TREATMENT OF AIR TO A CATALYST REGENERATOR TO MAINTAIN CATALYST ACTIVITY

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a conversion process for making olefin(s) using a molecular sieve catalyst composition in the presence of a hydrocarbon feedstock. More particularly, the present invention relates to a conversion process for making light olefins in a high salt environment by removing salts from the air being fed to a catalyst regenerator.

[0002] Olefins are traditionally produced from petroleum feedstock by catalytic or steam cracking processes. These cracking processes, especially steam cracking, produce light olefins such as ethylene or propylene from a variety of hydrocarbon feedstocks. Ethylene and propylene are important commodity petrochemicals useful in a variety of processes for making plastics and other chemical compounds.

[0003] The petrochemical industry has known for some time that oxygenates, especially alcohols, are convertible into light olefins. There are numerous technologies available for producing oxygenates including fermentation or reaction of synthesis gas derived from natural gas, petroleum liquids, carbonaceous materials including coal, recycled plastics, municipal waste or any other organic material.

[0004] The preferred methanol conversion process is generally referred to as a methanol-to-olefin process, where methanol is converted primarily to ethylene and/or propylene in the presence of a molecular sieve. Molecular sieves have a crystalline pore structure with uniform sized pores of molecular dimensions that selectively adsorb molecules that can enter the pores, and exclude those molecules that are too large.

[0005] There are many different types of molecular sieves to convert a feedstock, especially an oxygenate containing feedstock, into one or more olefins. For example, US 4,310,440 describes producing light olefin(s) from an alcohol using crystalline aluminophosphates, often represented by $ALPO_4$. The most useful molecular sieves for converting methanol to olefin(s) are silicoaluminophosphate molecular sieves. Silicoaluminophosphate (SAPO) molecular sieves contain a three-dimensional microporous crystalline framework structure of $[SiO_2]$, $[AlO_2]$ and $[PO_2]$ corner sharing tetrahedral units. SAPO molecular sieves have been found to be useful in converting hydrocarbon feedstocks

into light olefin(s), particularly where the feedstock is methanol. See for example, US 4,440,871; US 4,499,327; US 4,677,242; US 4,677,243; US 4,873,390; US 5,095,163; US 5,714,662 and US 6,166,282.

[0006] These molecular sieves have been found to be sensitive to various contaminants resulting in the lowering of the yield of light olefins and even affecting the operability of a conversion process. Such contaminants are introduced to a particular conversion process in a variety of ways. Sometimes the molecular sieve itself produces contaminants affecting the conversion performance of the molecular sieve. In addition, in large scale processes, it is more likely that the effect of various contaminants entering into commercial conversion processes is higher. Contaminants can be introduced into the oxygenate feedstock or in the air that is introduced, especially into the catalyst regeneration unit. Unfortunately, it has been found that contaminants such as salts become concentrated over time to the extent that olefin yields are significantly impacted.

[0007] Therefore, it would be highly desirable to control contamination so as not to adversely affect the molecular sieve catalyst. Controlling contamination is particularly desirable in oxygenate to olefin reactions, particularly in methanol to olefin reactions, where feedstocks and catalysts are relatively expensive. It has been previously reported by Janssen et al. in US 2004/0034264 A1 and US 2004/0034265 A1, that feedstocks need to be free or substantially free of salts. However, it has now been found that serious damage to the catalyst can be caused by exposure of the catalyst to the sodium chloride that is present in the air in coastal areas such as where petrochemical plants are frequently located. The present invention provides a process to protect the catalyst from harm from this and other salts that may be unexpectedly present in the air entering the reactor and particularly regarding air entering the catalyst regeneration vessel.

SUMMARY OF THE INVENTION

[0008] In one embodiment, the present invention relates to a process of regenerating a molecular sieve catalyst comprising: introducing a spent molecular sieve catalyst into a regeneration vessel; introducing a flow of gas into said regeneration vessel, wherein said gas comprises 0 to 100 ppb sodium; and heating said molecular sieve catalyst for a sufficient period of time and at a sufficient temperature to regenerate said molecular sieve catalyst.

[0009] This invention provides for a process for converting a feedstock in the presence of a molecular sieve into one or more olefin(s), while controlling contamination of the catalyst. Contamination of the catalyst can be controlled by providing a regeneration air feed having an appropriately low content of salt.

[0010] The invention is directed to a process for converting a feedstock in the presence of a molecular sieve into one or more olefin(s). Preferably the feedstock comprises an oxygenate such as an alcohol and/or an ether, for example methanol and/or dimethyl ether. The preferred molecular sieve is synthesized from a combination of at least two, preferably at least three, of the group consisting of a silicon source, a phosphorous source and an aluminum source, optionally in the presence of a templating agent. In the most preferred embodiment, the molecular sieve is a silicoaluminophosphate or aluminophosphate, most preferably a silicoaluminophosphate.

[0011] In the practice of the present invention, there is provided a process for converting oxygenates to olefins, which comprises contacting the oxygenate composition with a molecular sieve to convert such oxygenates to olefins. These molecular sieve catalysts require periodic regeneration in order to maintain the catalyst activity. The catalyst regenerators need to have a stream of air entering the regenerator since the most common method for regeneration is to burn off carbonaceous deposits on the catalyst, so that oxygen is necessary. It has been found advantageous to remove salt from the air entering the regenerator. There are several effective methods for removing the salt. The air stream may be passed through a cooler in which water condenses and salt is removed along with the water. Another method for removing the salt is to pass the air stream over an adsorbent bed in which again water is removed as well as salts and other contaminants.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The invention is directed toward a conversion process of a hydrocarbon feedstock, particularly methanol, in the presence of molecular sieve catalyst composition to one or more olefin(s). In this invention, gas fed to a catalyst regeneration unit is low in contaminants and particularly low in salts, so as not to significantly have an adverse effect on catalyst life or selectivity to desired product.

[0013] According to this invention, some reduction in catalyst life is acceptable as a result of regeneration air containing contaminants, particularly contaminants that are present

in the regeneration air due to exposure to seawater. These contaminants are more particularly the Group IA and/or Group IIA metal contaminants such as sodium, lithium or potassium ions and even more particularly, sodium ions. Generally, it is preferred that catalyst life be reduced by an amount of not greater than 20% relative to that of a regeneration air containing a low level of contaminants. Preferably, catalyst life is reduced by an amount of not greater, than 15%, more preferably not greater than 10% relative to that of a regeneration gas containing a low level of contaminants. The typical life for a given quantity of catalyst is a number of months or even years.

[0014] Molecular sieves have various chemical and physical, framework, characteristics. Molecular sieves have been well classified by the Structure Commission of the International Zeolite Association according to the rules of the IUPAC Commission on Zeolite Nomenclature. A framework-type describes the connectivity, topology, of the tetrahedrally coordinated atoms constituting the framework, and making an abstraction of the specific properties for those materials. Framework-type zeolite and zeolite-type molecular sieves for which a structure has been established, are assigned a three letter code and are described in the ATLAS OF ZEOLITE FRAMEWORK TYPES, 5th edition, Elsevier, London, England (2001), which is herein fully incorporated by reference.

[0015] Examples of these molecular sieves are the small pore molecular sieves, AEI, AFT, APC, ATN, ATT, ATV, AWW, BIK, CAS, CHA, CHI, DAC, DDR, EDI, ERI, GOO, KFI, LEV, LOV, LTA, MON, PAU, PHI, RHO, ROG, THO, and substituted forms thereof; the medium pore molecular sieves, AFO, AEL, EUO, HEU, FER, MEL, MFI, MTW, MTT, TON, and substituted forms thereof; and the large pore molecular sieves, EMT, FAU, and substituted forms thereof. Other molecular sieves include ANA, BEA, CFI, CLO, DON, GIS, LTL, MER, MOR, MWW and SOD. Non-limiting examples of the preferred molecular sieves, particularly for converting an oxygenate containing feedstock into olefin(s), include AEI, AEL, AFY, BEA, CHA, EDI, FAU, FER, GIS, LTA, LTL, MER, MFI, MOR, MTT, MWW, TAM and TON. In the preferred embodiment, the molecular sieve has an AEI topology or a CHA topology, or a combination thereof, most preferably a CHA topology.

[0016] The small, medium and large pore molecular sieves have from a 4-ring to a 12-ring or greater framework-type. In a preferred embodiment, the zeolitic molecular sieves have 8-, 10- or 12-ring structures or larger and an average pore size in the range of from 3 to 15 angstroms. In the most preferred embodiment, the molecular sieves of the invention,

preferably silicoaluminophosphate molecular sieves have eight rings and an average pore size less than 5 angstroms, preferably in the range of from 3 to 5 angstroms, more preferably from 3 to 4.5 angstroms, and most preferably from 3.5 to 4.2 angstroms.

[0017] The more preferred silicon, aluminum and/or phosphorous containing molecular sieves, and aluminum, phosphorous, and optionally silicon, containing molecular sieves include aluminophosphate (ALPO) molecular sieves and silicoaluminophosphate (SAPO) molecular sieves and substituted, preferably metal substituted, ALPO and SAPO molecular sieves. The most preferred molecular sieves are SAPO molecular sieves, and metal substituted SAPO molecular sieves. The metal is selected from the group consisting of Co, Cr, Cu, Fe, Ga, Ge, Mg, Mn, Ni, Sn, Ti, Zn and Zr, and mixtures thereof. In another preferred embodiment, these metal atoms discussed above are inserted into the framework of a molecular sieve through a tetrahedral unit, such as $[MeO_2]$, and carry a net charge depending on the valence state of the metal substituent. For example, in one embodiment, when the metal substituent has a valence state of +2, +3, +4, +5, or +6, the net charge of the tetrahedral unit is between -2 and +2.

[0018] The molecular sieve, as described in many U.S. patents, is represented by the empirical formula, on an anhydrous basis:

$$mR: (M_xAl_yP_z)O_2$$

wherein R represents at least one templating agent, preferably an organic templating agent; m is the number of moles of R per mole of $(M_xAl_yP_z)O_2$ and m has a value from 0 to 1, preferably 0 to 0.5, and most preferably from 0 to 0.3; x, y, and z represent the mole fraction of Al, P and M as tetrahedral oxides, where M is a metal selected from one of Group IA, IIA, IB, IIIB, IVB, VB, VIB, VIIB, VIIIB and Lanthanides of the Periodic Table of Elements, preferably M is selected from one of the group consisting of Co, Cr, Cu, Fe, Ga, Ge, Mg, Mn, Ni, Sn, Ti, Zn and Zr. In one embodiment, m is greater than or equal to 0.2, and x, y and z are greater than or equal to 0.0 1. In another embodiment, m is greater than 0.1 to 1, x is greater than 0 to 0.25, y is in the range of from 0.4 to 0.5, and z is in the range of from 0.25 to 0.5, more preferably m is from 0.15 to 0.7, x is from 0.01 to 0.2, y is from 0.4 to 0.5, and z is from 0.3 to 0.5.

[0019] Examples of SAPO and ALPO molecular sieves of the invention include one or a combination of SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42,

SAPO-44 (US 6,162,415), SAPO-47, SAPO-56, ALPO-5, ALPO-11, ALPO-18, ALPO-31, ALPO-34, ALPO-36, ALPO-37, ALPO-46, and metal-containing molecular sieves thereof. The more preferred zeolite-type molecular sieves include one or a combination of SAPO-18, SAPO-34, SAPO-35, SAPO-44, SAPO-56, ALPO-18 and ALPO-34, even more preferably one or a combination of SAPO-18, SAPO-34, ALPO-34 and ALPO-18, and metal containing molecular sieves thereof, and most preferably one or a combination of SAPO-34 and ALPO-18, and metal-containing molecular sieves thereof.

[0020] The molecular sieve is an intergrowth material having two or more distinct phases of crystalline structures within one molecular sieve composition. For example, SAPO-18, ALPO-18 and RUW-18 have an AEI framework-type, and SAPO-34 has a CHA framework-type. In another embodiment, the molecular sieve comprises at least one intergrown phase of AEI and CHA framework-types, preferably the molecular sieve has a greater amount of CHA framework-type to AEI framework-type, and more preferably the ratio of CHA to AEI is greater than 1:1. Most preferably, the ratio of CHA to AEI is greater than 6:4.

[0021] Synthesis of molecular sieves is described in many of the references discussed above and is well known in the art. Generally, molecular sieves are synthesized by the hydrothermal crystallization of one or more of a source of aluminum, a source of phosphorous, and a source of silicon, a templating agent, and a metal containing compound. Typically, a combination of sources of silicon, aluminum and phosphorous, optionally with one or more templating agents and/or one or more metal containing compounds are placed in a sealed pressure vessel, optionally lined with an inert plastic such as polytetrafluoroethylene, and heated, under a crystallization pressure and temperature, until a crystalline material is formed, and then recovered by filtration, centrifugation and/or decanting.

[0022] The molecular sieves are synthesized by forming a reaction product of a source of silicon, a source of aluminum, a source of phosphorous, an organic templating agent, preferably a nitrogen containing organic templating agent. This particularly preferred embodiment results in the synthesis of a silicoaluminophosphate crystalline material that is then isolated by filtration, centrifugation and/or decanting.

[0023] A preferred source of aluminum is pseudo-boehmite, particularly when producing a silicoaluminophosphate molecular sieve. The preferred source of phosphorous is phosphoric acid, particularly when producing a silicoaluminophosphate.

[0024] Templating agents are generally compounds that contain elements of Group VB of the Periodic Table of Elements, particularly nitrogen, phosphorus, arsenic and antimony, more preferably nitrogen or phosphorous, and most preferably nitrogen. Such templating agents also contain at least one alkyl or aryl group, preferably an alkyl or aryl group having from 1 to 10 carbon atoms, and more preferably from 1 to 8 carbon atoms. The preferred templating agents are nitrogen-containing compounds such as amines and quaternary ammonium compounds.

[0025] In one embodiment, the templating agents include a combination of one or more quaternary ammonium compound(s) and one or more of a mono-, di- or tri-amine.

[0026] The preferred templating agent or template is a tetraethylammonium compound, such as tetraethyl ammonium hydroxide (TEAOH), tetraethyl ammonium phosphate, tetraethyl ammonium fluoride, tetraethyl ammonium bromide, tetraethyl ammonium chloride and tetraethyl ammonium acetate. The most preferred templating agent is tetraethyl ammonium hydroxide and salts thereof, particularly when producing a silicoaluminophosphate molecular sieve. In some instances, a combination of two or more of any of the above templating agents is used in combination with one or more of a silicon-, aluminum-, and phosphorous-source.

[0027] In one embodiment, when a templating agent is used in the synthesis of a molecular sieve, the templating agent is substantially, preferably completely, removed after crystallization by numerous well known techniques, for example, heat treatments such as calcination

[0028] Molecular sieves may have either a high silicon (Si) to aluminum (Al) ratio or a low silicon to aluminum ratio, however, a low Si/Al ratio is preferred for SAPO synthesis

[0029] Once the molecular sieve is synthesized, depending on the requirements of the particular conversion process, the molecular sieve is then formulated into a molecular sieve catalyst composition, particularly for commercial use. The molecular sieves synthesized above are made or formulated into molecular sieve catalyst compositions by combining the synthesized molecular sieve(s) with a binder and optionally, but preferably, a matrix material to form a molecular sieve catalyst composition or a formulated molecular sieve catalyst composition. This formulated molecular sieve catalyst composition is formed into useful shape and sized particles by well-known techniques such as spray drying, pelletizing, extrusion, and the like.

[0030] There are many different binders that are useful in forming the molecular sieve catalyst composition. Examples of binders that are useful alone or in combination include various types of hydrated alumina, silicas, and/or other inorganic oxide sol. One preferred alumina containing sol is aluminum chlorohydrate.

[0031] The molecular sieve described above, in a preferred embodiment, is combined with one or more matrix material(s). Matrix materials are typically effective in reducing overall catalyst cost, act as thermal sinks assisting in shielding heat from the catalyst composition for example during regeneration, densifying the catalyst composition, increasing catalyst strength such as crush strength and attrition resistance, and to control the rate of conversion in a particular process.

[0032] Non-limiting examples of matrix materials include one or more of: rare earth metals, non-active, metal oxides including titania, zirconia, magnesia, thoria, beryllia, quartz, silica or sols, and mixtures thereof, for example silica-magnesia, silica-zirconia, silica-titania, silica-alumina and silica-alumina-thoria. In an embodiment, matrix materials are natural clays such as those from the families of montmorillonite and kaolin.

[0033] In one preferred embodiment, the matrix material is a clay or a clay-type composition, preferably the clay or clay-type composition having a low iron or titania content, and most preferably the matrix material is kaolin.

[0034] In one embodiment, the slurry of the molecular sieve, the binder and the matrix materials is mixed or milled to achieve a sufficiently uniform slurry of sub-particles of the molecular sieve catalyst composition that is then fed to a forming unit that produces the molecular sieve catalyst composition in the form of microspheres.

[0035] Once the molecular sieve catalyst composition is formed in a substantially dry or dried state, to further harden and/or activate the formed catalyst composition, a heat treatment such as calcination, at an elevated temperature is usually performed. A conventional calcination environment is air that typically includes a small amount of water vapor. Typical calcination temperatures are in the range from 400° to 1000°C, preferably from 500° to 800°C, and most preferably from 550° to 700°C, preferably in a calcination environment such as air, nitrogen, helium, flue gas (combustion product lean in oxygen), or any combination thereof. Calcination time is typically dependent on the degree of hardening of the molecular sieve catalyst composition and the temperature ranges from 15 minutes to 20 hours, preferably 1 hour to 2 hours. In a preferred embodiment, the molecular sieve catalyst

composition is heated in nitrogen at a temperature of from 600° to 700°C. Heating is carried out for a period of time typically from 30 minutes to 15 hours, preferably from 1 hour to 10 hours, more preferably from 1 hour to 5 hours, and most preferably from 2 hours to 4 hours.

[0036] The molecular sieve catalyst compositions described above are useful in a variety of processes including: cracking, of for example a naphtha feed to light olefin(s) or higher molecular weight (MW) hydrocarbons to lower MW hydrocarbons; hydrocracking, of for example heavy petroleum and/or cyclic feedstock; isomerization, of for example aromatics such as xylene, polymerization, of for example one or more olefin(s) to produce a polymer product; reforming; hydrogenation; dehydrogenation; dewaxing, of for example hydrocarbons to remove straight chain paraffins; absorption, of for example alkyl aromatic compounds for separating out isomers thereof; alkylation, of for example aromatic hydrocarbons such as benzene and alkyl benzene, optionally with propylene to produce cumene or with long chain olefins; transalkylation, of for example a combination of aromatic and polyalkylaromatic hydrocarbons; dealkylation; hydrodecylization; disproportionation, of for example toluene to make benzene and paraxylene; oligomerization, of for example straight and branched chain olefin(s); and dehydrocyclization.

[0037] Preferred processes are conversion processes including: naphtha to highly aromatic mixtures; light olefin(s) to gasoline, distillates and lubricants; oxygenates to olefin(s); light paraffins to olefins and/or aromatics; and unsaturated hydrocarbons (ethylene and/or acetylene) to aldehydes for conversion into alcohols, acids and esters. The most preferred process of the invention is a process directed to the conversion of a feedstock comprising one or more oxygenates to one or more olefin(s).

[0038] The molecular sieve catalyst compositions described above are particularly useful in conversion processes of different feedstock. Typically, the feedstock contains one or more aliphatic-containing compounds that include alcohols, amines, carbonyl compounds for example aldehydes, ketones and carboxylic acids, ethers, halides, mercaptans, sulfides, and the like, and mixtures thereof. The aliphatic moiety of the aliphatic-containing compounds typically contains from 1 to 50 carbon atoms, preferably from 1 to 20 carbon atoms, more preferably from 1 to 10 carbon atoms, and most preferably from 1 to 4 carbon atoms.

[0039] Non-limiting examples of aliphatic-containing compounds include: alcohols such as methanol and ethanol, alkyl-mercaptans such as methyl mercaptan and ethyl mercaptan, alkyl-sulfides such as methyl sulfide, alkyl-amines such as methyl amine, alkyl-ethers such as

dimethyl ether, diethyl ether and methylethyl ether, alkyl-halides such as methyl chloride and ethyl chloride, alkyl ketones such as dimethyl ketone, formaldehydes, and various acids such as acetic acid.

[0040] In a preferred embodiment of the process of the invention, the feedstock contains one or more oxygenates, more specifically, one or more organic compound(s) containing at least one oxygen atom. In the most preferred embodiment of the process of invention, the oxygenate in the feedstock is one or more alcohol(s), preferably aliphatic alcohol(s) where the aliphatic moiety of the alcohol(s) has from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms, and most preferably from 1 to 4 carbon atoms. The alcohols useful as feedstock in the process of the invention include lower straight and branched chain aliphatic alcohols and their unsaturated counterparts. In the most preferred embodiment, the feedstock is selected from one or more of methanol, ethanol, dimethyl ether, diethyl ether or a combination thereof, more preferably methanol and dimethyl ether, and most preferably methanol.

[0041] The feedstock containing an oxygenate, more particularly a feedstock containing an alcohol, is converted primarily into one or more olefin(s). The olefin(s) or olefin monomer(s) produced from the feedstock typically have 2 to 4 carbons atoms, with some higher carbon byproducts, and most preferably are ethylene and/or propylene.

[0042] In the most preferred embodiment, the oxygenate feedstock, preferably an alcohol, most preferably methanol, is converted to the preferred olefin(s) ethylene and/or propylene.

[0043] There are many processes used to convert feedstock into olefin(s) including various cracking processes such as steam cracking, thermal regenerative cracking, fluidized bed cracking, fluid catalytic cracking, deep catalytic cracking, and visbreaking. The most preferred process is generally referred to as gas-to-olefins (GTO) or alternatively, methanol-to-olefins (MTO). In an MTO process, typically an oxygenated feedstock, most preferably a methanol containing feedstock, is converted in the presence of a molecular sieve catalyst composition thereof into one or more olefin(s), preferably and predominantly, ethylene and/or propylene, often referred to as light olefin(s).

[0044] The process for conversion of an oxygenate feedstock typically produces an amount of olefin(s) produced based on the total weight of hydrocarbon produced that is greater than 50 wt-%, preferably greater than 60 wt-%, more preferably greater than 70 wt-%, and most preferably greater than 75 wt-%.

[0045] The feedstock often contains one or more diluent(s), typically used to reduce the concentration of the feedstock, that are generally non-reactive to the feedstock or molecular sieve catalyst composition. The most preferred diluents are water and nitrogen, with water being particularly preferred.

[0046] The diluent, water, is used either in a liquid or a vapor form, or a combination thereof. The diluent is either added directly to a feedstock entering into a reactor or added directly into a reactor, or added with a molecular sieve catalyst composition. The amount of diluent in the feedstock is in the range of from 1 to 99 mol-% based on the total number of moles of the feedstock and diluent.

[0047] In one embodiment, other hydrocarbons are added to a feedstock either directly or indirectly, and include olefin(s), paraffin(s), aromatic(s) (see for example US 4,677,242, addition of aromatics) or mixtures thereof, preferably propylene, butylene, pentylene, and other hydrocarbons having 4 or more carbon atoms, or mixtures thereof.

[0048] The process for converting a feedstock, especially a feedstock containing one or more oxygenates, in the presence of a molecular sieve catalyst composition of the invention, is carried out in a reaction process in a reactor, where the process is a fixed bed process, a fluidized bed process (includes a turbulent bed process), preferably a continuous fluidized bed process, and most preferably a continuous high velocity fluidized bed process.

[0049] The reaction processes can take place in a variety of catalytic reactors such as hybrid reactors that have a dense bed or fixed bed reaction zones and/or fast fluidized bed reaction zones coupled together, circulating fluidized bed reactors, riser reactors, and the like. Suitable conventional reactor types are described in for example US 4,076,796, US 6,287,522 (dual riser), and Fluidization Engineering, D. Kunii and O. Levenspiel, Robert E. Krieger Publishing Company, New York, New York 1977. In the preferred embodiment, a fluidized bed process or high velocity fluidized bed process includes a reactor system, a regeneration system and a recovery system.

[0050] The reactor system preferably is a fluid bed reactor system having a first reaction zone within one or more riser reactor(s) and a second reaction zone within at least one disengaging vessel, preferably comprising one or more cyclones. In one embodiment, the one or more riser reactor(s) and disengaging vessel is contained within a single reactor vessel. Fresh feedstock, preferably containing one or more oxygenates, optionally with one or more diluent(s), is fed to the one or more riser reactor(s) in which a molecular sieve catalyst

composition or coked version thereof is introduced. In one embodiment, the molecular sieve catalyst composition or coked version thereof is contacted with a liquid or gas, or combination thereof, prior to being introduced to the riser reactor(s), preferably the liquid is water or methanol, and the gas is an inert gas such as nitrogen.

[0051] In an embodiment, the amount of fresh liquid fed separately or jointly with a vapor feedstock, to a reactor system is in the range of from 0.1 to 85 wt.

[0052] The feedstock entering the reactor system is preferably converted, partially or fully, in the first reactor zone into a gaseous effluent that enters the disengaging vessel along with a coked molecular sieve catalyst composition. Cyclone(s) or other separation devices within the disengaging vessel are designed to separate the coked molecular sieve catalyst composition, from the gaseous effluent containing one or more olefin(s) within the disengaging zone.

[0053] The conversion temperature employed in the conversion process, specifically within the reactor system, is in the range of from 200° to 1000°C, preferably from 250° to 800°C, most preferably from 350° to 550°C.

[0054] The conversion pressure employed in the conversion process, specifically within the reactor system, varies over a wide range including autogenous pressure. The conversion pressure is based on the partial pressure of the feedstock exclusive of any diluent therein. Typically the conversion pressure employed in the process is in the range of from 0.1 kPa to 5 MPa.

[0055] The weight hourly space velocity (WHSV), particularly in a process for converting a feedstock containing one or more oxygenates in the presence of a molecular sieve catalyst composition within a reaction zone, is defined as the total weight of the feedstock excluding any diluents to the reaction zone per hour per weight of molecular sieve in the molecular sieve catalyst composition in the reaction zone. The WHSV is maintained at a level sufficient to keep the catalyst composition in a fluidized state within a reactor.

[0056] Typically, the WHSV ranges from 1 to 5000 hr^{-1} preferably the WHSV for conversion of a feedstock containing methanol and dimethyl ether is in the range of from 20 to 300 hr^{-1}.

[0057] The superficial gas velocity (SGV) of the feedstock including diluent and reaction products within the reactor system is preferably sufficient to fluidize the molecular sieve catalyst composition within a reaction zone in the reactor. The SGV in the process,

particularly within the reactor system, more particularly within the riser reactor(s), is at least 0.1 meter per second (m/sec) and preferably greater than 4 m/sec.

[0058] The coked molecular sieve catalyst composition is withdrawn from the disengaging vessel, preferably by one or more cyclones(s), and introduced to the regeneration system. The regeneration system comprises a regenerator where the coked catalyst composition is contacted with a regeneration medium, preferably a gas containing oxygen, under general regeneration conditions of temperature, pressure and residence time. Non-limiting examples of the regeneration medium include one or more of oxygen, O_3, SO_3, N_2O, NO, NO_2, N_2O_5, air, air diluted with nitrogen or carbon dioxide, oxygen and water (US 6,245,703), carbon monoxide and/or hydrogen. The regeneration conditions are those capable of burning coke from the coked catalyst composition, preferably to a level less than 0.5 wt-% based on the total weight of the coked molecular sieve catalyst composition entering the regeneration system. The coked molecular sieve catalyst composition withdrawn from the regenerator forms a regenerated molecular sieve catalyst composition. Air being fed to a catalyst regenerator can be dried to reduce the level of hydrothermal damage on the catalyst due to the combination of moisture and high temperatures. For example, if the inlet air is humid with 4.0 mol-% moisture content, the outlet gas from a regenerator will contain 7.5 mol-% moisture. At 625°C, exposure of the catalyst to this hot and humid gas may result in a relative activity loss of 0.4 to 0.6% per day. However, if the inlet air is dried, the offgas from the regenerator will only contain 3.5 mol-% moisture. At 625°C, exposure of the catalyst to these conditions will result in a relative activity loss of 0.1 to 0.3% per day.

[0059] Air entering the regeneration vessel can also be a significant source of undesired salt. For example, if the air salinity contains 0.5 ppm sodium, over time without catalyst withdrawals or additions, the level of sodium on the catalyst could reach 4500 wt ppm, which would result in a significant loss of active sites. Preferably, the air salinity is from 0 to 100 wt-ppb sodium. If, for example, the air salinity can be reduced to 30 wt ppb, the buildup of sodium on the catalyst under similar conditions would be only 20 to 250 wt ppm, which has no significant effect on the activity of the catalyst. Most preferably, the air salinity is less than 30 wt-ppb sodium. For long-term catalyst stability, it is desirable to maintain the sodium level that builds up on the catalyst below 500 wt-ppm.

[0060] Various means are available to reduce the moisture and the salinity in the inlet air. For example, if the air is cooled down sufficiently, excess moisture will condense out and the

air salinity will be entrained with the condensate. This is especially useful in treating the air going to cryogenic air separation plants, or similar, such that a side stream can be recovered for use as catalyst regenerent.

[0061] Adsorptive means can also be used, either in the form of low pressure drop fixed bed adsorbents that will remove both moisture and entrained aerosols of saline particles, and the adsorbent can later be regenerated, or also in the form of "drying wheels" in which the moist, saline air flows axially through a segment of a circular device loaded with a suitable adsorbent, while another segment of the device is undergoing regeneration – by slowly rotating such devices a continuous and simultaneous adsorptive and regenerative effect can be accomplished.

[0062] The regeneration temperature is in the range of from 200° to 1500°C and the regeneration pressure is in the range of from 103 to 3448 kPa. The preferred residence time of the molecular sieve catalyst composition in the regenerator is in the range of from one minute to several hours, most preferably one minute to 100 minutes, and the preferred volume of oxygen in the gas exiting the regenerator is in the range of from 0.01 to 5 mol-% based on the total volume of the gas.

[0063] The burning of coke is an exothermic reaction so that the temperature within the regeneration system is controlled by various techniques in the art. A preferred technique involves withdrawing the regenerated molecular sieve catalyst composition from the regeneration system and passing the regenerated molecular sieve catalyst composition through a catalyst cooler that forms a cooled regenerated molecular sieve catalyst composition.

[0064] The regenerated molecular sieve catalyst composition withdrawn from the regeneration system, preferably from the catalyst cooler, is combined with a fresh molecular sieve catalyst composition and/or re-circulated molecular sieve catalyst composition and/or feedstock and/or fresh gas or liquids, and returned to the riser reactor(s). In another embodiment, the regenerated molecular sieve catalyst composition withdrawn from the regeneration system is returned to the riser reactor(s) directly, preferably after passing through a catalyst cooler.

[0065] By controlling the flow of the regenerated molecular sieve catalyst composition or cooled regenerated molecular sieve catalyst composition from the regeneration system to the reactor system, the optimum level of coke on the molecular sieve catalyst composition

entering the reactor is maintained. Typical levels of coke on the molecular sieve catalyst composition, after regeneration is in the range of from 0.01 to 15 wt-%, and preferably from 0.3 to 2 wt-% based on the total weight of the molecular sieve and not the total weight of the molecular sieve catalyst composition.

[0066] The gaseous effluent is from the reaction zone is withdrawn from the disengaging system and is passed through a recovery system. There are many well known recovery systems, techniques and sequences that are useful in separating olefin(s) and purifying olefin(s) from the gaseous effluent. Recovery systems generally comprise one or more or a combination of a various separation, fractionation and/or distillation towers, columns, splitters, or trains, reaction systems such as ethylbenzene manufacture and other derivative processes such as aldehydes, ketones and ester manufacture.

[0067] The preferred light olefin(s) produced by any one of the processes described above are high purity prime olefin(s) products that contains a single carbon number olefin in an amount greater than 80 wt-%, preferably greater than 90 wt-%, more preferably greater than 95 wt-%, and most preferably no less than 99 wt-%, based on the total weight of the olefin.

[0068] Polymerization processes for conversion of the olefin products include solution, gas phase, slurry phase and a high pressure processes, or a combination thereof. Particularly preferred is a gas phase or a slurry phase polymerization of one or more olefin(s) at least one of which is ethylene or propylene. These polymerization processes utilize a polymerization catalyst that can include any one or a combination of the molecular sieve catalysts discussed above, however, the preferred polymerization catalysts are those Ziegler-Natta, Phillips-type, metallocene, metallocene-type and advanced polymerization catalysts, and mixtures thereof. The polymers produced by the polymerization processes described above include linear low density polyethylene, elastomers, plastomers, high density polyethylene, low density polyethylene, polypropylene and polypropylene copolymers. The propylene based polymers produced by the polymerization processes include atactic polypropylene, isotactic polypropylene, syndiotactic polypropylene, and propylene random, block or impact copolymers.

[0069] In preferred embodiment, the integrated process comprises a polymerizing process of one or more olefin(s) in the presence of a polymerization catalyst system in a polymerization reactor to produce one or more polymer products, wherein the one or more

olefin(s) having been made by converting an alcohol, particularly methanol, using a molecular sieve catalyst composition. The preferred polymerization process is a gas phase polymerization process and at least one of the olefins(s) is either ethylene or propylene, and preferably the polymerization catalyst system is a supported metallocene catalyst system.

CLAIMS:

1. A process of regenerating a molecular sieve catalyst comprising:
   a) introducing a spent SAPO or ALPO molecular sieve catalyst into a regeneration vessel;
   b) introducing a flow of gas comprising 10 to 50 ppb sodium into said regeneration vessel; and
   c) heating said molecular sieve catalyst for a sufficient period of time and at a sufficient temperature to regenerate said molecular sieve catalyst wherein said molecular sieve is used to convert oxygenates to ethylene and/or propylene.
2. The process of claim 1 wherein said gas comprises 20 to 40 ppb sodium.
3. The process of claim 1 or 2 wherein said gas comprises 20 to 30 ppb sodium.
4. The process of any one of claims 1 to 3 wherein said gas is subjected to a purification step prior to entering said regeneration vessel.
5. The process of claim 4 wherein said purification step comprises cooling said gas to condense and remove impurities including water and said sodium and then sending a purified gas flow to said regeneration vessel.
6. The process of claim 4 wherein said purification step comprises passing said gas through an adsorbent bed to remove impurities including water and salts followed by sending a resulting purified gas flow to said regeneration vessel.
7. The process of any one of claims 1 to 6 wherein said gas is selected from the group consisting of oxygen, O_3, SO_3, N_2O, NO, NO_2, N_2O_5, air, air diluted with nitrogen or carbon dioxide, oxygen and water carbon monoxide and hydrogen.
8. The process of any one of claims 1 to 7 wherein said gas is air.
9. The process of any one of claims 4 to 8 wherein prior to purification said gas contains at least one lithium, sodium, or potassium salt.