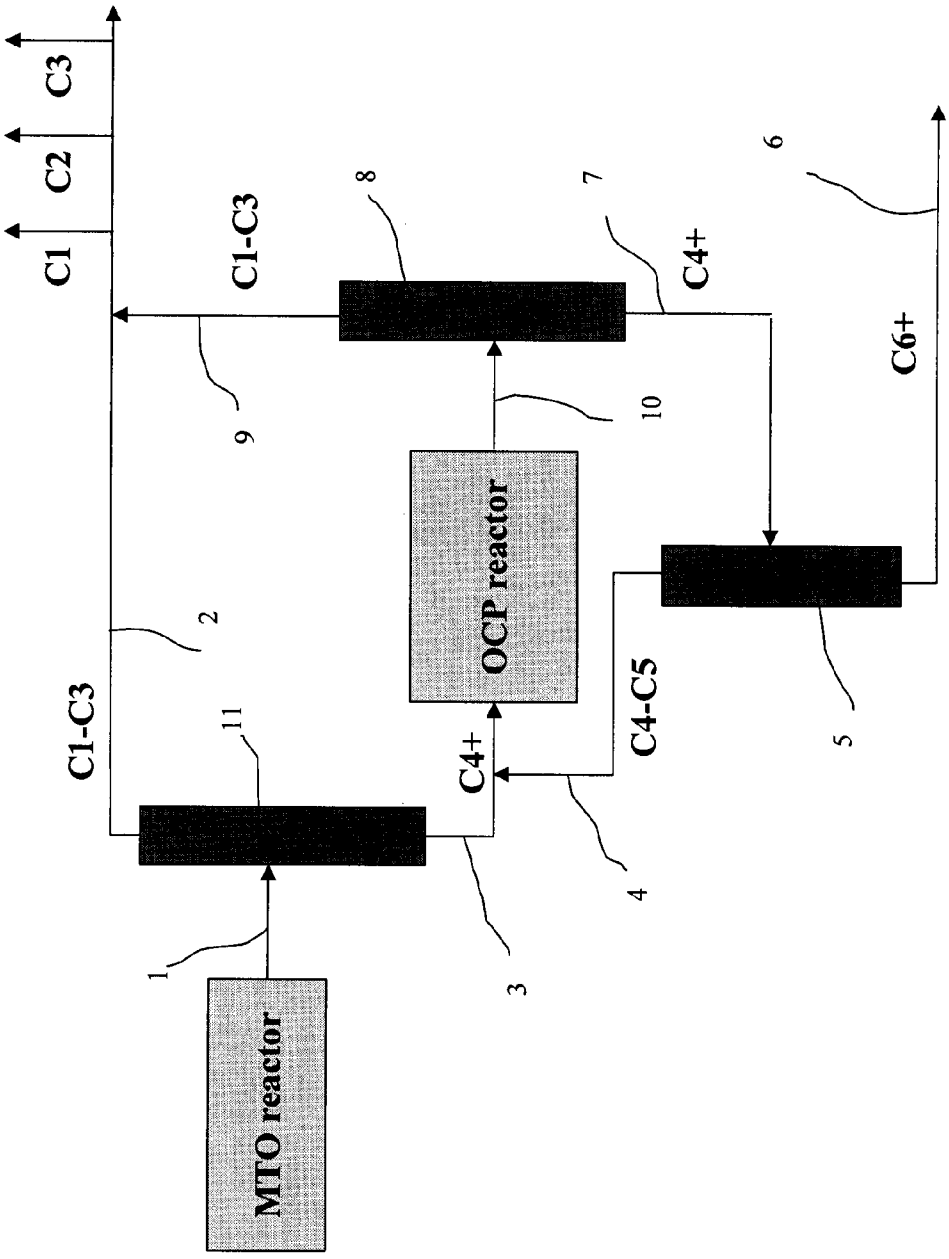
34. Process according to any one of claims 24 to 32 wherein propylene is further polymerized optionally with one or more comonomers.

35. Process for the catalytic cracking of an olefin-rich feedstock which is selective towards light olefins in the effluent, the process comprising contacting a hydrocarbon feedstock containing one or more olefins with a catalyst composite comprising

- at least 10 wt % of a molecular sieve having pores of 10-or more-membered rings
- at least one metal silicate different from said molecular sieve comprising at least one alkaline earth metal, such that the catalyst composite comprises at least 0.1 wt % of silicate
- optionally metal phosphate
- optionally matrix material
- optionally binder

, to produce an effluent with an olefin content of lower molecular weight than that of the feedstock.

Fig. 1


MTO reactor
OCP reactor
C1-C3
C4+
C4-C5
C6+
C1
C2
C3
1
2
3
4
5
6
7
8
9
10
11