

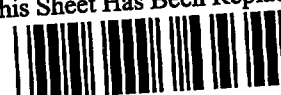
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REPLACED**PRODUCTION OF HIGH PURITY OLEFINS****BACKGROUND OF THE INVENTION**

5 This invention relates to a process for
converting an oxygenate to high purity olefins by
contacting the oxygenate with a molecular sieve
catalyst. More particularly, the invention relates to
a process for converting a methanol or methanol-water
mixture to polymer-grade propylene by contacting the
10 feed with zeolite or silicoaluminophosphate catalysts.

High purity olefins such as propylene have
traditionally been produced through the process of
steam and/or catalytic cracking. Because of the
limited availability and high cost of petroleum
15 sources, the cost of producing high purity olefins
from such petroleum sources has been steadily
increasing. Curtailment in the availability of
inexpensive petroleum raw materials threatens the
supply of high purity olefins such as polymer-grade
20 propylene. Polymer-grade propylene is used in the
production of many types of plastics such as
polypropylene.

The search for alternative materials for high
purity olefin production has led to the use of
25 oxygenates such as alcohols, and more particularly to
methanol and higher alcohols or their derivatives.
These alcohols may be produced by fermentation or from
synthesis gas. Synthesis gas can be produced from
natural gas, petroleum liquids, carbonaceous materials
30 including coal, recycled plastics, municipal wastes,
or any organic material. Thus, alcohol and alcohol
derivatives may provide non-petroleum based feeds for
high purity olefin production.

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- 2 -

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Molecular sieves, such as crystalline zeolite catalysts, are known to promote the conversion of oxygenates to olefin-containing hydrocarbon mixtures. US-A-4,025,575 and US-A-4,083,889 disclose processes
5 for conversion of methanol and/or methyl ether to olefin-containing products using ZSM-5-type zeolite catalysts.

Chang et al., US-A-4,724,270, describe a process for converting methanol feedstocks to aromatic
10 hydrocarbons using zeolite catalysts (having a silica-to-alumina ratio of at least 12) at a temperature of at least 725°C (1337°F). By conducting the reaction at elevated temperatures, zeolite dehydroxylation can occur. This can lead to zeolite decomposition to
15 amorphous silica and alumina.

US-A-4,433,189 to Young teaches conversion of methanol to light olefins over zeolite catalysts having a silica-to-alumina molar ratio of at least 12, and at a temperature of from about 200°C (392°F) to
20 500°C (932°F). The Young patent does not teach conversion of methanol to products such as polymer-grade propylene.

US-A-4,677,243 to Kaiser teaches the formation of light olefins using silicoaluminophosphate catalysts
25 at a temperature of from about 200°C (392°F) to 700°C (1292°F). Kaiser does not teach the formation of high purity olefins or polymer-grade propylene.

High purity olefins are generally recognized by those skilled in the art as products, excluding
30 methane, which have a paraffin to-olefin weight ratio of less than or equal to about 0.05. Purification of high purity olefins traditionally requires removal of low-level impurities which interfere with polymerization catalysis, or which interfere with

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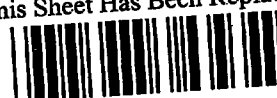
- 3 -

other processes requiring high-purity reactants. Low-level contaminants include, but are not limited to polar molecules, oxygenates such as water, alcohols, carbon monoxide, carbon dioxide, carbonyl sulfide (COS), oxygen, and other miscellaneous contaminants including hydrogen sulfide, mercaptans, ammonia, arsine phosphine, chlorides. Low-level contaminants are removed by a variety of processes including, but not limited to adsorption and fractional distillation. Lighter or heavier hydrocarbon molecules having fewer or more carbon atoms than the desired olefin product must also be removed. These hydrocarbons are typically removed by fractional distillation techniques.

One such high purity olefin is polymer-grade propylene. Polymer-grade propylene is required for the production of polypropylene and useful for the production of other propylene derivatives. Polymer-grade propylene is characterized by very low concentrations of impurities, including low levels of paraffins (saturated hydrocarbons) such as propane, ethane, and butane.

Commercial chemical-grade propylene, unlike polymer-grade propylene, is characterized by higher concentrations of saturated hydrocarbons. Propane is the most difficult of the saturated hydrocarbons to remove from propylene, due in large part to the proximity of the boiling points for propane and propylene. Typical polymer-grade propylene purities range from 95% to 99.5% propylene, and are more preferably above 99%. This degree of purity corresponds to propane-to-propylene ratios of about 0.05 to about 0.01 or lower. Hitherto, this low propane level could only be practically achieved

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- 4 -

through the use of the well known art of fractional distillation. The fractional distillation scheme employed for effecting the difficult separation of propane from propylene is called "superfractionation."

5 However, superfractionation requires a substantial investment in facilities and consumes copious amounts of energy. Alternative means for removing paraffin impurities, such as membrane techniques and adsorbent techniques, are as costly as the superfractionation

10 techniques. The present invention teaches a means for producing high purity olefins having the required range of paraffin-to-olefin ratios, without the need to resort to superfractionation or other expensive purification techniques. According to the teachings

15 of the present invention, a superfractionator is not required, thereby significantly reducing the cost of producing high purity olefins such as polymer-grade propylene.

20 SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a process for selectively catalytically converting oxygenate starting material to high purity olefins which comprises contacting the oxygenate

25 starting material with a molecular sieve catalyst having a preselected silica-to- Me_2O_3 molar ratio, at a preselected weight hourly space velocity (WHSV), and at a temperature of from 350°C to 550°C, and recovering the high purity olefins. The high purity

30 olefins are preferably polymer-grade propylene. The process employs molecular sieves such as the crystalline aluminosilicate, ferrosilicate zeolites, and silicoaluminophosphate (SAPO) catalysts. Preferred embodiments employ ZSM-5, ZSM-48, FeZSM-5,



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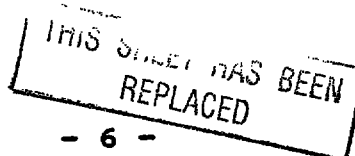
- 5 -

and SAPO-34 as the molecular sieve. It is to be noted that the process of the invention is performed at temperatures above those usually employed with molecular sieves; it is this, together with selection
5 of the nature of the catalyst and the matching temperature and flow conditions, which enables the selective conversions to high purity olefins characteristic of the invention. The reaction is conducted at a temperature preferably within a
10 narrower range, more preferably about 450°C (842°F). Oxygenate conversion under such conditions produces a product, substantially rich in high purity olefins, such as polymer-grade propylene.

By employing the teachings of the present
15 invention, a person having ordinary skill in the catalysis or olefin art should be able to produce a high purity olefin product from oxygenates without needing to resort to purification techniques such as adsorption or superfractionation. However, such
20 additional purification techniques may be employed to produce olefins having even higher degrees of purity than high purity olefins.

The invention is distinguished from the teachings of US-A-4,638,106 to Pieters, et al. which teaches a
25 process of converting alcohols to olefins using ZSM-5 having a silica-to-alumina ratio of about 400 because inter alia the ZSM-5 is modified by depositing carbonaceous materials on the catalyst (column 11, line 57 et seq.). This post-synthesis modification is
30 a requirement of the Pieters, et al. invention (claim 1). In contrast, the instant invention does not require such a limitation, and the process is able to obtain high purity olefins without the post-synthesis modification described by Pieters, et al. Pieters, et





- 6 -

al. defines selectivity (column 22, line 1 et seq.) in such a manner that it is clear that production of both olefins and paraffins is anticipated by the invention. In contrast, the process of the invention is for the
5 production of high purity olefins, such as polymer grade olefins having a paraffin-to-olefin weight ratio of less than or equal to about 0.05. This paraffin-to-olefin weight ratio is possible by using catalysts having a high, preselected silica-to-metal ratio, at a
10 preselected flow rate, and at temperatures outside those taught by Pieters, which are optimized to achieve the conversion.

DETAILED DESCRIPTION OF THE INVENTION

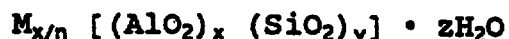
15 In accordance with the present invention, an oxygenate feed is catalytically converted to high purity olefins by contacting this feed with a molecular sieve zeolite and/or silicoaluminophosphate catalyst. The process obviates the need for a
20 conventional superfractionator to separate paraffins from olefins. It is within the scope of the present invention to use additional purification steps well known in the art to remove impurities other than paraffins having the same number of carbon atoms as
25 olefins. Additionally, superfractionation may be used with the present invention to achieve still higher degrees of olefin purity. More particularly, the present invention relates to a process for catalytically converting oxygenates to high purity
30 olefins such as polymer-grade propylene.

Zeolites are a class of molecular sieve catalysts and are porous, crystalline-hydrated metallo-silicates of Group IIIA and VIII elements (Me) interconnected through shared oxygen atoms.



Preferable metals include aluminum, iron, gallium, nickel, cobalt, and boron. The rigid three dimensional network of silica and metal (hereinafter "Me₂O₃") creates a tetrahedral form which comprises the primary building unit of the zeolites. The metal constituents in zeolites include, but are not limited to, aluminum, iron, gallium, and boron. Because the oxygen atoms in zeolites are shared by tetrahedra, the framework possesses a net negative charge.

For example, the net negative charge of aluminosilicate zeolites is balanced by exchangeable cations in the crystalline structure, leading to the representation:



where M is the cation, n is the cation charge, and z represents the water of hydration. The silica-to-alumina molar ratio is controlled by the amounts of alumina "x" and silica "y" in the zeolite. When M is a proton, the zeolite acquires the characteristics of a Broensted acid (e.g., HZSM-5).

Other positive ion-containing catalysts include ferrosilicates, borosilicates, and gallosilicates. Of the ferrosilicates, FeZSM-5 may be employed in the process of the present invention. FeZSM-5 is composed of silicon and iron oxide (Fe₂O₃) in a manner similar to the aluminosilicate zeolites.

Zeolites generally have ordered, porous crystalline structures containing a small number of cavities that are interconnected by a number of still smaller channels. The cavities and channels are uniform in size within a certain type of zeolitic material. The dimensions of the pores or cavities allow for adsorption of molecules of certain dimensions while excluding molecules of larger



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- 8 -

dimensions. The crystal structure of zeolites provides a selective constrained access to and egress from the intracrystalline free space. This phenomenon, also called "shape-selective catalysis,"
5 derives from zeolite geometry.

An important component of zeolite geometry derives from the proportions of silicon and Me_2O_3 atoms comprising the tetrahedra. The molar ratio of silica-to- Me_2O_3 may be determined by conventional
10 analysis, such as wet chemical analysis (e.g., Atomic Absorption Spectrometry or Inductively Coupled Plasma Emission Spectrometry;) or by the stoichiometry of silica and Me_2O_3 used to synthesize the zeolite. The silica-to- Me_2O_3 molar ratio is meant to represent, as
15 closely as possible, the silica-to- Me_2O_3 ratio in the rigid anionic framework of the molecular sieve crystal. Me_2O_3 in the binder or in cationic or other form within the porous channels is not considered in calculating the silica-to- Me_2O_3 ratio. The ratio of
20 silica-to- Me_2O_3 in the molecular sieve imparts selective catalytic and adsorptive properties. The catalytic and adsorptive properties of the molecular sieve may also be varied by changing the ions within the catalyst. Conventional ion exchange techniques
25 may be used to change the cations.

To those skilled in the zeolite catalyst art, ZSM-5 is generally considered a siliceous zeolite. This is because it may have a "high" silica-to- Me_2O_3 , or more specifically, silica-to-alumina molar ratio.
30 ZSM-5 is particularly advantageous for converting methanol-containing feedstocks to light olefins. Siliceous zeolites (i.e., zeolites having a high silica-to- Me_2O_3 ratio), such as those described for use in the processes of the present invention, are



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- 9 -

most effectively synthesized using templates such as alkylammonium cations. For example, the tetramethylammonium (TMA) cation is particularly advantageous in synthesizing a siliceous zeolite such as ZSM-5 having a silica-to-alumina ratio of about 1000. It is thought that silica forms hydrogen bonds with the TMA and traps or clathrates the organic cation within the silica. Alumina is less efficient in hydrogen bond formation, so the zeolites formed with organic templates such as TMA have a higher silica-to-alumina molar ratio. The presence of a trivalent metal site within the silicate structure provides the desired acidity in an environment which limits access to the site by molecules of appropriate size. This limits the acid catalyzed reactions to those which are carried out in a "shape selective" manner. Template cations which are usually present in these materials when they are synthesized may be removed, and the zeolite converted to the hydrogen form by exchange with ammonium ions, followed by heating to drive off ammonia, or by direct exchange with an acid such as hydrochloric acid, provided the zeolite is not degraded by the acidic treatment.

The silicoaluminophosphate (SAPO) molecular sieve catalysts exhibit properties characteristic of both aluminosilicate zeolites and aluminophosphates. The SAPO molecular sieves have a microporous crystal framework structure of PO_2^+ , AlO_2^- and SiO_2 tetrahedral units. The composition (anhydrous) is:



wherein "R" represents at least one organic templating agent present in the intracrystalline pore system, "m" represents the moles of "R" present per mole of $(Si_xAl_yP_z)O_2$ and has a value of from zero to 0.3, the

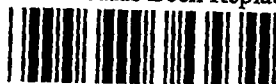


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- 10 -

maximum value in each case depending upon the molecular dimensions of the templating agent and the available void volume of the pore system of the particular SAPO species involved, and "x," "y," and
5 "z" represent the mole fractions of silicon, aluminum, and phosphorous, respectively. As will be understood, the nature of SAPO catalysts means that any preselected silica-to-Me₂O₃ value may be used. Representative SAPO molecular sieves, as described in
10 US-A-4,440,871, include SAPO-5, SAPO-11, SAPO-17, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-37, SAPO-40, SAPO-41, and SAPO-42.

The oxygenate starting material or feed comprises hydrocarbons containing aliphatic moieties such as,
15 but not limited to, alcohols, halides, mercaptans, sulfides, amines, ethers, and carbonyl compounds (aldehydes, ketones, carboxylic acids, and the like) or mixtures thereof. The aliphatic moiety preferably contains from about 1 to about 10 carbon atoms, and
20 more preferably 1 to 4 carbon atoms. Thus the term "oxygenate starting material" is intended to mean not only what might be considered "true" oxygenates, e.g., alcohols, ethers, carbonyl compounds; but also those compounds which behave in a similar fashion to "true"
25 oxygenates in the presence of the specified catalysts, such as substituted paraffins, e.g., halides, mercaptans, sulfides, amines. Representative oxygenates include methanol, isopropanol, n-propanol, ethanol, fuel alcohols, dimethyl ether, diethyl ether,
30 methyl mercaptan, methyl sulfide, methyl amine, ethyl mercaptan, ethylchloride, formaldehyde, dimethylketone, acetic acid, n-alkylamines, n-alkylhalides, and n-alkylsulfides having alkyl groups of 1 to 10 carbon atoms or mixtures thereof. In a



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- 11 -

preferred embodiment of the present invention, the feed comprises methanol. In another embodiment, the feed, e.g., methanol, contains a diluent. The addition of a diluent to the total feed charge
5 decreases paraffin production relative to olefin production.

The term "oxygenate starting material" or "oxygenate feed" as employed in the present invention and described herein designates only the organic
10 material used as the feed. However, the total charge to the reaction zone may contain additional compounds such as diluents. Use of a diluent as part of the feed, which is miscible with the oxygenate, imparts as a non-limiting example, a smaller propane to propylene
15 ($C_3O/C_3=$) ratio than the use of essentially anhydrous oxygenate. However, even anhydrous oxygenates contain trace quantities of diluents. Even though the process described herein may employ a diluent, computable quantities of the oxygenate feed (i.e, composition and
20 Weight Hourly Space Velocity (WHSV) are to be computed as an essentially diluent-free oxygenate feed unless otherwise stated.

The process is generally conducted in the presence of one or more diluents which may for example
25 be present in the feed in an amount between about 1 and about 99 molar percent, based on the total number of moles of all feed and diluent components fed to the reaction zone (or catalyst). The amount of diluent added to the oxygenate feed will depend in part on the
30 type of catalyst selected, the silica-to- Me_2O_3 ratio, and the reaction temperature. Preferably, the molar ratio of oxygenate feed-to-diluent (feed:diluent) is about 1:1 to about 1:4. Diluents include, but are not limited to, helium, argon, nitrogen, carbon monoxide,



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- 12 -

hydrocarbons (such as methane and the like), aromatic compounds, and mixtures thereof. Preferably, the diluent is water.

5 The instant process is preferably conducted in the vapor phase such that the oxygenate feed is contacted in the vapor phase in a reaction zone with the molecular sieve at effective process conditions to produce a paraffin/olefin, e.g., propane/propylene ratio characteristic of high purity olefins or
10 polymer-grade propylene, i.e., an effective temperature, silica-to-Me₂O₃ ratio, pressure, WHSV and, optionally, an effective amount of diluent, correlated to produce high purity olefins or polymer-grade propylene. Alternatively, the process may be
15 conducted in a liquid phase.

The process may be effectively carried out over a wide range of pressures including autogeneous pressures. At pressures between about 0.001 atmospheres (0.76 torr) and about 1000 atmospheres
20 (760,000 torr), the formation of light olefin products will be effected although the optimum amount of product will not necessarily form at all pressures. The preferred pressure is between 0.01 atmospheres (7.6 torr) and 100 atmospheres (76,000 torr). The
25 pressures referred to herein for the process are exclusive of the inert diluent, if any, that is present, and refer to the partial pressure of the feedstock as it relates to oxygenate compounds and/or mixtures thereof. Pressures outside the stated range
30 are not excluded from the scope of this invention, although such pressures do not fall within certain desirable embodiments of the invention. At the lower and upper end of the pressure range, and beyond, the selectivities, conversions, and/or rates to light



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- 13 -

olefin products may not be optimal, although light olefins such as ethylene may still be formed.

5 The process is effected for a period of time sufficient to produce the desired light olefin (and high purity olefin) products. In general, the residence time employed to produce the desired product can vary from seconds to a number of hours. It will be readily appreciated that the residence time will be determined to a significant extent by the reaction
10 temperature, the molecular sieve selected, the WHSV, the phase (liquid or vapor), and process design characteristics selected.

The olefin production process may be carried out in a batch, semi-continuous, or continuous fashion.
15 The process can be conducted in a single reaction zone, or a number of reaction zones arranged in series or in parallel, or it may be conducted intermittently or continuously in an elongated tubular zone or a number of such zones. When multiple reaction zones
20 are employed, it may be advantageous to employ one or more of such molecular sieves in series to provide for a desired product mixture. Owing to the nature of the process, it may be desirable to carry out the process of the present invention by use of the molecular sieve
25 catalysts in a dynamic (e.g., fluidized or moving) bed system or any system of a variety of transport beds rather than in a fixed bed system. Such systems would readily provide for any regeneration (if required) of the molecular sieve catalyst after a given period of
30 time. If regeneration is required, the molecular sieve catalyst can be continuously introduced as a moving bed to a regeneration zone where it can be regenerated, such as for example by removing carbonaceous materials or by oxidation in an oxygen-

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- 14 -

carbonaceous materials or by oxidation in an oxygen-containing atmosphere. In the preferred practice of the invention, the catalyst will be subject to a regeneration step by the burning of carbonaceous deposits accumulated during reactions.

5 The effect of feedstock flow rate over molecular sieves is well known to those skilled in the art. Increasing the flow rate (WHSV) enhances olefin production relative to paraffin production. However,
10 the enhanced olefin production relative to paraffin production is offset by a diminished conversion of oxygenate to hydrocarbons at the higher flow rates.

According to the invention, the process for conversion of an oxygenate feed to high purity olefins
15 such as polymer-grade propylene using molecular sieves is for example conducted at temperatures of from approximately 350°C (662°F) to about 550°C (1022°F), preferably 450°C (842°F) to 550°C (1022°F), and more preferably at 440°C (824°F) to 460°C (860°F). The
20 silica-to-Me₂O₃ molar ratio is preselected according to the type of molecular sieve employed, the reaction temperature used, and the degree of high purity olefin, e.g., polymer-grade propylene, production required. The WHSV of this reaction is for example
25 approximately 0.01 hr.⁻¹ to about 100 hr.⁻¹, preferably 0.5 hr.⁻¹ to 10 hr.⁻¹, and more preferably 0.8 hr.⁻¹ to 1.2 hr.⁻¹. For ZSM-5, at 0.8 hr.⁻¹ to 1.2 hr.⁻¹, approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur.

30 In the process using ZSM-5, which zeolite is described in US-A-3,702,886, the process temperature is preferably 400°C to 550°C, more preferably 440°C to 460°C; and the silica-to-Me₂O₃ molar ratio is preferably 350 to 2500, more preferably 950 to 1050.

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- 15 -

The WHSV of the process is preferably 0.1 hr.^{-1} to 10 hr.^{-1} , and more preferably 0.8 hr.^{-1} to 1.2 hr.^{-1} . Using ZSM-5, at 0.8 hr.^{-1} to 1.2 hr.^{-1} , approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur.

In the process using ZSM-48, which zeolite is described more fully in US-A-4,397,827, the process temperature is also preferably 400°C to 550°C , and more preferably 440°C to 460°C . The preferred silica-to- Me_2O_3 molar ratio is however from 300 to 2500, more preferably 320 to 353. The WHSV of the process using ZSM-48 is preferably 0.5 hr.^{-1} to 10 hr.^{-1} , and more preferably 0.8 hr.^{-1} to 1.2 hr.^{-1} . With ZSM-48, at 0.8 hr.^{-1} to 1.2 hr.^{-1} , approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur, comprising approximately 30% propylene and <1% propane in the case where the olefin is propylene.

In the process using FeZSM-5, which zeolite is described in US-A-4,843,183, the preferred process temperatures are as recited for ZSM-48. However, the silica-to- Me_2O_3 molar ratio is preferably from 332 to 368, more preferably about 350. The WHSV of the process using FeZSM-5 is preferably 0.1 hr.^{-1} to 10 hr.^{-1} , more preferably 0.8 hr.^{-1} to 1.2 hr.^{-1} . With ZSM-48 at 0.8 hr.^{-1} to 1.2 hr.^{-1} , approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur, comprising approximately 25% propylene with no propane production, in the case where the olefin is propylene.

In the process using SAPO-34, which catalyst is described in US-A-4,440,871, the process for conversion of an oxygenate feed to high purity olefins such as polymer-grade propylene may be conducted for example at temperatures of 350°C to 550°C , preferably



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- 16 -

400°C to 550°C, and more preferably at 440°C to 460°C .
The WHSV of this process is preferably from 0.01 hr.⁻¹
to 100 hr.⁻¹, more preferably 0.1 hr.⁻¹ to 10 hr.⁻¹,
and most preferably 0.8 hr.⁻¹ to 1.2 hr.⁻¹. With
5 SAPO-34 at 0.8 hr.⁻¹ to 1.2 hr.⁻¹, approximately 98%
to 100% conversion of the feed to hydrocarbons has
been found to occur.

The following examples illustrate the invention.

10 Example 1

Zeolites ZSM-5, having silica-to-Me₂O₃ molar
ratios (silica-to-alumina molar ratios) of 35, 350,
and 1000 (determined stoichiometrically), were
produced as described in US-A-3,702,886.

15 Each ZSM-5 was calcined at 510°C (950°F) and the
calcined material was ion exchanged with an ammonium
nitrate solution (85°C, 185°F; 12 hours). Generally,
the ion exchange was repeated two or three times, with
a calcination at 510°C (950°F) between each ion
20 exchange step.

The catalytic conversion of methanol or
methanol/water to hydrocarbons using each ZSM-5 having
a preselected silica-to-alumina ratio of 35, 350, and
1000 was carried out in a fixed bed (1/2", 1.27 cm
25 diameter), stainless steel reactor, equipped with a
1/8" (0.32 cm) coiled preheater. In addition, the
reactor was equipped with a 1/8" (0.32 cm)
thermocouple well running axially through the reactor.
The reactor was heated in an Applied Test Systems 3
30 zone tube furnace (12", 30.5 cm long; 1 1/4", 3.18 cm
I.D.) having the reactor with three spaced zones. The
first reactor zone is used as a preheater zone, and
the catalyst bed is heated in the second reactor zone.
The third reactor zone operates as a quench zone



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- 17 -

maintained at a temperature of about 200°C (392°F) to about 300°C (572°F).

Generally, 2 grams (0.07 ounces) catalyst (-14/+20 mesh) were mixed with 2.5 grams (0.09 ounces) of quartz (-20/+60); the first and third reactor zone were filled with quartz chips (-10/+20 mesh). To improve the heat transfer between the second reactor zone (containing the catalyst bed) and the furnace heating coils, the second reactor zone was equipped with a cylindrical (4", 10.2 cm long; 1 1/4", 3.18 cm O.D.) aluminum or stainless steel block. This block contained a central hole in order to be able to measure the block temperature.

Gas flows (nitrogen or hydrogen) were controlled by mass flow controllers, while liquid feed rates were controlled by a Beckmann 114M pump or a Sage 341B syringe pump.

The product emerging from the reactor was analyzed on line for (i) carbon monoxide; carbon dioxide; water; dimethyl ether; methanol; C₁-C₃ hydrocarbons with a Poropak Q column using a thermal conductivity detector and (ii) C₁-A₁₀ hydrocarbons with a DB-1 column using a flame ionization detector. The feed was either methanol or methanol:water (1:1 or 1:4 molar ratio as denoted in Table I) at a WHSV=1.0 hr.⁻¹. The reaction was conducted at 450°C (842°F). The results are shown in Table I.

The same procedures as recited in Example 1, using the same equipment, conditions and measurement techniques, were employed with several different catalysts. These catalysts, and the analyses of the products made employing the process of the invention, are further described in Examples 2 - 4 and Table 1.

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- 18 -

Example 2

The zeolite ZSM-48, having a silica-to-Me₂O₃ molar ratio of 336 (determined by wet chemical analysis), was produced as described in US-A-4,423,021.

ZSM-48 was calcined at 510°C (950°F) and the calcined material was ion exchanged with ammonium nitrate solution (85°C, 185°F; 12 hours). Generally, the ion exchange was repeated two or three times, with a calcination at 510°C (950°F) between each ion exchange step.

The feed was methanol:water (1:1 molar ratio) at a WHSV=1.0 hr.⁻¹. The reaction was conducted at 450°C (842°F). The results are shown in Table I.

Example 3

The zeolite FeZSM-5, having a silica-to-Me₂O₃ ratio of 350 (determined stoichiometrically), was produced as described in US-A-4,843,183.

FeZSM-5 was calcined at 510°C (950°F) and the calcined material was ion exchanged with an ammonium nitrate solution (85°C, 185°F; 12 hours). Generally, the ion exchange was repeated two or three times, with a calcination at 510°C (950°F) between each ion exchange step.

The feed was methanol:water (1:1 molar ratio) at a WHSV=1.0 hr.⁻¹. The reaction was conducted at 450°C (842°F). The results are shown in Table I.

Example 4

SAPO-34 was calcined at 510°C (950°F) and the calcined material was ion exchanged with an ammonium nitrate solution (85°C, 185°F; 12 hours). Generally, the ion exchange was repeated two or three times, with



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- 19 -

a calcination at 510°C (950°F) between each ion exchange step.

The feed was methanol:water (1:4 molar ratio) at a WHSV=1.0 hr.⁻¹. The reaction was conducted at 450°C (842°F). The results are shown in Table I.

Table I
Polymer-Grade Propylene Production

	<u>Molecular Sieve</u>	<u>Silica-to-Me₂O₃</u>	<u>Feed/Diluent (molar ratio)</u>	<u>Propane/propylene (C₃O/C₃=)</u>
10	ZSM-5	35	Methanol/Water (1:1)	0.770**
	ZSM-5	1000	Methanol (NA)	0.044
15	ZSM-5	350	Methanol/Water (1:4)	0.037
	ZSM-5	1000	Methanol/Water (1:1)	0.000
	ZSM-48	336	Methanol/Water (1:1)	0.038
	Fe ZSM-5	350	Methanol/Water (1:1)	0.039
20	SAPO-34	NA*	Methanol/Water (1:4)	0.001

*NA signifies "not applicable."

** signifies comparative.

As shown in Table I, olefins are formed by contacting the oxygenate feed with a molecular sieve at a temperature of between 350°C (662°F) to 550°C (1022°F). By preselecting the silica-to-Me₂O₃ ratio and/or diluent, a product having a propane/propylene ratio characteristic of high purity olefins can be produced. This can be achieved without the need of superfractionation to remove propane.

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CLAIMS:

1. A process for selectively catalytically converting oxygenate starting material to high purity olefins which comprises contacting the oxygenate starting material with a molecular sieve catalyst having a preselected silica-to-Me₂O₃ molar ratio, at a preselected weight hourly space velocity (WHSV), and at a temperature of from 350°C to 550°C, and recovering the high purity olefins.
2. A process according to claim 1 wherein the temperature is from 450°C to 550°C, preferably from 440°C to 460°C.
3. A process according to claim 1 or 2 wherein the WHSV is from 0.01 hr.⁻¹ to 100 hr.⁻¹, preferably 0.5 hr.⁻¹ to 10 hr.⁻¹, more preferably 0.8 hr.⁻¹ to 1.2 hr.⁻¹.
4. A process according to any preceding claim wherein the molecular sieve catalyst comprises a crystalline aluminosilicate zeolite, a ferrosilicate zeolite or a silicoaluminophosphate (SAPO) catalyst.
5. A process according to claim 4 wherein the catalyst comprises ZSM-5, ZSM-48, FeZSM-5 or SAPO-5, 11, 17, 20, 31, 34, 35, 37, 40, 41 or 42, or a mixture of any two or more thereof.
6. A process according to any preceding claim wherein the silica-to-Me₂O₃ ratio of the catalyst is from 300 to 2500.





- 21 -

7. A process according to claim 6 wherein (a) the catalyst is ZSM-5 and the ratio is from 350 to 2500, preferably from 950 to 1050; or (b) the catalyst is ZSM-48 and the ratio is from 320 to 353; or (c) the catalyst is FeZSM-5 and the ratio is from 332 to 368, preferably about 350.

8. A process according to any preceding claim wherein the oxygenate starting material is selected from the group consisting of methanol, ethanol, propanol, dimethyl ether, diethyl ether, and mixtures of any two or more thereof.

9. A process according to any preceding claim wherein the oxygenate starting material additionally comprises a diluent.

10. A process according to claim 9 wherein the diluent is water.

11. A process according to any preceding claim wherein the high purity olefin product comprises olefin and its corresponding paraffin in a paraffin to olefin weight ratio of not more than 0.05.

12. A process according to any preceding claim wherein the high purity olefin comprises polymer grade propylene containing not more than 5 wt%, preferably not more than 1 wt%, of propane.

13. A process according to any preceding claim wherein the high purity olefins are subjected to additional purification by superfractionation.



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- 22 -

14. The use of (a) ZSM-5 having a silica-to- Me_2O_3 ratio of from 350 to 2500, preferably from 950 to 1050; or (b) ZSM-48 having such ratio of from 300 to 2500, preferably from 320 to 353; or (c) FeZSM-5
5 having such ratio of from 332 to 368; or (d) a silicoaluminophosphate (SAPO), as catalyst for selectively converting oxygenate starting materials to high purity olefins by the process as defined in claim 1.

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REPLACEMENT SHEET

27 NOV 1996

- 1 -

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PRODUCTION OF HIGH PURITY OLEFINS

BACKGROUND OF THE INVENTION

This invention relates to a process for converting an oxygenate to high purity olefins by contacting the oxygenate with a molecular sieve catalyst. More particularly, the invention relates to a process for converting a methanol or methanol-water mixture to polymer-grade propylene by contacting the feed with zeolite or silicoaluminophosphate catalysts.

High purity olefins such as propylene have traditionally been produced through the process of steam and/or catalytic cracking. Because of the limited availability and high cost of petroleum sources, the cost of producing high purity olefins from such petroleum sources has been steadily increasing. Curtailment in the availability of inexpensive petroleum raw materials threatens the supply of high purity olefins such as polymer-grade propylene. Polymer-grade propylene is used in the production of many types of plastics such as polypropylene.

The search for alternative materials for high purity olefin production has led to the use of oxygenates such as alcohols, and more particularly to methanol and higher alcohols or their derivatives. These alcohols may be produced by fermentation or from synthesis gas. Synthesis gas can be produced from natural gas, petroleum liquids, carbonaceous materials including coal, recycled plastics, municipal wastes, or any organic material. Thus, alcohol and alcohol derivatives may provide non-petroleum based feeds for high purity olefin production.

THIS SHEET HAS BEEN
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REPLACEMENT SHEET
27 NOV 1996

- 2 -

Molecular sieves, such as crystalline zeolite catalysts, are known to promote the conversion of oxygenates to olefin-containing hydrocarbon mixtures. US-A-4,025,575 and US-A-4,083,889 disclose processes for conversion of methanol and/or methyl ether to olefin-containing products using ZSM-5-type zeolite catalysts.

Chang et al., US-A-4,724,270, describe a process for converting methanol feedstocks to aromatic hydrocarbons using zeolite catalysts (having a silica-to-alumina ratio of at least 12) at a temperature of at least 725°C (1337°F). By conducting the reaction at elevated temperatures, zeolite dehydroxylation can occur. This can lead to zeolite decomposition to amorphous silica and alumina.

US-A-4,433,189 to Young teaches conversion of methanol to light olefins over zeolite catalysts having a silica-to-alumina molar ratio of at least 12, and at a temperature of from about 200°C (392°F) to 500°C (932°F). The Young patent does not teach conversion of methanol to products such as polymer-grade propylene.

US-A-4,677,243 to Kaiser teaches the formation of light olefins using silicoaluminophosphate catalysts at a temperature of from about 200°C (392°F) to 700°C (1292°F). Kaiser does not teach the formation of high purity olefins or polymer-grade propylene.

High purity olefins are generally recognized by those skilled in the art as products, excluding methane, which have a paraffin-to-olefin weight ratio of less than or equal to about 0.05. Purification of high purity olefins traditionally requires removal of low-level impurities which interfere with polymerization catalysis, or which interfere with

THIS SHEET HAS BEEN
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REPLACEMENT SHEET

27 NOV 1996

- 3 -

other processes requiring high-purity reactants. Low-level contaminants include, but are not limited to polar molecules, oxygenates such as water, alcohols, carbon monoxide, carbon dioxide, carbonyl sulfide (COS), oxygen, and other miscellaneous contaminants including hydrogen sulfide, mercaptans, ammonia, arsine phosphine, chlorides. Low-level contaminants are removed by a variety of processes including, but not limited to adsorption and fractional distillation. Lighter or heavier hydrocarbon molecules having fewer or more carbon atoms than the desired olefin product must also be removed. These hydrocarbons are typically removed by fractional distillation techniques.

One such high purity olefin is polymer-grade propylene. Polymer-grade propylene is required for the production of polypropylene and useful for the production of other propylene derivatives. Polymer-grade propylene is characterized by very low concentrations of impurities, including low levels of paraffins (saturated hydrocarbons) such as propane, ethane, and butane.

Commercial chemical-grade propylene, unlike polymer-grade propylene, is characterized by higher concentrations of saturated hydrocarbons. Propane is the most difficult of the saturated hydrocarbons to remove from propylene, due in large part to the proximity of the boiling points for propane and propylene. Typical polymer-grade propylene purities range from 95% to 99.5% propylene, and are more preferably above 99%. This degree of purity corresponds to propane-to-propylene ratios of about 0.05 to about 0.01 or lower. Hitherto, this low propane level could only be practically achieved

THIS SHEET HAS BEEN
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REPLACEMENT SHEET

27 NOV 1996

- 4 -

through the use of the well known art of fractional distillation. The fractional distillation scheme employed for effecting the difficult separation of propane from propylene is called "superfractionation." However, superfractionation requires a substantial investment in facilities and consumes copious amounts of energy. Alternative means for removing paraffin impurities, such as membrane techniques and adsorbent techniques, are as costly as the superfractionation techniques. The present invention teaches a means for producing high purity olefins having the required range of paraffin-to-olefin ratios, without the need to resort to superfractionation or other expensive purification techniques. According to the teachings of the present invention, a superfractionator is not required, thereby significantly reducing the cost of producing high purity olefins such as polymer-grade propylene.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a process for selectively catalytically converting oxygenate starting material to high purity olefins which comprises contacting the oxygenate starting material with a molecular sieve catalyst having a preselected silica-to- Me_2O_3 molar ratio, at a preselected weight hourly space velocity (WHSV), and at a temperature of from 350°C to 550°C , and recovering the high purity olefins. The high purity olefins are preferably polymer-grade propylene. The process employs molecular sieves such as the crystalline aluminosilicate, ferrosilicate zeolites, and silicoaluminophosphate (SAPO) catalysts. Preferred embodiments employ ZSM-5, ZSM-48, FeZSM-5,

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REPLACEMENT SHEET

27 NOV 1996

and SAPO-34 as the molecular sieve. It is to be noted that the process of the invention is performed at temperatures above those usually employed with molecular sieves; it is this, together with selection of the nature of the catalyst and the matching temperature and flow conditions, which enables the selective conversions to high purity olefins characteristic of the invention. The reaction is conducted at a temperature preferably within a narrower range, more preferably about 450°C (842°F). Oxygenate conversion under such conditions produces a product, substantially rich in high purity olefins, such as polymer-grade propylene.

By employing the teachings of the present invention, a person having ordinary skill in the catalysis or olefin art should be able to produce a high purity olefin product from oxygenates without needing to resort to purification techniques such as adsorption or superfractionation. However, such additional purification techniques may be employed to produce olefins having even higher degrees of purity than high purity olefins.

The invention is distinguished from the teachings of US-A-4,638,106 to Pieters, et al. which teaches a process of converting alcohols to olefins using ZSM-5 having a silica-to-alumina ratio of about 400 because inter alia the ZSM-5 is modified by depositing carbonaceous materials on the catalyst (column 11, line 57 et seq.). This post-synthesis modification is a requirement of the Pieters, et al. invention (claim 1). In contrast, the instant invention does not require such a limitation, and the process is able to obtain high purity olefins without the post-synthesis modification described by Pieters, et al. Pieters, et

THIS SHEET HAS BEEN
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REPLACEMENT SHEET

27 NOV 1996

- 6 -

al. defines selectivity (column 22, line 1 et seq.) in such a manner that it is clear that production of both olefins and paraffins is anticipated by the invention. In contrast, the process of the invention is for the production of high purity olefins, such as polymer grade olefins having a paraffin-to-olefin weight ratio of less than or equal to about 0.05. This paraffin-to-olefin weight ratio is possible by using catalysts having a high, preselected silica-to-metal ratio, at a preselected flow rate, and at temperatures outside those taught by Pieters, which are optimized to achieve the conversion.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, an oxygenate feed is catalytically converted to high purity olefins by contacting this feed with a molecular sieve zeolite and/or silicoaluminophosphate catalyst. The process obviates the need for a conventional superfractionator to separate paraffins from olefins. It is within the scope of the present invention to use additional purification steps well known in the art to remove impurities other than paraffins having the same number of carbon atoms as olefins. Additionally, superfractionation may be used with the present invention to achieve still higher degrees of olefin purity. More particularly, the present invention relates to a process for catalytically converting oxygenates to high purity olefins such as polymer-grade propylene.

Zeolites are a class of molecular sieve catalysts and are porous, crystalline-hydrated metallo-silicates of Group IIIA and VIII elements (Me) interconnected through shared oxygen atoms.

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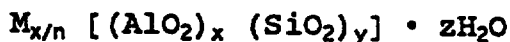
REPLACEMENT SHEET

27 NOV 1996

- 7 -

Preferable metals include aluminum, iron, gallium, nickel, cobalt, and boron. The rigid three dimensional network of silica and metal (hereinafter " Me_2O_3 ") creates a tetrahedral form which comprises the primary building unit of the zeolites. The metal constituents in zeolites include, but are not limited to, aluminum, iron, gallium, and boron. Because the oxygen atoms in zeolites are shared by tetrahedra, the framework possesses a net negative charge.

For example, the net negative charge of aluminosilicate zeolites is balanced by exchangeable cations in the crystalline structure, leading to the representation:



where M is the cation, n is the cation charge, and z represents the water of hydration. The silica-to-alumina molar ratio is controlled by the amounts of alumina "x" and silica "y" in the zeolite. When M is a proton, the zeolite acquires the characteristics of a Broensted acid (e.g., HZSM-5).

Other positive ion-containing catalysts include ferrosilicates, borosilicates, and gallosilicates. Of the ferrosilicates, FeZSM-5 may be employed in the process of the present invention. FeZSM-5 is composed of silicon and iron oxide (Fe_2O_3) in a manner similar to the aluminosilicate zeolites.

Zeolites generally have ordered, porous crystalline structures containing a small number of cavities that are interconnected by a number of still smaller channels. The cavities and channels are uniform in size within a certain type of zeolitic material. The dimensions of the pores or cavities allow for adsorption of molecules of certain dimensions while excluding molecules of larger

THIS SHEET HAS BEEN
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REPLACEMENT SHEET

27 NOV 1996

- 8 -

dimensions. The crystal structure of zeolites provides a selective constrained access to and egress from the intracrystalline free space. This phenomenon, also called "shape-selective catalysis," derives from zeolite geometry.

An important component of zeolite geometry derives from the proportions of silicon and Me_2O_3 atoms comprising the tetrahedra. The molar ratio of silica-to- Me_2O_3 may be determined by conventional analysis, such as wet chemical analysis (e.g., Atomic Absorption Spectrometry or Inductively Coupled Plasma Emission Spectrometry;) or by the stoichiometry of silica and Me_2O_3 used to synthesize the zeolite. The silica-to- Me_2O_3 molar ratio is meant to represent, as closely as possible, the silica-to- Me_2O_3 ratio in the rigid anionic framework of the molecular sieve crystal. Me_2O_3 in the binder or in cationic or other form within the porous channels is not considered in calculating the silica-to- Me_2O_3 ratio. The ratio of silica-to- Me_2O_3 in the molecular sieve imparts selective catalytic and adsorptive properties. The catalytic and adsorptive properties of the molecular sieve may also be varied by changing the ions within the catalyst. Conventional ion exchange techniques may be used to change the cations.

To those skilled in the zeolite catalyst art, ZSM-5 is generally considered a siliceous zeolite. This is because it may have a "high" silica-to- Me_2O_3 , or more specifically, silica-to-alumina molar ratio. ZSM-5 is particularly advantageous for converting methanol-containing feedstocks to light olefins. Siliceous zeolites (i.e., zeolites having a high silica-to- Me_2O_3 ratio), such as those described for use in the processes of the present invention, are

THIS SHEET HAS BEEN
REPLACED

- 9 -

REPLACEMENT SHEET

27 NOV 1996

most effectively synthesized using templates such as alkylammonium cations. For example, the tetramethylammonium (TMA) cation is particularly advantageous in synthesizing a siliceous zeolite such as ZSM-5 having a silica-to-alumina ratio of about 1000. It is thought that silica forms hydrogen bonds with the TMA and traps or clathrates the organic cation within the silica. Alumina is less efficient in hydrogen bond formation, so the zeolites formed with organic templates such as TMA have a higher silica-to-alumina molar ratio. The presence of a trivalent metal site within the silicate structure provides the desired acidity in an environment which limits access to the site by molecules of appropriate size. This limits the acid catalyzed reactions to those which are carried out in a "shape selective" manner. Template cations which are usually present in these materials when they are synthesized may be removed, and the zeolite converted to the hydrogen form by exchange with ammonium ions, followed by heating to drive off ammonia, or by direct exchange with an acid such as hydrochloric acid, provided the zeolite is not degraded by the acidic treatment.

The silicoaluminophosphate (SAPO) molecular sieve catalysts exhibit properties characteristic of both aluminosilicate zeolites and aluminophosphates. The SAPO molecular sieves have a microporous crystal framework structure of PO_2^+ , AlO_2^- and SiO_2 tetrahedral units. The composition (anhydrous) is:



wherein "R" represents at least one organic templating agent present in the intracrystalline pore system, "m" represents the moles of "R" present per mole of $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$ and has a value of from zero to 0.3, the

THIS SHEET HAS BEEN
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REPLACEMENT SHEET

27 NOV 1996

- 10 -

maximum value in each case depending upon the molecular dimensions of the templating agent and the available void volume of the pore system of the particular SAPO species involved, and "x," "y," and "z" represent the mole fractions of silicon, aluminum, and phosphorous, respectively. As will be understood, the nature of SAPO catalysts means that any preselected silica-to-Me₂O₃ value may be used. Representative SAPO molecular sieves, as described in US-A-4,440,871, include SAPO-5, SAPO-11, SAPO-17, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-37, SAPO-40, SAPO-41, and SAPO-42.

The oxygenate starting material or feed comprises hydrocarbons containing aliphatic moieties such as, but not limited to, alcohols, halides, mercaptans, sulfides, amines, ethers, and carbonyl compounds (aldehydes, ketones, carboxylic acids, and the like) or mixtures thereof. The aliphatic moiety preferably contains from about 1 to about 10 carbon atoms, and more preferably 1 to 4 carbon atoms. Thus the term "oxygenate starting material" is intended to mean not only what might be considered "true" oxygenates, e.g., alcohols, ethers, carbonyl compounds; but also those compounds which behave in a similar fashion to "true" oxygenates in the presence of the specified catalysts, such as substituted paraffins, e.g., halides, mercaptans, sulfides, amines. Representative oxygenates include methanol, isopropanol, n-propanol, ethanol, fuel alcohols, dimethyl ether, diethyl ether, methyl mercaptan, methyl sulfide, methyl amine, ethyl mercaptan, ethylchloride, formaldehyde, dimethylketone, acetic acid, n-alkylamines, n-alkylhalides, and n-alkylsulfides having alkyl groups of 1 to 10 carbon atoms or mixtures thereof. In a

THIS SHEET HAS BEEN
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REPLACEMENT SHEET

27 NOV 1996

- 11 -

preferred embodiment of the present invention, the feed comprises methanol. In another embodiment, the feed, e.g., methanol, contains a diluent. The addition of a diluent to the total feed charge decreases paraffin production relative to olefin production.

The term "oxygenate starting material" or "oxygenate feed" as employed in the present invention and described herein designates only the organic material used as the feed. However, the total charge to the reaction zone may contain additional compounds such as diluents. Use of a diluent as part of the feed, which is miscible with the oxygenate, imparts as a non-limiting example, a smaller propane to propylene ($C_3O/C_3=$) ratio than the use of essentially anhydrous oxygenate. However, even anhydrous oxygenates contain trace quantities of diluents. Even though the process described herein may employ a diluent, computable quantities of the oxygenate feed (i.e., composition and Weight Hourly Space Velocity (WHSV) are to be computed as an essentially diluent-free oxygenate feed unless otherwise stated.

The process is generally conducted in the presence of one or more diluents which may for example be present in the feed in an amount between about 1 and about 99 molar percent, based on the total number of moles of all feed and diluent components fed to the reaction zone (or catalyst). The amount of diluent added to the oxygenate feed will depend in part on the type of catalyst selected, the silica-to- Me_2O_3 ratio, and the reaction temperature. Preferably, the molar ratio of oxygenate feed-to-diluent (feed:diluent) is about 1:1 to about 1:4. Diluents include, but are not limited to, helium, argon, nitrogen, carbon monoxide,

THIS SHEET HAS BEEN
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REPLACEMENT SHEET

27 NOV 1996

- 12 -

hydrocarbons (such as methane and the like), aromatic compounds, and mixtures thereof. Preferably, the diluent is water.

The instant process is preferably conducted in the vapor phase such that the oxygenate feed is contacted in the vapor phase in a reaction zone with the molecular sieve at effective process conditions to produce a paraffin/olefin, e.g., propane/propylene ratio characteristic of high purity olefins or polymer-grade propylene, i.e., an effective temperature, silica-to-Me₂O₃ ratio, pressure, WHSV and, optionally, an effective amount of diluent, correlated to produce high purity olefins or polymer-grade propylene. Alternatively, the process may be conducted in a liquid phase.

The process may be effectively carried out over a wide range of pressures including autogeneous pressures. At pressures between about 0.001 atmospheres (0.76 torr) and about 1000 atmospheres (760,000 torr), the formation of light olefin products will be effected although the optimum amount of product will not necessarily form at all pressures. The preferred pressure is between 0.01 atmospheres (7.6 torr) and 100 atmospheres (76,000 torr). The pressures referred to herein for the process are exclusive of the inert diluent, if any, that is present, and refer to the partial pressure of the feedstock as it relates to oxygenate compounds and/or mixtures thereof. Pressures outside the stated range are not excluded from the scope of this invention, although such pressures do not fall within certain desirable embodiments of the invention. At the lower and upper end of the pressure range, and beyond, the selectivities, conversions, and/or rates to light

THIS SHEET HAS BEEN
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- 13 -

REPLACEMENT SHEET

27 NOV 1996

olefin products may not be optimal, although light olefins such as ethylene may still be formed.

The process is effected for a period of time sufficient to produce the desired light olefin (and high purity olefin) products. In general, the residence time employed to produce the desired product can vary from seconds to a number of hours. It will be readily appreciated that the residence time will be determined to a significant extent by the reaction temperature, the molecular sieve selected, the WHSV, the phase (liquid or vapor), and process design characteristics selected.

The olefin production process may be carried out in a batch, semi-continuous, or continuous fashion. The process can be conducted in a single reaction zone, or a number of reaction zones arranged in series or in parallel, or it may be conducted intermittently or continuously in an elongated tubular zone or a number of such zones. When multiple reaction zones are employed, it may be advantageous to employ one or more of such molecular sieves in series to provide for a desired product mixture. Owing to the nature of the process, it may be desirable to carry out the process of the present invention by use of the molecular sieve catalysts in a dynamic (e.g., fluidized or moving) bed system or any system of a variety of transport beds rather than in a fixed bed system. Such systems would readily provide for any regeneration (if required) of the molecular sieve catalyst after a given period of time. If regeneration is required, the molecular sieve catalyst can be continuously introduced as a moving bed to a regeneration zone where it can be regenerated, such as for example by removing carbonaceous materials or by oxidation in an oxygen-

THIS SHEET HAS BEEN
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- 14 -

REPLACEMENT SHEET

27 NOV 1996

carbonaceous materials or by oxidation in an oxygen-containing atmosphere. In the preferred practice of the invention, the catalyst will be subject to a regeneration step by the burning of carbonaceous deposits accumulated during reactions.

The effect of feedstock flow rate over molecular sieves is well known to those skilled in the art. Increasing the flow rate (WHSV) enhances olefin production relative to paraffin production. However, the enhanced olefin production relative to paraffin production is offset by a diminished conversion of oxygenate to hydrocarbons at the higher flow rates.

According to the invention, the process for conversion of an oxygenate feed to high purity olefins such as polymer-grade propylene using molecular sieves is for example conducted at temperatures of from approximately 350°C (662°F) to about 550°C (1022°F), preferably 450°C (842°F) to 550°C (1022°F), and more preferably at 440°C (824°F) to 460°C (860°F). The silica-to-Me₂O₃ molar ratio is preselected according to the type of molecular sieve employed, the reaction temperature used, and the degree of high purity olefin, e.g., polymer-grade propylene, production required. The WHSV of this reaction is for example approximately 0.01 hr.⁻¹ to about 100 hr.⁻¹, preferably 0.5 hr.⁻¹ to 10 hr.⁻¹, and more preferably 0.8 hr.⁻¹ to 1.2 hr.⁻¹. For ZSM-5, at 0.8 hr.⁻¹ to 1.2 hr.⁻¹, approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur.

In the process using ZSM-5, which zeolite is described in US-A-3,702,886, the process temperature is preferably 400°C to 550°C, more preferably 440°C to 460°C; and the silica-to-Me₂O₃ molar ratio is preferably 350 to 2500, more preferably 950 to 1050.

THIS SHEET HAS BEEN
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REPLACEMENT SHEET

27 NOV 1996

- 15 -

The WHSV of the process is preferably 0.1 hr.^{-1} to 10 hr.^{-1} , and more preferably 0.8 hr.^{-1} to 1.2 hr.^{-1} . Using ZSM-5, at 0.8 hr.^{-1} to 1.2 hr.^{-1} , approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur.

In the process using ZSM-48, which zeolite is described more fully in US-A-4,397,827, the process temperature is also preferably 400°C to 550°C , and more preferably 440°C to 460°C . The preferred silica-to- Me_2O_3 molar ratio is however from 300 to 2500, more preferably 320 to 353. The WHSV of the process using ZSM-48 is preferably 0.5 hr.^{-1} to 10 hr.^{-1} , and more preferably 0.8 hr.^{-1} to 1.2 hr.^{-1} . With ZSM-48, at 0.8 hr.^{-1} to 1.2 hr.^{-1} , approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur, comprising approximately 30% propylene and <1% propane in the case where the olefin is propylene.

In the process using FeZSM-5, which zeolite is described in US-A-4,843,183, the preferred process temperatures are as recited for ZSM-48. However, the silica-to- Me_2O_3 molar ratio is preferably from 332 to 368, more preferably about 350. The WHSV of the process using FeZSM-5 is preferably 0.1 hr.^{-1} to 10 hr.^{-1} , more preferably 0.8 hr.^{-1} to 1.2 hr.^{-1} . With ZSM-48 at 0.8 hr.^{-1} to 1.2 hr.^{-1} , approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur, comprising approximately 25% propylene with no propane production, in the case where the olefin is propylene.

In the process using SAPO-34, which catalyst is described in US-A-4,440,871, the process for conversion of an oxygenate feed to high purity olefins such as polymer-grade propylene may be conducted for example at temperatures of 350°C to 550°C , preferably

THIS SHEET HAS BEEN
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REPLACEMENT SHEET

27 NOV 1996

- 16 -

400°C to 550°C, and more preferably at 440°C to 460°C. The WHSV of this process is preferably from 0.01 hr.⁻¹ to 100 hr.⁻¹, more preferably 0.1 hr.⁻¹ to 10 hr.⁻¹, and most preferably 0.8 hr.⁻¹ to 1.2 hr.⁻¹. With SAPO-34 at 0.8 hr.⁻¹ to 1.2 hr.⁻¹, approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur.

The following examples illustrate the invention.

Example 1

Zeolites ZSM-5, having silica-to-Me₂O₃ molar ratios (silica-to-alumina molar ratios) of 35, 350, and 1000 (determined stoichiometrically), were produced as described in US-A-3,702,886.

Each ZSM-5 was calcined at 510°C (950°F) and the calcined material was ion exchanged with an ammonium nitrate solution (85°C, 185°F; 12 hours). Generally, the ion exchange was repeated two or three times, with a calcination at 510°C (950°F) between each ion exchange step.

The catalytic conversion of methanol or methanol/water to hydrocarbons using each ZSM-5 having a preselected silica-to-alumina ratio of 35, 350, and 1000 was carried out in a fixed bed (1/2", 1.27 cm diameter), stainless steel reactor, equipped with a 1/8" (0.32 cm) coiled preheater. In addition, the reactor was equipped with a 1/8" (0.32 cm) thermocouple well running axially through the reactor. The reactor was heated in an Applied Test Systems 3 zone tube furnace (12", 30.5 cm long; 1 1/4", 3.18 cm I.D.) having the reactor with three spaced zones. The first reactor zone is used as a preheater zone, and the catalyst bed is heated in the second reactor zone. The third reactor zone operates as a quench zone.

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REPLACEMENT SHEET

27 NOV 1996

- 17 -

maintained at a temperature of about 200°C (392°F) to about 300°C (572°F).

Generally, 2 grams (0.07 ounces) catalyst (-14/+20 mesh) were mixed with 2.5 grams (0.09 ounces) of quartz (-20/+60); the first and third reactor zone were filled with quartz chips (-10/+20 mesh). To improve the heat transfer between the second reactor zone (containing the catalyst bed) and the furnace heating coils, the second reactor zone was equipped with a cylindrical (4", 10.2 cm long; 1 1/4", 3.18 cm O.D.) aluminum or stainless steel block. This block contained a central hole in order to be able to measure the block temperature.

Gas flows (nitrogen or hydrogen) were controlled by mass flow controllers, while liquid feed rates were controlled by a Beckmann 114M pump or a Sage 341B syringe pump.

The product emerging from the reactor was analyzed on line for (i) carbon monoxide; carbon dioxide; water; dimethyl ether; methanol; C₁-C₃ hydrocarbons with a Poropak Q column using a thermal conductivity detector and (ii) C₁-A₁₀ hydrocarbons with a DB-1 column using a flame ionization detector. The feed was either methanol or methanol:water (1:1 or 1:4 molar ratio as denoted in Table I) at a WHSV=1.0 hr.⁻¹. The reaction was conducted at 450°C (842°F). The results are shown in Table I.

The same procedures as recited in Example 1, using the same equipment, conditions and measurement techniques, were employed with several different catalysts. These catalysts, and the analyses of the products made employing the process of the invention, are further described in Examples 2 - 4 and Table 1.

27 NOV 1996

Example 2

The zeolite ZSM-48, having a silica-to- Me_2O_3 molar ratio of 336 (determined by wet chemical analysis), was produced as described in US-A-4,423,021.

ZSM-48 was calcined at 510°C (950°F) and the calcined material was ion exchanged with ammonium nitrate solution (85°C , 185°F ; 12 hours). Generally, the ion exchange was repeated two or three times, with a calcination at 510°C (950°F) between each ion exchange step.

The feed was methanol:water (1:1 molar ratio) at a $\text{WHSV}=1.0 \text{ hr.}^{-1}$. The reaction was conducted at 450°C (842°F). The results are shown in Table I.

Example 3

The zeolite FeZSM-5, having a silica-to- Me_2O_3 ratio of 350 (determined stoichiometrically), was produced as described in US-A-4,843,183.

FeZSM-5 was calcined at 510°C (950°F) and the calcined material was ion exchanged with an ammonium nitrate solution (85°C , 185°F ; 12 hours). Generally, the ion exchange was repeated two or three times, with a calcination at 510°C (950°F) between each ion exchange step.

The feed was methanol:water (1:1 molar ratio) at a $\text{WHSV}=1.0 \text{ hr.}^{-1}$. The reaction was conducted at 450°C (842°F). The results are shown in Table I.

Example 4

SAPO-34 was calcined at 510°C (950°F) and the calcined material was ion exchanged with an ammonium nitrate solution (85°C , 185°F ; 12 hours). Generally, the ion exchange was repeated two or three times, with

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REPLACEMENT SHEET

27 NOV 1996

- 19 -

a calcination at 510°C (950°F) between each ion exchange step.

The feed was methanol:water (1:4 molar ratio) at a WHSV=1.0 hr.⁻¹. The reaction was conducted at 450°C (842°F). The results are shown in Table I.

Table I
Polymer-Grade Propylene Production

<u>Molecular Sieve</u>	<u>Silica-to-Me₂O₃</u>	<u>Feed/Diluent (molar ratio)</u>	<u>Propane/propylene (C₃0/C₃=)</u>
ZSM-5	35	Methanol/Water (1:1)	0.770**
ZSM-5	1000	Methanol (NA)	0.044
ZSM-5	350	Methanol/Water (1:4)	0.037
ZSM-5	1000	Methanol/Water (1:1)	0.000
ZSM-48	336	Methanol/Water (1:1)	0.038
Fe ZSM-5	350	Methanol/Water (1:1)	0.039
SAPO-34	NA*	Methanol/Water (1:4)	0.001

*NA signifies "not applicable."

** signifies comparative.

As shown in Table I, olefins are formed by contacting the oxygenate feed with a molecular sieve at a temperature of between 350°C (662°F) to 550°C (1022°F). By preselecting the silica-to-Me₂O₃ ratio and/or diluent, a product having a propane/propylene ratio characteristic of high purity olefins can be produced. This can be achieved without the need of superfractionation to remove propane.



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- 20 -

REPLACEMENT SHEET

27 NOV 1996

CLAIMS:

1. A process for selectively catalytically converting oxygenate starting material to high purity olefins which comprises contacting the oxygenate starting material with a molecular sieve catalyst having a preselected silica-to-Me₂O₃ molar ratio, at a preselected weight hourly space velocity (WHSV), and at a temperature of from 350°C to 550°C, and recovering the high purity olefins.
2. A process according to claim 1 wherein the temperature is from 450°C to 550°C, preferably from 440°C to 460°C.
3. A process according to claim 1 or 2 wherein the WHSV is from 0.01 hr.⁻¹ to 100 hr.⁻¹, preferably 0.5 hr.⁻¹ to 10 hr.⁻¹, more preferably 0.8 hr.⁻¹ to 1.2 hr.⁻¹.
4. A process according to any preceding claim wherein the molecular sieve catalyst comprises a crystalline aluminosilicate zeolite, a ferrosilicate zeolite or a silicoaluminophosphate (SAPO) catalyst.
5. A process according to claim 4 wherein the catalyst comprises ZSM-5, ZSM-48, FeZSM-5 or SAPO-5, 11, 17, 20, 31, 34, 35, 37, 40, 41 or 42, or a mixture of any two or more thereof.
6. A process according to any preceding claim wherein the silica-to-Me₂O₃ ratio of the catalyst is from 300 to 2500.



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- 21 -

REPLACEMENT SHEET

27 NOV 1996

7. A process according to claim 6 wherein (a) the catalyst is ZSM-5 and the ratio is from 350 to 2500, preferably from 950 to 1050; or (b) the catalyst is ZSM-48 and the ratio is from 320 to 353; or (c) the catalyst is FeZSM-5 and the ratio is from 332 to 368, preferably about 350.

8. A process according to any preceding claim wherein the oxygenate starting material is selected from the group consisting of methanol, ethanol, propanol, dimethyl ether, diethyl ether, and mixtures of any two or more thereof.

9. A process according to any preceding claim wherein the oxygenate starting material additionally comprises a diluent.

10. A process according to claim 9 wherein the diluent is water.

11. A process according to any preceding claim wherein the high purity olefin product comprises olefin and its corresponding paraffin in a paraffin to olefin weight ratio of not more than 0.05.

12. A process according to any preceding claim wherein the high purity olefin comprises polymer grade propylene containing not more than 5 wt%, preferably not more than 1 wt%, of propane.

13. A process according to any preceding claim wherein the high purity olefins are subjected to additional purification by superfractionation.



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REPLACEMENT SHEET

27 NOV 1996

- 22 -

14. The use of (a) ZSM-5 having a silica-to- Me_2O_3 ratio of from 350 to 2500, preferably from 950 to 1050; or (b) ZSM-48 having such ratio of from 300 to 2500, preferably from 320 to 353; or (c) FeZSM-5 having such ratio of from 332 to 368; or (d) a silicoaluminophosphate (SAPO), as catalyst for selectively converting oxygenate starting materials to high purity olefins by the process as defined in claim 1.

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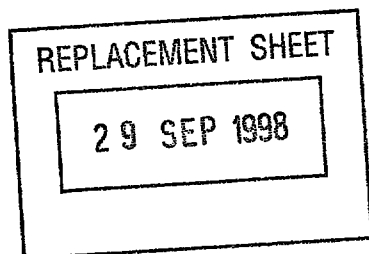
- 23 -

PRODUCTION OF HIGH PURITY OLEFINS

ABSTRACT

A process for converting an oxygenate feed to high purity olefins such as polymer-grade propylene ($C_3O/C_3 = \leq 0.05$) at a temperature of about 450 °C (842 °F), using a molecular sieve catalyst having a high preselected Si/Al₂ ratio (such as ZSM-5, ZSM-48) or preselected Si/Fe₂ ratio (such as FeZSM-5), or SAPO-34.

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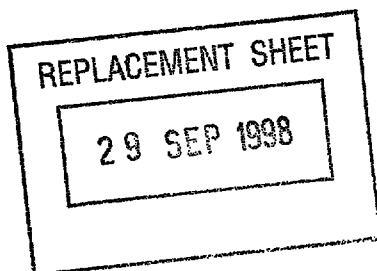
PRODUCTION OF HIGH PURITY OLEFINS

BACKGROUND OF THE INVENTION

This invention relates to a process for converting an oxygenate to high purity olefins by contacting the oxygenate with a molecular sieve catalyst. More particularly, the invention relates to a process for converting a methanol or methanol-water mixture to polymer-grade propylene by contacting the feed with zeolite or silicoaluminophosphate catalysts.

High purity olefins such as propylene have traditionally been produced through the process of steam and/or catalytic cracking. Because of the limited availability and high cost of petroleum sources, the cost of producing high purity olefins from such petroleum sources has been steadily increasing. Curtailment in the availability of inexpensive petroleum raw materials threatens the supply of high purity olefins such as polymer-grade propylene. Polymer-grade propylene is used in the production of many types of plastics such as polypropylene.

The search for alternative materials for high purity olefin production has led to the use of oxygenates such as alcohols, and more particularly to methanol and higher alcohols or their derivatives. These alcohols may be produced by fermentation or from synthesis gas. Synthesis gas can be produced from natural gas, petroleum liquids, carbonaceous materials including coal, recycled plastics, municipal wastes, or any organic material. Thus, alcohol and alcohol derivatives may provide non-petroleum based feeds for high purity olefin production.



- 2 -

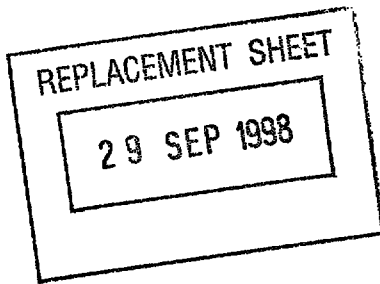
Molecular sieves, such as crystalline zeolite catalysts, are known to promote the conversion of oxygenates to olefin-containing hydrocarbon mixtures. US-A-4,025,575 and US-A-4,083,889 disclose processes for conversion of methanol and/or methyl ether to olefin-containing products using ZSM-5-type zeolite catalysts.

Chang et al., US-A-4,724,270, describe a process for converting methanol feedstocks to aromatic hydrocarbons using zeolite catalysts (having a silica-to-alumina ratio of at least 12) at a temperature of at least 725°C (1337°F). By conducting the reaction at elevated temperatures, zeolite dehydroxylation can occur. This can lead to zeolite decomposition to amorphous silica and alumina.

US-A-4,433,189 to Young teaches conversion of methanol to light olefins over zeolite catalysts having a silica-to-alumina molar ratio of at least 12, and at a temperature of from about 200°C (392°F) to 500°C (932°F). The Young patent does not teach conversion of methanol to products such as polymer-grade propylene.

US-A-4,677,243 to Kaiser teaches the formation of light olefins using silicoaluminophosphate catalysts at a temperature of from about 200°C (392°F) to 700°C (1292°F). Kaiser does not teach the formation of high purity olefins or polymer-grade propylene.

High purity olefins are generally recognized by those skilled in the art as products, excluding methane, which have a paraffin-to-olefin weight ratio of less than or equal to about 0.05. Purification of high purity olefins traditionally requires removal of low-level impurities which interfere with polymerization catalysis, or which interfere with



- 3 -

other processes requiring high-purity reactants. Low-level contaminants include, but are not limited to polar molecules, oxygenates such as water, alcohols, carbon monoxide, carbon dioxide, carbonyl sulfide (COS), oxygen, and other miscellaneous contaminants including hydrogen sulfide, mercaptans, ammonia, arsine phosphine, chlorides. Low-level contaminants are removed by a variety of processes including, but not limited to adsorption and fractional distillation. Lighter or heavier hydrocarbon molecules having fewer or more carbon atoms than the desired olefin product must also be removed. These hydrocarbons are typically removed by fractional distillation techniques.

One such high purity olefin is polymer-grade propylene. Polymer-grade propylene is required for the production of polypropylene and useful for the production of other propylene derivatives. Polymer-grade propylene is characterized by very low concentrations of impurities, including low levels of paraffins (saturated hydrocarbons) such as propane, ethane, and butane.

Commercial chemical-grade propylene, unlike polymer-grade propylene, is characterized by higher concentrations of saturated hydrocarbons. Propane is the most difficult of the saturated hydrocarbons to remove from propylene, due in large part to the proximity of the boiling points for propane and propylene. Typical polymer-grade propylene purities range from 95% to 99.5% propylene, and are more preferably above 99%. This degree of purity corresponds to propane-to-propylene ratios of about 0.05 to about 0.01 or lower. Hitherto, this low propane level could only be practically achieved

29 SEP 1998

- 4 -

through the use of the well known art of fractional distillation. The fractional distillation scheme employed for effecting the difficult separation of propane from propylene is called "superfractionation." However, superfractionation requires a substantial investment in facilities and consumes copious amounts of energy. Alternative means for removing paraffin impurities, such as membrane techniques and adsorbent techniques, are as costly as the superfractionation techniques. The present invention teaches a means for producing high purity olefins having the required range of paraffin-to-olefin ratios, without the need to resort to superfractionation or other expensive purification techniques. According to the teachings of the present invention, a superfractionator is not required, thereby significantly reducing the cost of producing high purity olefins such as polymer-grade propylene.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a process for selectively catalytically converting a starting material comprising an oxygenate, or a substituted paraffin which is a halide, a mercaptan, a sulfide or an amine, to high purity olefins, which process comprises contacting the starting material at a weight hourly space velocity (WHSV) of from 0.01 hr.⁻¹ to 100 hr.⁻¹, and at a temperature of from 350°C to 550°C, with a molecular sieve catalyst comprising ZSM-48, a ferrosilicate zeolite or a silicoaluminophosphate (SAPO), which molecular sieve catalyst, in the case of ZSM-48 or ferrosilicate zeolites, has a silica-to-Me₂O₃ molar ratio (where Me is a Group IIIA or VIII element) of from 300 to 2500, and recovering the high purity olefins. The high purity olefins are preferably polymer-grade propylene. Preferred embodiments employ FeZSM-5,



- 5 -

and SAPO-34 as the molecular sieve. It is to be noted that the process of the invention is performed at temperatures above those usually employed with molecular sieves; it is this, together with selection of the nature of the catalyst and the matching temperature and flow conditions, which enables the selective conversions to high purity olefins characteristic of the invention. The reaction is conducted at a temperature preferably within a narrower range, more preferably about 450°C (842°F). Oxygenate conversion under such conditions produces a product, substantially rich in high purity olefins, such as polymer-grade propylene.

By employing the teachings of the present invention, a person having ordinary skill in the catalysis or olefin art should be able to produce a high purity olefin product from oxygenates without needing to resort to purification techniques such as adsorption or superfractionation. However, such additional purification techniques may be employed to produce olefins having even higher degrees of purity than high purity olefins.

~~The invention is distinguished from the teachings~~
of US-A-4,638,106 to Pieters, et al. ~~which~~ teaches a process of converting alcohols to olefins using ZSM-5 having a silica-to-alumina ratio of about 400 because inter alia the ZSM-5 is modified by depositing carbonaceous materials on the catalyst (column 11, line 57 et seq.). This post-synthesis modification is a requirement of the Pieters, et al. invention (claim 1). In contrast, the instant invention does not encompass use of ZSM-5, and the process is able to obtain high purity olefins without the post-synthesis modification described by Pieters, et al. Pieters, et al. defines selectivity (column 22, line 1 et seq.) in such a manner that it is clear that production of both olefins and paraffins is anticipated by the invention. In contrast, the process of the invention is for the

REPLACEMENT SHEET

29 SEP 1998

- 6 -

production of high purity olefins, such as polymer grade olefins having a paraffin-to-olefin weight ratio of less than or equal to about 0.05. This paraffin-to-olefin weight ratio is possible by using catalysts having a high, preselected silica-to-metal ratio, at a preselected flow rate, and at temperatures outside those taught by Pieters, which are optimized to achieve the conversion.

DE-A-2935863 (equivalent US-A-4,849,573) describes a process for the conversion of alcohols (like methanol) in presence of a crystalline aluminosilicate (ZSM-5) used as catalyst. The ratio silicon oxide/aluminium oxide in the zeolite is at least 140, the range 298 to 2000 being preferred. The WHSV is from 1 to 5. The reaction temperature is between 350 and 600°C, with the range between 400 and 550°C being preferred. Water vapor can be used as diluent. According to example 11, the ratio of olefin to paraffin is 29.7 at 500°C and 35.3 at 550°C. DE-A-2935863 also teaches processes employing ZSM-11, 12, 35 and 38 as catalyst.

DETAILED DESCRIPTION OF THE INVENTION

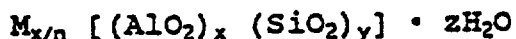
In accordance with the present invention, an oxygenate feed is catalytically converted to high purity olefins by contacting this feed with a ZSM-48, or ferro silicate zeolite and/or silicoaluminophosphate catalyst. The process obviates the need for a conventional superfractionator to separate paraffins from olefins. It is within the scope of the present invention to use additional purification steps well known in the art to remove impurities other than paraffins having the same number of carbon atoms as olefins. Additionally, superfractionation may be used with the present invention to achieve still higher degrees of olefin purity. More particularly, the present invention relates to a process for catalytically converting oxygenates to high purity olefins such as polymer-grade propylene.

29 SEP 1998

- 7 -

Zeolites are a class of molecular sieve catalysts and are porous, crystalline-hydrated metallo-silicates of Group IIIA and VIII elements (Me) interconnected through shared oxygen atoms. Preferable metals include aluminum, iron, gallium, nickel, cobalt, and boron. The rigid three dimensional network of silica and metal (hereinafter "Me₂O₃") creates a tetrahedral form which comprises the primary building unit of the zeolites. The metal constituents in zeolites include, but are not limited to, aluminum, iron, gallium, and boron. Because the oxygen atoms in zeolites are shared by tetrahedra, the framework possesses a net negative charge.

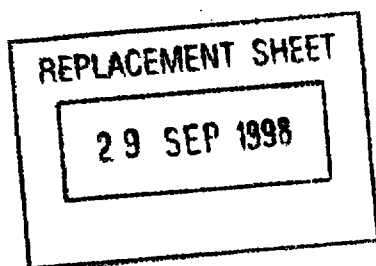
For example, the net negative charge of aluminosilicate zeolites is balanced by exchangeable cations in the crystalline structure, leading to the representation:



where M is the cation, n is the cation charge, and z represents the water of hydration. The silica-to-alumina molar ratio is controlled by the amounts of alumina "x" and silica "y" in the zeolite. When M is a proton, the zeolite acquires the characteristics of a Broensted acid (~~e.g., HZSM-5~~).

Other positive ion-containing catalysts include ferrosilicates, borosilicates, and gallosilicates. Of the ferrosilicates, FeZSM-5 may be employed in the process of the present invention. FeZSM-5 is composed of silicon and iron oxide (Fe₂O₃) in a manner similar to the aluminosilicate zeolites.

Zeolites generally have ordered, porous crystalline structures containing a small number of cavities that are interconnected by a number of still smaller channels. The cavities and channels are uniform in size within a certain type of zeolitic material. The dimensions of the pores or cavities allow for adsorption of molecules of certain dimensions while excluding molecules of larger

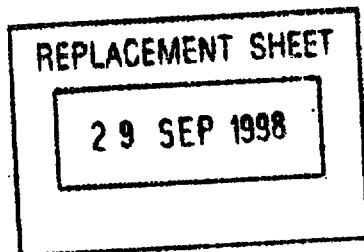


- 8 -

dimensions. The crystal structure of zeolites provides a selective constrained access to and egress from the intracrystalline free space. This phenomenon, also called "shape-selective catalysis," derives from zeolite geometry.

An important component of zeolite geometry derives from the proportions of silicon and Me_2O_3 atoms comprising the tetrahedra. The molar ratio of silica-to- Me_2O_3 may be determined by conventional analysis, such as wet chemical analysis (e.g., Atomic Absorption Spectrometry or Inductively Coupled Plasma Emission Spectrometry;) or by the stoichiometry of silica and Me_2O_3 used to synthesize the zeolite. The silica-to- Me_2O_3 molar ratio is meant to represent, as closely as possible, the silica-to- Me_2O_3 ratio in the rigid anionic framework of the molecular sieve crystal. Me_2O_3 in the binder or in cationic or other form within the porous channels is not considered in calculating the silica-to- Me_2O_3 ratio. The ratio of silica-to- Me_2O_3 in the molecular sieve imparts selective catalytic and adsorptive properties. The catalytic and adsorptive properties of the molecular sieve may also be varied by changing the ions within the catalyst. Conventional ion exchange techniques may be used to change the cations.

~~To those skilled in the zeolite catalyst art,~~
ZSM-5 is generally considered a siliceous zeolite. This is because it may have a "high" silica-to- Me_2O_3 , or more specifically, silica-to-alumina molar ratio. ZSM-5 is particularly advantageous for converting ~~methanol-containing feedstocks to light olefins.~~ Siliceous zeolites (i.e., zeolites having a high silica-to- Me_2O_3 ratio), such as those described for use in the processes of the present invention, are



- 9 -

most effectively synthesized using templates such as alkylammonium cations. For example, the tetramethylammonium (TMA) cation is particularly advantageous in synthesizing a siliceous zeolite ~~such as ZSM-5~~ having a silica-to-alumina ratio of about 1000. It is thought that silica forms hydrogen bonds with the TMA and traps or clathrates the organic cation within the silica. Alumina is less efficient in hydrogen bond formation, so the zeolites formed with organic templates such as TMA have a higher silica-to-alumina molar ratio. The presence of a trivalent metal site within the silicate structure provides the desired acidity in an environment which limits access to the site by molecules of appropriate size. This limits the acid catalyzed reactions to those which are carried out in a "shape selective" manner. Template cations which are usually present in these materials when they are synthesized may be removed, and the zeolite converted to the hydrogen form by exchange with ammonium ions, followed by heating to drive off ammonia, or by direct exchange with an acid such as hydrochloric acid, provided the zeolite is not degraded by the acidic treatment.

The silicoaluminophosphate (SAPO) molecular sieve catalysts exhibit properties characteristic of both aluminosilicate zeolites and aluminophosphates. The SAPO molecular sieves have a microporous crystal framework structure of PO_2^+ , AlO_2^- and SiO_2 tetrahedral units. The composition (anhydrous) is:



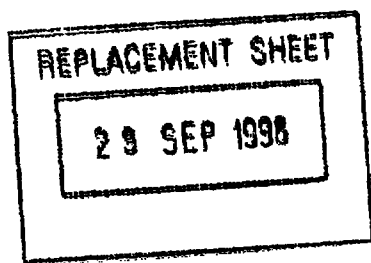
wherein "R" represents at least one organic templating agent present in the intracrystalline pore system, "m" represents the moles of "R" present per mole of $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$ and has a value of from zero to 0.3, the

29 SEP 1998

- 10 -

maximum value in each case depending upon the molecular dimensions of the templating agent and the available void volume of the pore system of the particular SAPO species involved, and "x," "y," and "z" represent the mole fractions of silicon, aluminum, and phosphorous, respectively. As will be understood, the nature of SAPO catalysts means that any preselected silica-to-Me₂O₃ value may be used. Representative SAPO molecular sieves, as described in US-A-4,440,871, include SAPO-5, SAPO-11, SAPO-17, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-37, SAPO-40, SAPO-41, and SAPO-42.

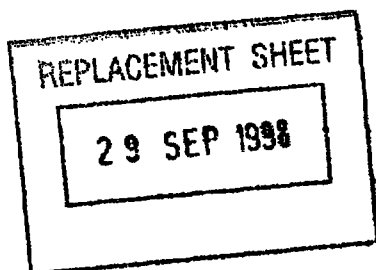
The ~~oxygenate~~ starting material or feed comprises hydrocarbons containing aliphatic moieties such as, but not limited to, alcohols, halides, mercaptans, sulfides, amines, ethers, and carbonyl compounds (aldehydes, ketones, carboxylic acids, and the like) or mixtures thereof. The aliphatic moiety preferably contains from about 1 to about 10 carbon atoms, and more preferably 1 to 4 carbon atoms. Thus the term "oxygenate starting material" is intended to mean not only what might be considered "true" oxygenates, e.g., alcohols, ethers, carbonyl compounds; but also those compounds which behave in a similar fashion to "true" oxygenates in the presence of the specified catalysts, such as substituted paraffins, e.g., halides, mercaptans, sulfides, amines. Representative oxygenates include methanol, isopropanol, n-propanol, ethanol, fuel alcohols, dimethyl ether, diethyl ether, methyl mercaptan, methyl sulfide, methyl amine, ethyl mercaptan, ethylchloride, formaldehyde, dimethylketone, acetic acid, n-alkylamines, n-alkylhalides, and n-alkylsulfides having alkyl groups of 1 to 10 carbon atoms or mixtures thereof. In a



preferred embodiment of the present invention, the feed comprises methanol. In another embodiment, the feed, e.g., methanol, contains a diluent. The addition of a diluent to the total feed charge decreases paraffin production relative to olefin production.

The term "~~oxygenate~~ starting material" or "~~oxygenate~~ feed" as employed in the present invention and described herein designates only the organic material used as the feed. However, the total charge to the reaction zone may contain additional compounds such as diluents. Use of a diluent as part of the feed, which is miscible with the oxygenate, imparts as a non-limiting example, a smaller propane to propylene ($C_3O/C_3=$) ratio than the use of essentially anhydrous oxygenate. However, even anhydrous oxygenates contain trace quantities of diluents. Even though the process described herein may employ a diluent, computable quantities of the oxygenate feed (i.e., composition and Weight Hourly Space Velocity (WHSV) are to be computed as an essentially diluent-free oxygenate feed unless otherwise stated.

The process is generally conducted in the presence of one or more diluents which may for example be present in the feed in an amount between about 1 and about 99 molar percent, based on the total number of moles of all feed and diluent components fed to the reaction zone (or catalyst). The amount of diluent added to the oxygenate feed will depend in part on the type of catalyst selected, the silica-to- Me_2O_3 ratio, and the reaction temperature. Preferably, the molar ratio of oxygenate feed-to-diluent (feed:diluent) is about 1:1 to about 1:4. Diluents include, but are not limited to, helium, argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, paraffins,

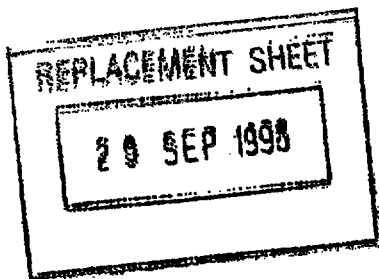


- 12 -

hydrocarbons (such as methane and the like), aromatic compounds, and mixtures thereof. Preferably, the diluent is water.

The instant process is preferably conducted in the vapor phase such that the oxygenate feed is contacted in the vapor phase in a reaction zone with the molecular sieve at effective process conditions to produce a paraffin/olefin, e.g., propane/propylene ratio characteristic of high purity olefins or polymer-grade propylene, i.e., an effective temperature, silica-to-Me₂O₃ ratio, pressure, WHSV and, optionally, an effective amount of diluent, correlated to produce high purity olefins or polymer-grade propylene. Alternatively, the process may be conducted in a liquid phase.

The process may be effectively carried out over a wide range of pressures including autogeneous pressures. At pressures between about 0.001 atmospheres (0.76 torr) and about 1000 atmospheres (760,000 torr), the formation of light olefin products will be effected although the optimum amount of product will not necessarily form at all pressures. The preferred pressure is between 0.01 atmospheres (7.6 torr) and 100 atmospheres (76,000 torr). The pressures referred to herein for the process are exclusive of the inert diluent, if any, that is present, and refer to the partial pressure of the feedstock as it relates to oxygenate compounds and/or mixtures thereof. Pressures outside the stated range are not excluded from the scope of this invention, although such pressures do not fall within certain desirable embodiments of the invention. At the lower and upper end of the pressure range, and beyond, the selectivities, conversions, and/or rates to light

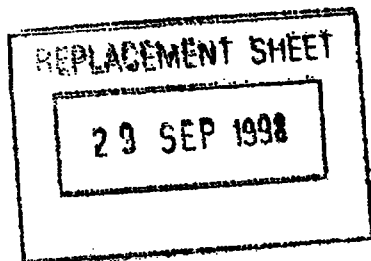


- 13 -

olefin products may not be optimal, although light olefins such as ethylene may still be formed.

The process is effected for a period of time sufficient to produce the desired light olefin (and high purity olefin) products. In general, the residence time employed to produce the desired product can vary from seconds to a number of hours. It will be readily appreciated that the residence time will be determined to a significant extent by the reaction temperature, the molecular sieve selected, the WHSV, the phase (liquid or vapor), and process design characteristics selected.

The olefin production process may be carried out in a batch, semi-continuous, or continuous fashion. The process can be conducted in a single reaction zone, or a number of reaction zones arranged in series or in parallel, or it may be conducted intermittently or continuously in an elongated tubular zone or a number of such zones. When multiple reaction zones are employed, it may be advantageous to employ one or more of such molecular sieves in series to provide for a desired product mixture. Owing to the nature of the process, it may be desirable to carry out the process of the present invention by use of the molecular sieve catalysts in a dynamic (e.g., fluidized or moving) bed system or any system of a variety of transport beds rather than in a fixed bed system. Such systems would readily provide for any regeneration (if required) of the molecular sieve catalyst after a given period of time. If regeneration is required, the molecular sieve catalyst can be continuously introduced as a moving bed to a regeneration zone where it can be regenerated, such as for example by removing carbonaceous materials or by oxidation in an oxygen-



- 14 -

~~carbonaceous materials or by oxidation in an oxygen~~ containing atmosphere. In the preferred practice of the invention, the catalyst will be subject to a regeneration step by the burning of carbonaceous deposits accumulated during reactions.

The effect of feedstock flow rate over molecular sieves is well known to those skilled in the art. Increasing the flow rate (WHSV) enhances olefin production relative to paraffin production. However, the enhanced olefin production relative to paraffin production is offset by a diminished conversion of oxygenate to hydrocarbons at the higher flow rates.

According to the invention, the process for conversion of an ~~oxygenate~~ feed to high purity olefins such as polymer-grade propylene using molecular sieves is for example conducted at temperatures of from approximately 350°C (662°F) to about 550°C (1022°F), preferably 450°C (842°F) to 550°C (1022°F), and more preferably at 440°C (824°F) to 460°C (860°F). The silica-to-Me₂O₃ molar ratio is preselected according to the type of molecular sieve employed, the reaction temperature used, and the degree of high purity olefin, e.g., polymer-grade propylene, production required. The WHSV of this reaction is for example approximately 0.01 hr.⁻¹ to about 100 hr.⁻¹, preferably 0.5 hr.⁻¹ to 10 hr.⁻¹, and more preferably 0.8 hr.⁻¹ to 1.2 hr.⁻¹. ~~For ZSM-5, at 0.8 hr.⁻¹ to 1.2 hr.⁻¹, approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur.~~

In the process using ZSM-48, which zeolite is described more fully in US-A-4,397,827, the process temperature is preferably 400°C to 550°C, and more preferably 440°C to 460°C. The preferred silica-to-Me₂O₃ molar ratio is 320 to 353.

29 SEP 1998

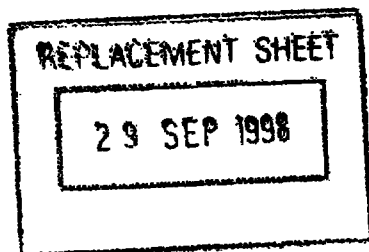
- 15 -

The WHSV of the process using ZSM-48 is preferably 0.5 hr.⁻¹ to 10 hr.⁻¹, and more preferably 0.8 hr.⁻¹ to 1.2 hr.⁻¹. With ZSM-48, at 0.8 hr.⁻¹ to 1.2 hr.⁻¹, approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur, comprising approximately 30% propylene and < 1% propane in the case where the olefin is propylene.

~~temperature is also preferably 400°C to 550°C, and more preferably 440°C to 460°C. The preferred silica-to-Me₂O₃ molar ratio is however from 300 to 2500, more preferably 320 to 353. The WHSV of the process using ZSM-48 is preferably 0.5 hr.⁻¹ to 10 hr.⁻¹, and more preferably 0.8 hr.⁻¹ to 1.2 hr.⁻¹. With ZSM-48, at 0.8 hr.⁻¹ to 1.2 hr.⁻¹, approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur, comprising approximately 30% propylene and < 1% propane in the case where the olefin is propylene.~~

In the process using FeZSM-5, which zeolite is described in US-A-4,843,183; the preferred process temperatures are as recited for ZSM-48. However, the silica-to-Me₂O₃ molar ratio is preferably from 332 to 368, more preferably about 350. The WHSV of the process using FeZSM-5 is preferably 0.1 hr.⁻¹ to 10 hr.⁻¹, more preferably 0.8 hr.⁻¹ to 1.2 hr.⁻¹. With ZSM-48 at 0.8 hr.⁻¹ to 1.2 hr.⁻¹, approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur, comprising approximately 25% propylene with no propane production, in the case where the olefin is propylene.

In the process using SAPO-34, which catalyst is described in US-A-4,440,871, the process for conversion of an oxygenate feed to high purity olefins such as polymer-grade propylene may be conducted ~~for example at temperatures of 350°C to 550°C, preferably~~



400°C to 550°C, and more preferably at 440°C to 460°C. The WHSV of this process is preferably from 0.1 hr.⁻¹ to 10 hr.⁻¹, and more preferably ~~0.1 hr.⁻¹ to 10 hr.⁻¹~~, and most preferably 0.8 hr.⁻¹ to 1.2 hr.⁻¹. With SAPO-34 at 0.8 hr.⁻¹ to 1.2 hr.⁻¹, approximately 98% to 100% conversion of the feed to hydrocarbons has been found to occur.

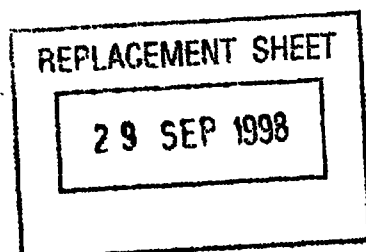
The following examples illustrate the invention.

Example 1

Zeolites ZSM-5, having silica-to-Me₂O₃ molar ratios (silica-to-alumina molar ratios) of 35, 350, and 1000 (determined stoichiometrically), were produced as described in US-A-3,702,886.

Each ZSM-5 was calcined at 510°C (950°F) and the calcined material was ion exchanged with an ammonium nitrate solution (85°C, 185°F; 12 hours). Generally, the ion exchange was repeated two or three times, with a calcination at 510°C (950°F) between each ion exchange step.

The catalytic conversion of methanol or methanol/water to hydrocarbons using each ZSM-5 having a preselected silica-to-alumina ratio of 35, 350, and 1000 was carried out in a fixed bed 1.27 cm (1/2") diameter, stainless steel reactor, equipped with a 0.32 cm (1/8") coiled preheater. In addition, the reactor was equipped with a 1/8" (0.32 cm) thermocouple well running axially through the reactor. The reactor was heated in an Applied Test Systems 3 zone tube furnace 30.5 cm (12") long; 3.18 cm (1 1/4") I.D.) having one reactor with three spaced zones. The first reactor zone is used as a preheater zone, and the catalyst bed is heated in the second reactor zone. The third reactor zone operates as a quench zone



- 17 -

maintained at a temperature of about 200°C (392°F) to about 300°C (572°F).

Generally, 2 grams (0.07 ounces) catalyst (-14/+20 mesh) were mixed with 2.5 grams (0.09 ounces) of quartz (-20/+60); the first and third reactor zone were filled with quartz chips (-10/+20 mesh). To improve the heat transfer between the second reactor zone (containing the catalyst bed) and the furnace heating coils, the second reactor zone was equipped with a cylindrical (10.2 cm (-4"); 3.18 cm (1¼") O.D.) aluminum or stainless steel block. This block contained a central hole in order to be able to measure the block temperature.

Gas flows (nitrogen or hydrogen) were controlled by mass flow controllers, while liquid feed rates were controlled by a Beckmann 114M pump or a Sage 341B syringe pump.

The product emerging from the reactor was analyzed on line for (i) carbon monoxide; carbon dioxide; water; dimethyl ether; methanol; C₁-C₃ hydrocarbons with a Porepack Q column using a thermal conductivity detector and (ii) C₁-A₁₀ hydrocarbons with a DB-1 column using a flame ionization detector. The feed was either methanol or methanol:water (1:1 or 1:4 molar ratio as denoted in Table I) at a WHSV=1.0 hr.⁻¹. The reaction was conducted at 450°C (842°F). The results are shown in Table I.

The same procedures as recited in Example 1, using the same equipment, conditions and measurement techniques, were employed with several different catalysts. These catalysts, and the analyses of the products made employing the process of the invention, are further described in Examples 2 - 4 and Table 1.

29 SEP 1998

- 18 -

Example 2

The zeolite ZSM-48, having a silica-to- Me_2O_3 molar ratio of 336 (determined by wet chemical analysis), was produced as described in US-A-4,423,021.

ZSM-48 was calcined at 510°C (950°F) and the calcined material was ion exchanged with ammonium nitrate solution (85°C , 185°F ; 12 hours). Generally, the ion exchange was repeated two or three times, with a calcination at 510°C (950°F) between each ion exchange step.

The feed was methanol:water (1:1 molar ratio) at a $\text{WHSV}=1.0 \text{ hr.}^{-1}$. The reaction was conducted at 450°C (842°F). The results are shown in Table I.

Example 3

The zeolite FeZSM-5, having a silica-to- Me_2O_3 ratio of 350 (determined stoichiometrically), was produced as described in US-A-4,843,183.

FeZSM-5 was calcined at 510°C (950°F) and the calcined material was ion exchanged with an ammonium nitrate solution (85°C , 185°F ; 12 hours). Generally, the ion exchange was repeated two or three times, with a calcination at 510°C (950°F) between each ion exchange step.

The feed was methanol:water (1:1 molar ratio) at a $\text{WHSV}=1.0 \text{ hr.}^{-1}$. The reaction was conducted at 450°C (842°F). The results are shown in Table I.

Example 4

SAPO-34 was calcined at 510°C (950°F) and the calcined material was ion exchanged with an ammonium nitrate solution (85°C , 185°F ; 12 hours). Generally, the ion exchange was repeated two or three times, with

29 SEP 1998

a calcination at 510°C (950°F) between each ion exchange step.

The feed was methanol:water (1:4 molar ratio) at a WHSV=1.0 hr.⁻¹. The reaction was conducted at 450°C (842°F). The results are shown in Table I.

Table I
Polymer-Grade Propylene Production

<u>Molecular Sieve</u>	<u>Silica-to-Me₂O₃</u>	<u>Feed/Diluent (molar ratio)</u>	<u>Propane/propylene (C₃O/C₃=)</u>
ZSM-5	35	Methanol/Water (1:1)	0.770**
ZSM-5	1000	Methanol (NA)	0.044
ZSM-5	350	Methanol/Water (1:4)	0.037
ZSM-5	1000	Methanol/Water (1:1)	0.000
ZSM-48	336	Methanol/Water (1:1)	0.038
Fe ZSM-5	350	Methanol/Water (1:1)	0.039
SAPO-34	NA*	Methanol/Water (1:4)	0.001

*NA signifies "not applicable."

** signifies comparative.

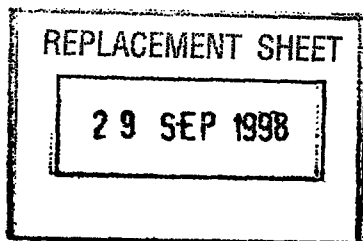
As shown in Table I, olefins are formed by contacting the oxygenate feed with a molecular sieve at a temperature of between 350°C (662°F) to 550°C (1022°F). By preselecting the silica-to-Me₂O₃ ratio and/or diluent, a product having a propane/propylene ratio characteristic of high purity olefins can be produced. This can be achieved without the need of superfractionation to remove propane.

29 SEP 1998

- 20 -

CLAIMS:

1. A process for selectively catalytically converting a starting material comprising an oxygenate, or a substituted paraffin which is a halide, a mercaptan, a sulfide or an amine, to high purity olefins, which process comprises contacting the starting material at a weight hourly space velocity (WHSV) of from 0.01^{hr.} to 100^{hr.}, and at a temperature of from 350°C to 550°C, with a molecular sieve catalyst comprising ZSM-48, a ferrosilicate zeolite or a silicoaluminophosphate (SAPO), which molecular sieve catalyst, in the case of ZSM-48 or ferrosilicate zeolites, has a silica-to-Me₂O₃ molar ratio (where Me is a Group IIIA or VIII element) of from 300 to 2500, and recovering the high purity olefins.
2. A process according to claim 1 wherein the temperature is from 450°C to 550°C, preferably from 440°C to 460°C.
3. A process according to claims 1 or 2 wherein the WHSV is from 0.01 hr.⁻¹ to 100 hr.⁻¹, preferably 0.5 hr.⁻¹ to 10 hr.⁻¹, more preferably 0.8 hr.⁻¹ to 1.2 hr.⁻¹.
- ~~4. A process according to any preceding claim wherein the molecular sieve catalyst comprises a crystalline aluminosilicate zeolite, a ferrosilicate zeolite or a silicoaluminophosphate (SAPO) catalyst.~~
4. A process according to any preceding claim, wherein the catalyst comprises ~~ZSM-5~~, ZSM-48, FeZSM-5 or SAPO-5, SAPO-11, SAPO-17, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-37, SAPO-40, SAPO-41, or SAPO-42 or a mixture of any two or more thereof.
- ~~6. A process according to any preceding claim wherein the silica-to-Me₂O₃ ratio of the catalyst is from 300 to 2500.~~



REPLACEMENT SHEET

- 21 -



5. A process according to claim 4, wherein (a) the catalyst is ZSM-~~48~~ and the ratio is from ~~350 to 2500~~, preferably from ~~950 to 1050~~; or ~~(b) the catalyst is ZSM-48 and the ratio is from 320 to 353~~; or (b) the catalyst is FeZSM-5 and the ratio is from 332 to 368, preferably about 350.

6. A process according to any preceding claim wherein the oxygenate starting material comprises ~~from the group consisting of methanol, ethanol, propanol, dimethyl ether, diethyl ether, and mixtures of any two or more thereof.~~

7. A process according to any preceding claim wherein the ~~oxygenate~~ starting material additionally comprises a diluent.

8. A process according to claim 7 wherein the diluent is water.

9. A process according to any preceding claim wherein the high purity olefin product comprises olefin and its corresponding paraffin in a paraffin to olefin weight ratio of not more than 0.05.

10. A process according to any preceding claim wherein the high purity olefin comprises polymer grade propylene containing not more than 5 wt%, preferably not more than 1 wt%, of propane.

11. A process according to any preceding claim wherein the high purity olefins are subjected to additional purification by superfractionation.

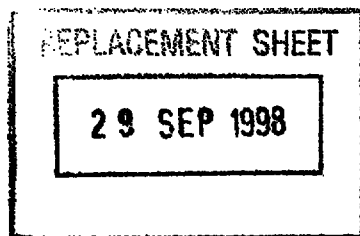
REPLACEMENT SHEET

23 SEP 1998



- 22 -

12. The use of (a) ZSM-~~40~~ having a silica-to-Me₂O₃ ratio of from 300 to 2500, preferably from 320 to 353 ; or (b) FeZSM-5 having such ratio of from 332 to 368 , ~~preferably from 320 to 353~~ ; or (c) ~~Fe~~ZSM-5 ~~having such ratio of from 332 to 368~~ ; or (c) a silicoaluminophosphate (SAPO), as catalyst for selectively converting a starting material comprising an oxygenate or a substituted paraffin which is a halide, a mercaptan, a sulfide or an amine, to high purity olefins by the process as defined in Claim 1.



REPLACEMENT SHEET

- 23 -

PRODUCTION OF HIGH PURITY OLEFINS

ABSTRACT

A process for converting an oxygenate feed to high purity olefins such as polymer-grade propylene ($C_3O/C_3 = \leq 0.05$) at a temperature of about 450 °C (842 °F), using a molecular sieve catalyst having a high preselected Si/Al₂ ratio (such as ZSM-5, ZSM-48) or preselected Si/Fe₂ ratio (such as FeZSM-5), or SAPO-34.