MOLECULAR SIEVE CATALYST COMPOSITION, ITS MAKING AND USE IN CONVERSION PROCESSES

Field Of The Invention

[0001] The present invention relates to a molecular sieve catalyst composition, to a method of making or forming the molecular sieve catalyst composition, and to a conversion process using the catalyst composition.

Background Of The Invention

[0002] Olefins are traditionally produced from petroleum feedstock by catalytic or steam cracking processes. These cracking processes, especially steam cracking, produce light olefin(s) such as ethylene and/or propylene from a variety of hydrocarbon feedstock. 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 olefin(s). 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. Generally, the production of synthesis gas involves a combustion reaction of natural gas, mostly methane, and an oxygen source into hydrogen, carbon monoxide and/or carbon dioxide. Syngas production processes are well known, and include conventional steam reforming, autothermal reforming, or a combination thereof.

[0004] Methanol, the preferred alcohol for light olefin production, is typically synthesized from the catalytic reaction of hydrogen, carbon monoxide and/or carbon dioxide in a methanol reactor in the presence of a heterogeneous catalyst. For example, in one synthesis process methanol is produced using a copper/zinc oxide catalyst in a water-cooled tubular methanol reactor. The preferred methanol conversion process is generally referred to as a methanol-to-

olefin(s) process, where methanol is converted to primarily ethylene and/or propylene in the presence of a molecular sieve.

[0005] Molecular sieves are porous solids having pores of different sizes such as zeolites or zeolite-type molecular sieves, carbons and oxides. The most commercially useful molecular sieves for the petroleum and petrochemical industries are known as zeolites, for example aluminosilicate molecular sieves. Zeolites in general have a one-, two- or three- dimensional crystalline pore structure having uniformly sized pores of molecular dimensions that selectively adsorb molecules that can enter the pores, and exclude those molecules that are too large.

[0006] There are many different types of molecular sieves well known to convert a feedstock, especially an oxygenate containing feedstock, into one or more olefin(s). For example, U.S. Patent No. 5,367,100 describes the use of a well known zeolite, ZSM-5, to convert methanol into olefin(s); U.S. Patent No. 4,062,905 discusses the conversion of methanol and other oxygenates to ethylene and propylene using crystalline aluminosilicate zeolites, for example Zeolite T, ZK5, erionite and chabazite; U.S. Patent No. 4,079,095 describes the use of ZSM-34 to convert methanol to hydrocarbon products such as ethylene and propylene; and U.S. Patent No. 4,310,440 describes producing light olefin(s) from an alcohol using a crystalline aluminophosphates, often represented by $ALPO_4$.

[0007] One of the most useful molecular sieves for converting methanol to olefin(s) is a 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 synthesis is described in U.S. Patent No. 4,440,871, which is herein fully incorporated by reference. SAPO is generally synthesized by the hydrothermal crystallization of a reaction mixture of silicon-, aluminum- and phosphorus-sources and at least one templating agent. Synthesis of a SAPO molecular sieve, its formulation into a SAPO catalyst, and its use in converting a hydrocarbon feedstock into olefin(s), particularly where the feedstock is methanol, is shown in

U.S. Patent Nos. 4,499,327, 4,677,242, 4,677,243, 4,873,390, 5,095,163, 5,714,662 and 6,166,282, all of which are herein fully incorporated by reference.

[0008] Typically, molecular sieves are formed into molecular sieve catalyst compositions to improve their durability in commercial conversion processes. The collisions within a commercial process between catalyst composition particles themselves, the reactor walls, and other reactor systems cause the particles to breakdown into smaller particles called fines. The physical breakdown of the molecular sieve catalyst composition particles is known as attrition. Fines often exit the reactor in the effluent stream resulting in problems in recovery systems. Catalyst compositions having a higher resistance to attrition generate fewer fines, less catalyst composition is required for conversion, and longer life times result in lower operating costs.

[0009] Molecular sieve catalyst compositions are formed by combining a molecular sieve and a matrix material usually in the presence of a binder. The purpose of the binder is to hold the matrix material, often a clay, to the molecular sieve. The use of binders and matrix materials in the formation of molecular sieve catalyst compositions is well known for a variety of commercial processes. It is also known that the way in which the molecular sieve catalyst composition is made or formulated affects catalyst composition attrition.

[0010] Example of methods of making catalyst compositions include: U.S. Patent No. 5,126,298 discusses a method for making a cracking catalyst having high attrition resistance by combining two different clay particles in separate slurries with a zeolite slurry and a source of phosphorous, and spray drying a mixture of the slurries having a pH below 3; U.S. Patent No. 4,987,110 and 5,298,153 relates to a catalytic cracking process using a spray dried attrition resistant catalyst containing greater than 25 weight percent molecular sieve dispersed in a clay matrix with a synthetic silica-alumina component; U.S. Patent Nos. 5,194,412 and 5,286,369 discloses forming a catalytic cracking catalyst of a molecular sieve and a crystalline aluminum phosphate binder having a surface area less than 20 m^2/g and a total pore volume less than 0.1 cc/g; U.S. Patent No.

4,542,118 relates to forming a particulate inorganic oxide composite of a zeolite and aluminum chlorhydrol that is reacted with ammonia to form a cohesive binder; U.S. Patent No. 6,153,552 claims a method of making a catalyst, by drying a slurry of a SAPO molecular sieve, an inorganic oxide sol, and an external phosphorous source; U.S. Patent No. 5,110,776 illustrates the formation of a zeolite containing catalytic catalyst by modifying the zeolite with a phosphate containing solution; U.S. Patent No. 5,348,643 relates to spray drying a zeolite slurry with a clay and source of phosphorous at a pH of below 3; U.S Patent Application No. 09/891,674 filed June 25, 2001 discusses a method for steaming a molecular sieve to remove halogen; U.S. Patent No. 5,248,647 illustrates spray drying a SAPO-34 molecular sieve admixed with kaolin and a silica sol; U.S. Patent No. 5,346,875 discloses a method for making a catalytic cracking catalyst by matching the isoelectric point of each component of the framework structure to the pH of the inorganic oxide sol; Mäurer, et al, *Aggregation and Peptization Behavior of Zeolite Crystals in Sols and Suspensions*, Ind. Eng. Chem. Vol. 40, pages 2573-2579, 2001 discusses zeolite aggregation at or near the isoelectric point; PCT Publication WO 99/21651 describes making a catalyst by drying a mixture of an alumina sol and a SAPO molecular sieve; PCT Publication WO 02/05950 describes making a catalyst composition of a molecular sieve containing attrition particles with fresh molecular sieve; and WO 02/05952 discloses a crystalline metallo-aluminophosphate molecular sieve and a matrix material of an inorganic oxide binder and filler where the molecular sieve is present in an amount less than 40 weight percent relative to the catalyst weight and a preferable weight ratio of the binder to molecular sieve close to 1.

[0011] Although these molecular sieve catalyst compositions described above are useful in hydrocarbon conversion processes, it would be desirable to have an improved molecular sieve catalyst composition having better attrition resistance and commercially desirable operability and cost advantages.

Summary Of The Invention

[0012] This invention provides for a method of making or formulating a molecular sieve catalyst composition and to its use in a conversion process for converting a feedstock into one or more olefin(s).

[0013] In one embodiment the invention is directed to a method for making a molecular sieve catalyst composition by combining, contacting, mixing, or the like, a molecular sieve, a binder, and a matrix material in a slurry, wherein the slurry has a pH above or below an isoelectric point (IEP) of, independently or in combination, the molecular sieve, the binder and/or the matrix material. In one preferred embodiment, the slurry has a pH at least 0.3 above or below the IEP of the molecular sieve. In a preferred embodiment, the molecular sieve is synthesized from the combination from at least two of the group consisting of a silicon source, a phosphorous source and an aluminum source, optionally in the presence of a templating agent, more preferably the molecular sieve is a silicoaluminophosphate or aluminophosphate, and most preferably a silicoaluminophosphate.

[0014] In one embodiment the invention is directed to a method for formulating a molecular sieve catalyst composition, the method comprising the steps of: (a) introducing a molecular sieve to form a slurry; (b) introducing a binder to the slurry; (c) introducing a matrix material to the slurry; and (d) spray drying the slurry to produce the formulated molecular sieve catalyst composition, wherein a pH of the slurry is above or below an IEP of the molecular sieve. In another embodiment, the pH of the slurry is at least 0.3 away, above or below, the isoelectric point of the molecular sieve. In another embodiment, the molecular sieve catalyst composition has an Attrition Rate Index (ARI) less than 2 weight percent per hour, preferably less than 1 weight percent per hour and most preferably less than 0.5 weight percent per hour. Preferably the molecular sieve is a silicoaluminophosphate, an aluminophosphate and/or a chabazite structure-type molecular sieve.

[0015] In yet another embodiment, the invention is directed to a process for producing olefin(s) in the presence of any of the above molecular sieve catalyst compositions. In particular, the process involves producing olefin(s) in a process for converting a feedstock, preferably a feedstock containing an oxygenate, more preferably a feedstock containing an alcohol, and most preferably a feedstock containing methanol in the presence of one or more of the molecular sieve catalyst compositions thereof.

Detailed Description Of The Invention

Introduction

[0016] The invention is directed toward a molecular sieve catalyst composition, its making and to its use in the conversion of a hydrocarbon feedstock into one or more olefin(s). The molecular sieve catalyst composition is made or formed from the combination of a molecular sieve, a binder, and optionally, most preferably, a matrix material. It has been known generally in the art that with solid/liquid dispersions that particle aggregation is prevented by overcoming the van der Waals attraction potential between the solid or particle surfaces. Stabilization of dispersions by electrostatic repulsion is described in E.J.W. Verwey, et al., *Theory of the Stabilization of Lyophobic Colloids*, Elsevier, Amsterdam, 1948. The oxide surfaces are either negatively or positively charged depending on the pH of the oxides in an aqueous media; see Th. F. Tadros, *Solid/Liquid Dispersions,* Academic Press, London, page 5, 1987, which is fully incorporated herein by reference. The isoelectric point (IEP) is that state where the surface of particles in a medium is not charged, which corresponds to a pH value for a particular material, for example a molecular sieve catalyst composition, in a particular medium, for example water; see J. Lyklema, *Structure of the Solid/Liquid Interface and Electrical Double Layer, in Solid/Liquid Dispersions (Edited by Th.F. Tadors)*, Academic Press, London, pages 63-90, 1987, which is fully incorporated herein by reference. It has been surprisingly discovered that by preparing a molecular sieve catalyst composition below or above the IEP of the

molecular sieve, a catalyst composition having improved attrition resistance is formed. The pH at the IEP of a given surface is also an important consideration in selecting a binder, weight ratio of binder to molecular sieve, and total solid particle content in a solid/liquid dispersion. Therefore, it has also been discovered that in addition to IEP, that the weight ratio of the binder to the molecular sieve is also important to producing an attrition resistance catalyst composition.

Molecular Sieves and Catalysts Thereof

[0017] 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.

[0018] Non-limiting 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 AEL, AFY, BEA, CHA, EDI, FAU, FER, GIS, LTA, LTL, MER, MFI, MOR, MTT, MWW, TAM and TON. In one preferred

embodiment, the molecular sieve of the invention has an AEI topology or a CHA topology, or a combination thereof, most preferably a CHA topology.

[0019] Molecular sieve materials all have 3-dimensional framework structure of corner-sharing TO_4 tetrahedra, where T is any tetrahedrally coordinated cation. These molecular sieves are typically described in terms of the size of the ring that defines a pore, where the size is based on the number of T atoms in the ring. Other framework-type characteristics include the arrangement of rings that form a cage, and when present, the dimension of channels, and the spaces between the cages. See van Bekkum, et al., *Introduction to Zeolite Science and Practice, Second Completely Revised and Expanded Edition*, Volume 137, pages 1-67, Elsevier Science, B.V., Amsterdam, Netherlands (2001).

[0020] 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 about 3Å to 15 Å. In the most preferred embodiment, the molecular sieves of the invention, preferably silicoaluminophosphate molecular sieves have 8- rings and an average pore size less than about 5Å, preferably in the range of from 3Å to about 5Å, more preferably from 3Å to about 4.5Å, and most preferably from 3.5Å to about 4.2Å.

[0021] Molecular sieves, particularly zeolitic and zeolitic-type molecular sieves, preferably have a molecular framework of one, preferably two or more corner-sharing $[TO_4]$ tetrahedral units, more preferably, two or more $[SiO_4]$, $[AlO_4]$ and/or $[PO_4]$ tetrahedral units, and most preferably $[SiO_4]$, $[AlO_4]$ and $[PO_4]$ tetrahedral units. These silicon, aluminum, and phosphorous based molecular sieves and metal containing silicon, aluminum and phosphorous based molecular sieves have been described in detail in numerous publications including for example, U.S. Patent No. 4,567,029 (MeAPO where Me is Mg, Mn, Zn, or Co), U.S. Patent No. 4,440,871 (SAPO), European Patent Application EP-A-0 159 624 (ELAPSO where El is As, Be, B, Cr, Co, Ga, Ge, Fe, Li, Mg, Mn, Ti or Zn), U.S. Patent No. 4,554,143 (FeAPO), U.S. Patents No. 4,822,478, 4,683,217,

4,744,885 (FeAPSO), EP-A-0 158 975 and U.S. Patent No. 4,935,216 (ZnAPSO, EP-A-0 161 489 (CoAPSO), EP-A-0 158 976 (ELAPO, where EL is Co, Fe, Mg, Mn, Ti or Zn), U.S. Patent No. 4,310,440 ($AlPO_4$), EP-A-0 158 350 (SENAPSO), U.S. Patent No. 4,973,460 (LiAPSO), U.S. Patent No. 4,789,535 (LiAPO), U.S. Patent No. 4,992,250 (GeAPSO), U.S. Patent No. 4,888,167 (GeAPO), U.S. Patent No. 5,057,295 (BAPSO), U.S. Patent No. 4,738,837 (CrAPSO), U.S. Patents Nos. 4,759,919, and 4,851,106 (CrAPO), U.S. Patents Nos. 4,758,419, 4,882,038, 5,434,326 and 5,478,787 (MgAPSO), U.S. Patent No. 4,554,143 (FeAPO), U.S. Patent No. 4,894,213 (AsAPSO), U.S. Patent No. 4,913,888 (AsAPO), U.S. Patents Nos. 4,686,092, 4,846,956 and 4,793,833 (MnAPSO), U.S. Patents Nos. 5,345,011 and 6,156,931 (MnAPO), U.S. Patent No. 4,737,353 (BeAPSO), U.S. Patent No. 4,940,570 (BeAPO), U.S. Patents Nos. 4,801,309, 4,684,617 and 4,880,520 (TiAPSO), U.S. Patents Nos. 4,500,651, 4,551,236 and 4,605,492 (TiAPO), U.S. Patents No. 4,824,554, 4,744,970 (CoAPSO), U.S. Patent No. 4,735,806 (GaAPSO) EP-A-0 293 937 (QAPSO, where Q is framework oxide unit [QO_2]), as well as U.S. Patents Nos. 4,567,029, 4,686,093, 4,781,814, 4,793,984, 4,801,364, 4,853,197, 4,917,876, 4,952,384, 4,956,164, 4,956,165, 4,973,785, 5,241,093, 5,493,066 and 5,675,050, all of which are herein fully incorporated by reference. Other molecular sieves are described in R. Szostak, *Handbook of Molecular Sieves*, Van Nostrand Reinhold, New York, New York (1992), which is herein fully incorporated by reference.

[0022] 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. In an embodiment, the metal is an alkali metal of Group IA of the Periodic Table of Elements, an alkaline earth metal of Group IIA of the Periodic Table of Elements, a rare earth metal of Group IIIB, including the

Lanthanides: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium; and scandium or yttrium of the Periodic Table of Elements, a transition metal of Groups IVB, VB, VIB, VIIB, VIIIB, and IB of the Periodic Table of Elements, or mixtures of any of these metal species. In one preferred embodiment, 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.

[0023] In one embodiment, the molecular sieve, as described in many of the U.S. Patents mentioned above, 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 Lanthanide's 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 an embodiment, m is greater than or equal to 0.2, and x, y and z are greater than or equal to 0.01. In another embodiment, m is greater than 0.1 to about 1, x is greater than 0 to about 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.

[0024] Non-limiting 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 (U.S. Patent No. 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 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.

[0025] In an embodiment, the molecular sieve is an intergrowth material having two or more distinct phases of crystalline structures within one molecular sieve composition. In particular, intergrowth molecular sieves are described in the U.S. Patent Application Serial No. 09/924,016 filed August 7, 2001 and PCT WO 98/15496 published April 16, 1998, both of which are herein fully incorporated by reference. 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.

Molecular Sieve Synthesis

[0026] The synthesis of molecular sieves is described in many of the references discussed above. Generally, molecular sieves are synthesized by the hydrothermal crystallization of one or more of a source of aluminum, a source of phosphorous, 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.

[0027] In a preferred embodiment 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.

[0028] Non-limiting examples of silicon sources include a silicates, fumed silica, for example, Aerosil-200 available from Degussa Inc., New York, New York, and CAB-O-SIL M-5, silicon compounds such as tetraalkyl orthosilicates, for example, tetramethyl orthosilicate (TMOS) and tetraethylorthosilicate (TEOS), colloidal silicas or aqueous suspensions thereof, for example Ludox-HS-40 sol available from E.I. du Pont de Nemours, Wilmington, Delaware, silicic acid, alkali-metal silicate, or any combination thereof. The preferred source of silicon is a silica sol.

[0029] Non-limiting examples of aluminum sources include aluminum-containing compositions such as aluminum alkoxides, for example aluminum isopropoxide, aluminum phosphate, aluminum hydroxide, sodium aluminate, pseudo-boehmite, gibbsite and aluminum trichloride, or any combinations thereof. A preferred source of aluminum is pseudo-boehmite, particularly when producing a silicoaluminophosphate molecular sieve.

[0030] Non-limiting examples of phosphorous sources, which may also include aluminum-containing phosphorous compositions, include phosphorous-containing, inorganic or organic, compositions such as phosphoric acid, organic phosphates such as triethyl phosphate, and crystalline or amorphous aluminophosphates such as $ALPO_4$, phosphorous salts, or combinations thereof. The preferred source of phosphorous is phosphoric acid, particularly when producing a silicoaluminophosphate.

[0031] Templating agents are generally compounds that contain elements of Group VA of the Periodic Table of Elements, particularly nitrogen, phosphorus, arsenic and antimony, more preferably nitrogen or phosphorous, and most preferably nitrogen. Typical templating agents of Group VA of the Periodic Table of elements 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.

[0032] The quaternary ammonium compounds, in one embodiment, are represented by the general formula R_4N^+, where each R is hydrogen or a hydrocarbyl or substituted hydrocarbyl group, preferably an alkyl group or an aryl group having from 1 to 10 carbon atoms. 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.

[0033] Non-limiting examples of templating agents include tetraalkyl ammonium compounds including salts thereof such as tetramethyl ammonium compounds including salts thereof, tetraethyl ammonium compounds including salts thereof, tetrapropyl ammonium including salts thereof, and tetrabutylammonium including salts thereof, cyclohexylamine, morpholine, di-n-propylamine (DPA), tripropylamine, triethylamine (TEA), triethanolamine, piperidine, cyclohexylamine, 2-methylpyridine, N,N-dimethylbenzylamine, N,N-diethylethanolamine, dicyclohexylamine, N,N-dimethylethanolamine, choline, N,N'-dimethylpiperazine, 1,4-diazabicyclo(2,2,2)octane, N', N',N,N-tetramethyl-(1,6)hexanediamine, N-methyldiethanolamine, N-methyl-ethanolamine, N-methyl piperidine, 3-methyl-piperidine, N-methylcyclohexylamine, 3-methylpyridine, 4-methyl-pyridine, quinuclidine, N,N'-dimethyl-1,4-diazabicyclo(2,2,2) octane ion; di-n-butylamine, neopentylamine, di-n-pentylamine, isopropylamine, t-butyl-amine, ethylenediamine, pyrrolidine, and 2-imidazolidone.

[0034] 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 one embodiment, 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.

[0035] A synthesis mixture containing at a minimum a silicon-, aluminum-, and/or phosphorous- composition, and a templating agent, should have a pH in the range of from 2 to 10, preferably in the range of from 4 to 9, and most preferably in the range of from 5 to 8. Generally, the synthesis mixture is sealed in a vessel and heated, preferably under autogenous pressure, to a temperature in the range of from about 80°C to about 250°C, and more preferably from about 150°C to about 180°C. The time required to form the crystalline product is typically from immediately up to several weeks, the duration of which is usually dependent on the temperature; the higher the temperature the shorter the duration. Typically, the crystalline molecular sieve product is formed, usually in a slurry state, and is recovered by any standard technique well known in the art, for example centrifugation or filtration. The isolated or separated crystalline product, in an embodiment, is washed, typically, using a liquid such as water, from one to many times. The washed crystalline product is then optionally dried, preferably in air.

[0036] In one preferred embodiment, when a templating agent is used in the synthesis of a molecular sieve, it is preferred that the templating agent is substantially, preferably completely, removed after crystallization by numerous well known techniques, for example, heat treatments such as calcination. Calcination involves contacting the molecular sieve containing the templating agent with a gas, preferably containing oxygen, at any desired concentration at an elevated temperature sufficient to either partially or completely decompose and oxidize the templating agent.

[0037] Molecular sieves 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. In one embodiment, the molecular sieve has a Si/Al ratio less than 0.65, preferably less than 0.40, more preferably less than 0.32, and most preferably less than 0.20. In another embodiment the molecular sieve has a Si/Al ratio in the range of from about 0.65 to about 0.10, preferably from about 0.40 to about 0.10, more preferably from about 0.32 to about 0.10, and more preferably from about 0.32 to about 0.15.

Method for Making Molecular Sieve Catalyst Compositions

[0038] 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.

[0039] The pH at the IEP for various materials including metal oxides are discussed in J. Lyklema, *Structure of the Solid/Liquid Interface and Electrical Double Layer, in Solid/Liquid Dispersions*, Academic Press, London, pages 63-90, 1987 and J.-E. Otterstedt and D. A. Brandreth, *Small Particles Technology*, page 258, Plenum, New York, 1998, which are herein fully incorporated by reference.

[0040] In one embodiment, the molecular sieve, preferably a silicoaluminophosphate molecular sieve, and more preferably a SAPO-34 molecular sieve, has a pH in the range of from about 3 to 7 at its IEP (measured as an aqueous slurry), preferably in the range of from 4 to 6, and more preferably in

the range of from 4.5 to 5.5. In another embodiment, the binder, preferably an alumina sol, has a pH of greater than about 9 at its IEP, preferably greater than 10. In yet another embodiment, the matrix material, preferably a clay, has a pH less than about 2 at its IEP.

[0041] In another embodiment, the slurry comprising a molecular sieve and one or more of a binder or a matrix material has a pH above or below, preferably below the IEP of the molecular sieve, and one or more of the binder or the matrix material. Preferably the slurry comprises the molecular sieve, the binder and the matrix material and has a pH different from, above or below, preferably below, the IEP of the molecular sieve, the binder and the matrix material. In an embodiment, the pH of the slurry is in the range of from 2 to 7, preferably from 2.3 to 6.2; the IEP of the molecular sieve is in the range of from 2.5 to less than 7, preferably from about 3.5 to 6.5; the IEP of the binder is greater than 10; and the IEP of the matrix material is less than 2. In a particularly preferred embodiment, the IEP of the molecular sieve is in the range of from 4.5 to 5.5.

[0042] In yet another embodiment, the binder, preferably a alumina sol, and more preferably an aluminum chlorohydrate, is positively charged and/or at a pH in the range of from greater than 2 to less than 10. In still a further embodiment, the matrix material, a clay is negatively charged and/or has pH of less than 2 at its IEP. In another embodiment, a binder and a matrix composition, preferably a 20 to 60 weight percent binder and 40 to 80 weight percent matrix material based on the total weight of the binder and matrix material, has a pH of about 9.8 at its IEP.

[0043] In one preferred embodiment, the slurry has a pH at least 0.3 above or below the IEP of the molecular sieve and/or the IEP of the binder and/or the IEP of the matrix material, preferably the slurry has a pH at least 0.5 above or below, preferably below, more preferably the slurry has a pH at least 1 above or below, preferably below, and most preferably the slurry has a pH at least 1.5 above or below, preferably a pH of at least 2 below. Preferably the pH of the slurry is different from the IEP of the molecular sieve, the binder and matrix material.

[0044] In one embodiment, the weight ratio of the binder to the molecular sieve is in the range of from about 0.1 to 0.5, preferably in the range of from 0.1 to less than 0.5, more preferably in the range of from 0.11 to 0.48, even more preferably from 0.12 to about 0.45, yet even more preferably from 0.13 to less than 0.45, and most preferably in the range of from 0.15 to about 0.4.

[0045] In another embodiment, the molecular sieve catalyst composition or formulated molecular sieve catalyst composition has a micropore surface area (MSA) measured in m^2/g-molecular sieve that is greater than about 70 percent, preferably greater than about 75 percent, more preferably greater than 80 percent, even more preferably greater than 85 percent, and most preferably greater than about 90 percent of the MSA of the molecular sieve itself. The MSA of the molecular sieve catalyst composition is the total MSA of the composition divided by the fraction of the molecular sieve contained in the molecular sieve catalyst composition.

[0046] In another embodiment in the formulation of a molecular sieve catalyst composition, that the amount of solids present in a slurry of the molecular sieve and the binder, optionally including a matrix material, used in a spray drying process for example is important. Also, it is preferred that the synthesized molecular sieve contain an amount of a liquid medium, preferably water, not calcined, prior to being used in the slurry. When the solids content of the slurry is too low or too high the attrition resistance properties of the molecular sieve catalyst composition is reduced. The molecular sieve catalyst composition in a preferred embodiment is made by preparing a slurry containing a molecular sieve, a binder, and, optionally while preferably, a matrix material. The solids content of the preferred slurry includes about 20% to about 50% by weight of the molecular sieve, preferably from about 30% to about 48% by weight of the molecular sieve, more preferably from about 40% to about 48% by weight molecular sieve, about 5% to about 20%, preferably from about 8% to about 15%, by weight of the binder, and about 30% to about 80%, preferably about 40% to about 60%, by weight of the matrix material.

[0047] There are many different binders that are useful in forming the molecular sieve catalyst composition. Non-limiting 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 chlorhydrate. The inorganic oxide sol acts like glue binding the synthesized molecular sieves and other materials such as the matrix together, particularly after thermal treatment. Upon heating, the inorganic oxide sol, preferably having a low viscosity, is converted into an inorganic oxide matrix component. For example, an alumina sol will convert to an aluminum oxide matrix following heat treatment.

[0048] Aluminum chlorhydrate, a hydroxylated aluminum based sol containing a chloride counter ion, has the general formula of $Al_mO_n(OH)_oCl_p \bullet x(H_2O)$ wherein m is 1 to 20, n is 1 to 8, o is 5 to 40, p is 2 to 15, and x is 0 to 30. In one embodiment, the binder is $Al_{13}O_4(OH)_{24}Cl_7 \bullet 12(H_2O)$ as is described in G.M. Wolterman, et al., Stud. Surf. Sci. and Catal., 76, pages 105-144 (1993), which is herein incorporated by reference. In another embodiment, one or more binders are combined with one or more other non-limiting examples of alumina materials such as aluminum oxyhydroxide, γ-alumina, boehmite, diaspore, and transitional aluminas such as α-alumina, β-alumina, γ-alumina, δ-alumina, ε-alumina, κ-alumina, and ρ-alumina, aluminum trihydroxide, such as gibbsite, bayerite, nordstrandite, doyelite, and mixtures thereof.

[0049] In another embodiment, the binders are alumina sols, predominantly comprising aluminum oxide, optionally including some silicon. In yet another embodiment, the binders are peptized alumina made by treating alumina hydrates such as pseudobohemite, with an acid, preferably an acid that does not contain a halogen, to prepare sols or aluminum ion solutions. Non-limiting examples of commercially available colloidal alumina sols include Nalco 8676 available from Nalco Chemical Co., Naperville, Illinois, and Nyacol AL20DW available from Nyacol Nano Technologies, Inc., Ashland, MA.

[0050] 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.

[0051] 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. These natural clays include sabbentonites and those kaolins known as, for example, Dixie, McNamee, Georgia and Florida clays. Non-limiting examples of other matrix materials include: haloysite, kaolinite, dickite, nacrite, or anauxite. In one embodiment, the matrix material, preferably any of the clays, are subjected to well known modification processes such as calcination and/or acid treatment and/or chemical treatment.

[0052] 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. Kaolin has been found to form a pumpable, high solid content slurry, it has a low fresh surface area, and it packs together easily due to its platelet structure. A preferred average particle size of the matrix material, most preferably kaolin, is from about 0.05 μm to about 0.6 μm with a D_{90} particle size distribution of less than about 1 μm.

[0053] In one embodiment, the binder, the molecular sieve, and the matrix material are combined in the presence of a liquid to form the catalyst composition, where the amount of binder is from about 2% by weight to about 30% by weight, preferably from about 5% by weight to about 20% by weight, and more preferably

from about 7% by weight to about 15% by weight, based on the total weight of the binder, the molecular sieve and matrix material, excluding the liquid.

[0054] Upon combining the molecular sieve, the binder, and optionally the matrix material, in a liquid to form a slurry, mixing, preferably rigorous mixing is needed to produce a substantially homogeneous mixture. Non-limiting examples of suitable liquids include one or a combination of water, alcohol, ketones, aldehydes, and/or esters. The most preferred liquid is water. In one embodiment, the slurry is subjected to high shear for a period of time sufficient to produce the desired slurry texture, sub-particle size, and/or sub-particle size distribution. Suitable means for subjecting the slurry to milling including colloid mills, inline mixers, and the like.

[0055] The preparation of the slurry comprising the molecular sieve, the binder and the matrix material is carried out by mixing the molecular sieve, the binder and optionally the matrix material at a temperature in the range of from about -10°C to about 80°C. Depending on the particle size of the molecular sieve and the binder, in one embodiment, a particle size reduction step is performed, either before or after mixing. There are many ways to perform particle size reduction on various powders using a variety of devices, including but not limited to an impingement mill (a micronizer available from Sturtevant, Inc. Boston, Massachusetts), or a dry or wet mill, for example an Eiger mill (a wet mill available from Eiger Machinery, In., Grayslake, Illinois), a jar rolling mill for both dry and wet milling (available from Paul O. Abbe, Inc., Little Falls, New Jersey), or by use of a high-shear mixer (available from Silverson Machines, Inc., East Longmeadow, Massachusetts). The particle size distribution in the slurry is measured using for example, a Microtrac laser scattering particle size analyzer S3000 available from MicroTrac, Clearwater, Florida. To ensure the quality of the slurry for spray drying to form the catalyst composition of the invention, measurements of pH, surface area, solid content, bulk density, and viscosity are also preferably monitored using respectively, for example, a Cole Palmer pH meter, Micromeritics Gemini 9375 surface area instrument available from

Micometrics Instrument Corporation, Norcross, Georgia, CEM MAS 700 microwave muffle furnace for solid content determination available from CEM Corporation, Mathews, North Carolina, and Brookfield LV-DVE viscometer for viscosity. Zeta potential measurements were made on a Matec 9800 electrokinetic instrument available from Matec Applied Science, Northboro, MA. Particle size is but one factor in the effectiveness of the slurry in the formation of the catalyst composition of the invention. In addition, the sequence of adding each individual component, the molecular sieve, binder, matrix material, and other ingredient, is also important. Sequence of addition is most important when the surface of the different particles, whether these are of the molecular sieve, the binder, or the matrix materials, have opposite charges, negative and positive, or different charge densities. As a general rule, after size reduction is completed, if necessary, the last step is the addition and mixing of the opposite charged particles. In one preferred embodiment, it is best to add the component selected from the molecular sieve, the binder or the matrix material, having a higher charge density per unit mass to a component having a lower charge density per unit mass.

[0056] The molecular sieve, the binder, and the matrix material, are in the same or different liquid, and are combined in any order, together, simultaneously, sequentially, or a combination thereof. In the preferred embodiment, the same liquid, preferably water is used. The molecular sieve, matrix material, and the binder, are added to a liquid as solids, or as slurries, together or separately. If solids are added together, it is preferable to add a limited and/or controlled amount of liquid.

[0057] 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 a preferred embodiment, the forming unit is a spray dryer. Typically, the forming unit is maintained at a temperature sufficient to dry most of the liquid from the slurry, and from the resulting molecular sieve catalyst particles. The resulting

catalyst composition when formed in this way preferably takes the form of microspheres.

[0058] When a spray dryer is used as the forming unit, typically, the slurry of the molecular sieve, the binder and the matrix material is co-fed to the spray drying volume with a drying gas with an average inlet temperature ranging from 100°C to 550°C, and a combined outlet temperature ranging from 50°C to about 225°C. In an embodiment, the average diameter of the spray dried formed catalyst composition is from about 10 μm to about 300 μm, preferably from about 30 μm to about 250 μm, more preferably from about 40 μm to about 150 μm, and most preferably from about 50 μm to about 120 μm.

[0059] During spray drying, the slurry is passed through a nozzle distributing the slurry into small droplets, resembling an aerosol spray into a drying chamber. Atomization is achieved by forcing the slurry through a single nozzle or multiple nozzles with a pressure drop in the range of from 100 psig to 2000 psig (690 kPag to 13790 kPag). In another embodiment, the slurry is co-fed through a single nozzle or multiple nozzles along with an atomization fluid such as air, steam, flue gas, or any other suitable gas with a pressure drop in the range of from 1 psig to 150 psig (6.9 kPag to 1034 kPag).

[0060] In yet another embodiment, the slurry described above is directed to the perimeter of a spinning wheel that distributes the slurry into small droplets, the size of which is controlled by many factors including slurry viscosity, surface tension, flow rate, pressure, and temperature of the slurry, the shape and dimension of the nozzle(s), or the spinning rate of the wheel. These droplets are then dried in a co-current or counter-current flow of air passing through a spray drier to form a substantially dried or dried molecular sieve catalyst composition, more specifically a molecular sieve catalyst composition in a microspherical form.

[0061] Generally, the size of the microspheres is controlled to some extent by the solids content of the slurry. However, control of the size of the catalyst composition and its spherical characteristics are also controllable by varying the slurry feed properties and conditions of atomization.

[0062] Other methods for forming a molecular sieve catalyst composition is described in U.S. Patent Application Serial No. 09/617,714 filed July 17, 2000 (spray drying using a recycled molecular sieve catalyst composition), which is herein incorporated by reference.

[0063] In another embodiment, the formulated molecular sieve catalyst composition contains from about 1% to about 99%, preferably from about 10 % to about 90%, more preferably from about 10% to about 80%, even more preferably from about 20% to about 70%, and most preferably from about 20% to about 60% by weight of the molecular sieve based on the total weight of the molecular sieve catalyst composition.

[0064] 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 about 400°C to about 1,000°C, preferably from about 500°C to about 800°C, and most preferably from about 550°C to about 700°C, preferably in a calcination environment such as air, nitrogen, helium, flue gas (combustion product lean in oxygen), or any combination thereof. In one embodiment, calcination of the formulated molecular sieve catalyst composition is carried out in any number of well known devices including rotary calciners, fluid bed calciners, batch ovens, and the like. Calcination time is typically dependent on the degree of hardening of the molecular sieve catalyst composition and the temperature ranges from about 1 minutes to about 10 hours, preferably 15 minutes to about 5 hours.

[0065] In one embodiment, the attrition resistance of a molecular sieve catalyst composition is measured using an Attrition Rate Index (ARI), measured in weight percent catalyst composition attrited per hour. An apparatus such as described in S.A. Weeks and P. Dumbill, in Oil & Gas Journal, pages 38 to 40, 1987, which is herein fully incorporated by reference. ARI is measured by adding

6.0g of catalyst composition having a particles size ranging from about 53 microns to about 125 microns to a hardened steel attrition cup. Approximately 23,700 cc/min of nitrogen gas is bubbled through a water-containing bubbler to humidify the nitrogen. The wet nitrogen passes through the attrition cup, and exits the attrition apparatus through a porous fiber thimble. The flowing nitrogen removes the finer particles, with the larger particles being retained in the cup. The porous fiber thimble separates the fine catalyst particles from the nitrogen that exits through the thimble. The fine particles remaining in the thimble represent the catalyst composition that has broken apart through attrition. The nitrogen flow passing through the attrition cup is maintained for 1 hour. The fines collected in the thimble are removed from the unit. A new thimble is then installed. The catalyst left in the attrition unit is attrited for an additional 3 hours, under the same gas flow and moisture levels. The fines collected in the thimble are recovered. The collection of fine catalyst particles separated by the thimble after the first hour are weighed. The amount in grams of fine particles divided by the original amount of catalyst charged to the attrition cup expressed on per hour basis is the ARI, in weight percent per hour (wt. %/hr). ARI is represented by the formula: ARI = C/(B+C)/D multiplied by 100%, wherein B is weight of catalyst composition left in the cup after the attrition test, C is the weight of collected fine catalyst particles after the first hour of attrition treatment, and D is the duration of treatment in hours after the first hour attrition treatment.

[0066] In one embodiment, the molecular sieve catalyst composition or formulated molecular sieve catalyst composition has an ARI less than 15 weight percent per hour, preferably less than 10 weight percent per hour, more preferably less than 5 weight percent per hour, and even more preferably less than 2 weight percent per hour, and most preferably less than 1 weight percent per hour. In one embodiment, the molecular sieve catalyst composition or formulated molecular sieve catalyst composition has an ARI in the range of from 0.1 weight percent per hour to less than 5 weight percent per hour, more preferably from about 0.2 weight

percent per hour to less than 3 weight percent per hour, and most preferably from about 0.2 weight percent per hour to less than 2 weight percent per hour.

Process For Using the Molecular Sieve Catalyst Compositions

[0067] 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) (U.S. Patent No. 6,300,537) 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 cumeme 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.

[0068] 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).

[0069] 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 about 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.

[0070] 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.

[0071] 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.

[0072] Non-limiting examples of oxygenates include methanol, ethanol, n-propanol, isopropanol, methyl ethyl ether, dimethyl ether, diethyl ether, di-isopropyl ether, formaldehyde, dimethyl carbonate, dimethyl ketone, acetic acid, and mixtures thereof. 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.

[0073] The various feedstocks discussed above, particularly a 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 from 2 to 30 carbon atoms, preferably 2 to 8 carbon atoms, more preferably 2 to 6 carbon atoms, still more preferably 2 to 4 carbons atoms, and most preferably ethylene an/or propylene. Non-limiting examples of olefin monomer(s) include ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1 and decene-1, preferably ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1 and isomers thereof. Other olefin monomer(s) include unsaturated monomers, diolefins having 4 to 18 carbon atoms, conjugated or nonconjugated dienes, polyenes, vinyl monomers and cyclic olefins.

[0074] In the most preferred embodiment, the feedstock, preferably of one or more oxygenates, is converted in the presence of a molecular sieve catalyst composition of the invention into olefin(s) having 2 to 6 carbons atoms, preferably 2 to 4 carbon atoms. Most preferably, the olefin(s), alone or combination, are converted from a feedstock containing an oxygenate, preferably an alcohol, most preferably methanol, to the preferred olefin(s) ethylene and/or propylene.

[0075] The 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 a 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).

[0076] In one embodiment of the process for conversion of a feedstock, preferably a feedstock containing one or more oxygenates, the amount of olefin(s) produced based on the total weight of hydrocarbon produced is greater than 50 weight percent, preferably greater than 60 weight percent, more preferably greater than 70 weight percent, and most preferably greater than 75 weight percent. In another embodiment of the process for conversion of one or more oxygenates to

one or more olefin(s), the amount of ethylene and/or propylene produced based on the total weight of hydrocarbon product produced is greater than 65 weight percent, preferably greater than 70 weight percent, more preferably greater than 75 weight percent, and most preferably greater than 78 weight percent.

[0077] In another embodiment of the process for conversion of one or more oxygenates to one or more olefin(s), the amount ethylene produced in weight percent based on the total weight of hydrocarbon product produced, is greater than 30 weight percent, more preferably greater than 35 weight percent, and most preferably greater than 40 weight percent. In yet another embodiment of the process for conversion of one or more oxygenates to one or more olefin(s), the amount of propylene produced in weight percent based on the total weight of hydrocarbon product produced is greater than 20 weight percent, preferably greater than 25 weight percent, more preferably greater than 30 weight percent, and most preferably greater than 35 weight percent.

[0078] The feedstock, in one embodiment, contains one or more diluent(s), typically used to reduce the concentration of the feedstock, and are generally non-reactive to the feedstock or molecular sieve catalyst composition. Non-limiting examples of diluents include helium, argon, nitrogen, carbon monoxide, carbon dioxide, water, essentially non-reactive paraffins (especially alkanes such as methane, ethane, and propane), essentially non-reactive aromatic compounds, and mixtures thereof. The most preferred diluents are water and nitrogen, with water being particularly preferred.

[0079] 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. In one embodiment, the amount of diluent in the feedstock is in the range of from about 1 to about 99 mole percent based on the total number of moles of the feedstock and diluent, preferably from about 1 to 80 mole percent, more preferably from about 5 to about 50, and most preferably from about 5 to about 25.

[0080] 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 U.S. Patent No. 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.

[0081] 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.

[0082] 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 U.S. Patent No. 4,076,796, U.S. Patent No. 6,287,522 (dual riser), and *Fluidization Engineering*, D. Kunii and O. Levenspiel, Robert E. Krieger Publishing Company, New York, New York 1977, which are all herein fully incorporated by reference. The preferred reactor type are riser reactors generally described in *Riser Reactor, Fluidization and Fluid-Particle Systems*, pages 48 to 59, F.A. Zenz and D.F. Othmo, Reinhold Publishing Corporation, New York, 1960, and U.S. Patent No. 6,166,282 (fast-fluidized bed reactor), and U.S. Patent Application Serial No. 09/564,613 filed May 4, 2000 (multiple riser reactor), which are all herein fully incorporated by reference.

[0083] 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.

[0084] 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.

[0085] In an embodiment, the amount of fresh feedstock fed separately or jointly with a vapor feedstock, to a reactor system is in the range of from 0.1 weight percent to about 85 weight percent, preferably from about 1 weight percent to about 75 weight percent, more preferably from about 5 weight percent to about 65 weight percent based on the total weight of the feedstock including any diluent contained therein. The liquid and vapor feedstocks are preferably the same composition, or contain varying proportions of the same or different feedstock with the same or different diluent.

[0086] 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. In the preferred embodiment, cyclone(s) within the disengaging vessel are designed to separate the molecular sieve catalyst composition, preferably a coked molecular sieve catalyst composition, from the gaseous effluent containing one or more olefin(s) within the disengaging zone. Cyclones are preferred, however, gravity effects within the disengaging vessel will also separate the catalyst compositions from the gaseous effluent. Other methods for separating the catalyst compositions from the gaseous effluent include the use of plates, caps, elbows, and the like.

[0087] In one embodiment of the disengaging system, the disengaging system includes a disengaging vessel, typically a lower portion of the disengaging vessel is a stripping zone. In the stripping zone the coked molecular sieve catalyst composition is contacted with a gas, preferably one or a combination of steam,

methane, carbon dioxide, carbon monoxide, hydrogen, or an inert gas such as argon, preferably steam, to recover adsorbed hydrocarbons from the coked molecular sieve catalyst composition that is then introduced to the regeneration system. In another embodiment, the stripping zone is in a separate vessel from the disengaging vessel and the gas is passed at a gas hourly superficial velocity (GHSV) of from 1 hr^{-1} to about 20,000 hr^{-1} based on the volume of gas to volume of coked molecular sieve catalyst composition, preferably at an elevated temperature from 250°C to about 750°C, preferably from about 350°C to 650°C, over the coked molecular sieve catalyst composition.

[0088] The conversion temperature employed in the conversion process, specifically within the reactor system, is in the range of from about 200°C to about 1000°C, preferably from about 250°C to about 800°C, more preferably from about 250°C to about 750 °C, yet more preferably from about 300°C to about 650°C, yet even more preferably from about 350°C to about 600°C most preferably from about 350°C to about 550°C.

[0089] 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 about 0.1 kPaa to about 5 MPaa, preferably from about 5 kPaa to about 1 MPaa , and most preferably from about 20 kPaa to about 500 kPaa.

[0090] 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.

[0091] Typically, the WHSV ranges from about 1 hr^{-1} to about 5000 hr^{-1}, preferably from about 2 hr^{-1} to about 3000 hr^{-1}, more preferably from about 5 hr^{-1} to about 1500 hr^{-1}, and most preferably from about 10 hr^{-1} to about 1000 hr^{-1}. In one preferred embodiment, the WHSV is greater than 20 hr^{-1}, preferably the WHSV for conversion of a feedstock containing methanol and dimethyl ether is in the range of from about 20 hr^{-1} to about 300 hr^{-1}.

[0092] 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), preferably greater than 0.5 m/sec, more preferably greater than 1 m/sec, even more preferably greater than 2 m/sec, yet even more preferably greater than 3 m/sec, and most preferably greater than 4 m/sec. See for example U.S. Patent Application Serial No. 09/708,753 filed November 8, 2000, which is herein incorporated by reference.

[0093] In one preferred embodiment of the process for converting an oxygenate to olefin(s) using a silicoaluminophosphate molecular sieve catalyst composition, the process is operated at a WHSV of at least 20 hr^{-1} and a Temperature Corrected Normalized Methane Selectivity (TCNMS) of less than 0.016, preferably less than or equal to 0.01. See for example U.S. Patent No. 5,952,538, which is herein fully incorporated by reference. In another embodiment of the processes for converting an oxygenate such as methanol to one or more olefin(s) using a molecular sieve catalyst composition, the WHSV is from 0.01 hr^{-1} to about 100 hr^{-1}, at a temperature of from about 350°C to 550°C, and silica to Me_2O_3 (Me is a Group IIIA or VIII element from the Periodic Table of Elements) molar ratio of from 300 to 2500. See for example EP-0 642 485 B1, which is herein fully incorporated by reference. Other processes for converting an oxygenate such as methanol to one or more olefin(s) using a molecular sieve catalyst composition are described in PCT WO 01/23500 published April 5, 2001

(propane reduction at an average catalyst feedstock exposure of at least 1.0), which is herein incorporated by reference.

[0094] 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 (U.S. Patent No. 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 weight percent 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.

[0095] The regeneration temperature is in the range of from about 200°C to about 1500°C, preferably from about 300°C to about 1000°C, more preferably from about 450°C to about 750°C, and most preferably from about 550°C to 700°C. The regeneration pressure is in the range of from about 15 psia (103 kPaa) to about 500 psia (3448 kPaa), preferably from about 20 psia (138 kPaa) to about 250 psia (1724 kPaa), more preferably from about 25 psia (172kPaa) to about 150 psia (1034 kPaa), and most preferably from about 30 psia (207 kPaa) to about 60 psia (414 kPaa). The preferred residence time of the molecular sieve catalyst composition in the regenerator is in the range of from about one minute to several hours, most preferably about one minute to 100 minutes, and the preferred volume of oxygen in the gas is in the range of from about 0.01 mole percent to about 5 mole percent based on the total volume of the gas.

[0096] In one embodiment, regeneration promoters, typically metal containing compounds such as platinum, palladium and the like, are added to the

regenerator directly, or indirectly, for example with the coked catalyst composition. Also, in another embodiment, a fresh molecular sieve catalyst composition is added to the regenerator containing a regeneration medium of oxygen and water as described in U.S. Patent No. 6,245,703, which is herein fully incorporated by reference. In yet another embodiment, a portion of the coked molecular sieve catalyst composition from the regenerator is returned directly to the one or more riser reactor(s), or indirectly, by pre-contacting with the feedstock, or contacting with fresh molecular sieve catalyst composition, or contacting with a regenerated molecular sieve catalyst composition or a cooled regenerated molecular sieve catalyst composition described below.

[0097] The burning of coke is an exothermic reaction, and in an embodiment, the temperature within the regeneration system is controlled by various techniques in the art including feeding a cooled gas to the regenerator vessel, operated either in a batch, continuous, or semi-continuous mode, or a combination thereof. 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. The catalyst cooler, in an embodiment, is a heat exchanger that is located either internal or external to the regeneration system. In one embodiment, the cooler regenerated molecular sieve catalyst composition is returned to the regenerator in a continuous cycle, alternatively, (see U.S. Patent Application Serial No. 09/587,766 filed June 6, 2000) a portion of the cooled regenerated molecular sieve catalyst composition is returned to the regenerator vessel in a continuous cycle, and another portion of the cooled molecular sieve regenerated molecular sieve catalyst composition is returned to the riser reactor(s), directly or indirectly, or a portion of the regenerated molecular sieve catalyst composition or cooled regenerated molecular sieve catalyst composition is contacted with by-products within the gaseous effluent (PCT WO 00/49106 published August 24, 2000), which are all herein fully incorporated by reference. In another embodiment, a regenerated molecular

sieve catalyst composition contacted with an alcohol, preferably ethanol, 1-propnaol, 1-butanol or mixture thereof, is introduced to the reactor system, as described in U.S. Patent Application Serial No. 09/785,122 filed February 16, 2001, which is herein fully incorporated by reference. Other methods for operating a regeneration system are in disclosed U.S. Patent No. 6,290,916 (controlling moisture), which is herein fully incorporated by reference.

[0098] 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. In one embodiment, a carrier, such as an inert gas, feedstock vapor, steam or the like, semi-continuously or continuously, facilitates the introduction of the regenerated molecular sieve catalyst composition to the reactor system, preferably to the one or more riser reactor(s).

[0099] 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. There are many techniques for controlling the flow of a molecular sieve catalyst composition described in Michael Louge, *Experimental Techniques*, *Circulating Fluidized Beds*, Grace, Avidan and Knowlton, eds., Blackie, 1997 (336-337), which is herein incorporated by reference. Coke levels on the molecular sieve catalyst composition is measured by withdrawing from the conversion process the molecular sieve catalyst composition at a point in the process and determining its carbon content. Typical levels of coke on the molecular sieve catalyst composition, after regeneration is in the range of from 0.01 weight percent to about 15 weight percent, preferably from about 0.1 weight percent to about 10

weight percent, more preferably from about 0.2 weight percent to about 5 weight percent, and most preferably from about 0.3 weight percent to about 2 weight percent based on the total weight of the molecular sieve and not the total weight of the molecular sieve catalyst composition.

[00100] In one preferred embodiment, the mixture of fresh molecular sieve catalyst composition and regenerated molecular sieve catalyst composition and/or cooled regenerated molecular sieve catalyst composition contains in the range of from about 1 to 50 weight percent, preferably from about 2 to 30 weight percent, more preferably from about 2 to about 20 weight percent, and most preferably from about 2 to about 10 coke or carbonaceous deposit based on the total weight of the mixture of molecular sieve catalyst compositions. See for example U.S. Patent No. 6,023,005, which is herein fully incorporated by reference.

[00101] The gaseous effluent 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 (U.S. Patent No. 5,476,978) and other derivative processes such as aldehydes, ketones and ester manufacture (U.S. Patent No. 5,675,041), and other associated equipment for example various condensers, heat exchangers, refrigeration systems or chill trains, compressors, knock-out drums or pots, pumps, and the like. Non-limiting examples of these towers, columns, splitters or trains used alone or in combination include one or more of a demethanizer, preferably a high temperature demethanizer, a dethanizer, a depropanizer, preferably a wet depropanizer, a wash tower often referred to as a caustic wash tower and/or quench tower, absorbers, adsorbers, membranes, ethylene (C2) splitter, propylene (C3) splitter, butene (C4) splitter, and the like.

[00102] Various recovery systems useful for recovering predominately olefin(s), preferably prime or light olefin(s) such as ethylene, propylene and/or

butene are described in U.S. Patent No. 5,960,643 (secondary rich ethylene stream), U.S. Patent Nos. 5,019,143, 5,452,581 and 5,082,481 (membrane separations), U.S. Patent 5,672,197 (pressure dependent adsorbents), U.S. Patent No. 6,069,288 (hydrogen removal), U.S. Patent No. 5,904,880 (recovered methanol to hydrogen and carbon dioxide in one step), U.S. Patent No. 5,927,063 (recovered methanol to gas turbine power plant), and U.S. Patent No. 6,121,504 (direct product quench), U.S. Patent No. 6,121,503 (high purity olefins without superfractionation), and U.S. Patent No. 6,293,998 (pressure swing adsorption), which are all herein fully incorporated by reference.

[00103] Generally accompanying most recovery systems is the production, generation or accumulation of additional products, by-products and/or contaminants along with the preferred prime products. The preferred prime products, the light olefins, such as ethylene and propylene, are typically purified for use in derivative manufacturing processes such as polymerization processes. Therefore, in the most preferred embodiment of the recovery system, the recovery system also includes a purification system. For example, the light olefin(s) produced particularly in a MTO process are passed through a purification system that removes low levels of by-products or contaminants. Non-limiting examples of contaminants and by-products include generally polar compounds such as water, alcohols, carboxylic acids, ethers, carbon oxides, sulfur compounds such as hydrogen sulfide, carbonyl sulfides and mercaptans, ammonia and other nitrogen compounds, arsine, phosphine and chlorides. Other contaminants or by-products include hydrogen and hydrocarbons such as acetylene, methyl acetylene, propadiene, butadiene and butyne.

[00104] Other recovery systems that include purification systems, for example for the purification of olefin(s), are described in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition*, Volume 9, John Wiley & Sons, 1996, pages 249-271 and 894-899, which is herein incorporated by reference. Purification systems are also described in for example, U.S. Patent No. 6,271,428 (purification of a diolefin hydrocarbon stream), U.S. Patent No.

6,293,999 (separating propylene from propane), and U.S. Patent Application No. 09/689,363 filed October 20, 2000 (purge stream using hydrating catalyst), which is herein incorporated by reference.

[00105] Typically, in converting one or more oxygenates to olefin(s) having 2 or 3 carbon atoms, an amount of hydrocarbons, particularly olefin(s), especially olefin(s) having 4 or more carbon atoms, and other by-products are formed or produced. Included in the recovery systems of the invention are reaction systems for converting the products contained within the effluent gas withdrawn from the reactor or converting those products produced as a result of the recovery system utilized.

[00106] In one embodiment, the effluent gas withdrawn from the reactor is passed through a recovery system producing one or more hydrocarbon containing stream(s), in particular, a three or more carbon atom (C_3^+) hydrocarbon containing stream. In this embodiment, the C_3^+ hydrocarbon containing stream is passed through a first fractionation zone producing a crude C_3 hydrocarbon and a C_4^+ hydrocarbon containing stream, the C_4^+ hydrocarbon containing stream is passed through a second fractionation zone producing a crude C_4 hydrocarbon and a C_5^+ hydrocarbon containing stream. The four or more carbon hydrocarbons include butenes such as butene-1 and butene-2, butadienes, saturated butanes, and isobutanes.

[00107] The effluent gas removed from a conversion process, particularly a MTO process, typically has a minor amount of hydrocarbons having 4 or more carbon atoms. The amount of hydrocarbons having 4 or more carbon atoms is typically in an amount less than 20 weight percent, preferably less than 10 weight percent, more preferably less than 5 weight percent, and most preferably less than 2 weight percent, based on the total weight of the effluent gas withdrawn from a MTO process, excluding water. In particular with a conversion process of oxygenates into olefin(s) utilizing a molecular sieve catalyst composition the resulting effluent gas typically comprises a majority of ethylene and/or propylene

and a minor amount of four carbon and higher carbon number products and other by-products, excluding water.

[00108] Suitable well known reaction systems as part of the recovery system primarily take lower value products and convert them to higher value products. For example, the C_4 hydrocarbons, butene-1 and butene-2 are used to make alcohols having 8 to 13 carbon atoms, and other specialty chemicals, isobutylene is used to make a gasoline additive, methyl-t-butylether, butadiene in a selective hydrogenation unit is converted into butene-1 and butene-2, and butane is useful as a fuel. Non-limiting examples of reaction systems include U.S. Patent No. 5,955,640 (converting a four carbon product into butene-1), U.S. Patent No. 4,774,375 (isobutane and butene-2 oligomerized to an alkylate gasoline), U.S. Patent No. 6,049,017 (dimerization of n-butylene), U.S. Patent Nos. 4,287,369 and 5,763,678 (carbonylation or hydroformulation of higher olefins with carbon dioxide and hydrogen making carbonyl compounds), U.S. Patent No. 4,542,252 (multistage adiabatic process), U.S. Patent No. 5,634,354 (olefin-hydrogen recovery), and Cosyns, J. et al., *Process for Upgrading C_3, C_4 and C_5 Olefinic Streams*, Pet. & Coal, Vol. 37, No. 4 (1995) (dimerizing or oligomerizing propylene, butylene and pentylene), which are all herein fully incorporated by reference.

[00109] The preferred light olefin(s) produced by any one of the processes described above, preferably conversion processes, are high purity prime olefin(s) products that contains a single carbon number olefin in an amount greater than 80 percent, preferably greater than 90 weight percent, more preferably greater than 95 weight percent, and most preferably no less than about 99 weight percent, based on the total weight of the olefin. In one embodiment, high purity prime olefin(s) are produced in the process of the invention at rate of greater than 5 kg per day, preferably greater than 10 kg per day, more preferably greater than 20 kg per day, and most preferably greater than 50 kg per day. In another embodiment, high purity ethylene and/or high purity propylene is produced by the process of the invention at a rate greater than 4,500 kg per day, preferably greater than 100,000

kg per day, more preferably greater than 500,000 kg per day, even more preferably greater than 1,000,000 kg per day, yet even more preferably greater than 1,500,000 kg per day, still even more preferably greater than 2,000,000 kg per day, and most preferably greater than 2,500,000 kg per day.

[00110] Other conversion processes, in particular, a conversion process of an oxygenate to one or more olefin(s) in the presence of a molecular sieve catalyst composition, especially where the molecular sieve is synthesized from a silicon-, phosphorous-, and alumina- source, include those described in for example: U.S. Patent No. 6,121,503 (making plastic with an olefin product having a paraffin to olefin weight ratio less than or equal to 0.05), U.S. Patent No. 6,187,983 (electromagnetic energy to reaction system), PCT WO 99/18055 publishes April 15, 1999 (heavy hydrocarbon in effluent gas fed to another reactor) PCT WO 01/60770 published August 23, 2001 and U.S. Patent Application Serial No. 09/627,634 filed July 28, 2000 (high pressure), U.S. Patent Application Serial No. 09/507,838 filed February 22, 2000 (staged feedstock injection), and U.S. Patent Application Serial No. 09/785,409 filed February 16, 2001 (acetone co-fed), which are all herein fully incorporated by reference.

[00111] In an embodiment, an integrated process is directed to producing light olefin(s) from a hydrocarbon feedstock, preferably a hydrocarbon gas feedstock, more preferably methane and/or ethane. The first step in the process is passing the gaseous feedstock, preferably in combination with a water stream, to a syngas production zone to produce a synthesis gas (syngas) stream. Syngas production is well known, and typical syngas temperatures are in the range of from about 700°C to about 1200°C and syngas pressures are in the range of from about 2 MPa to about 100 MPa. Synthesis gas streams are produced from natural gas, petroleum liquids, and carbonaceous materials such as coal, recycled plastic, municipal waste or any other organic material, preferably synthesis gas stream is produced via steam reforming of natural gas. Generally, a heterogeneous catalyst, typically a copper based catalyst, is contacted with a synthesis gas stream, typically carbon dioxide and carbon monoxide and hydrogen to produce an

alcohol, preferably methanol, often in combination with water. In one embodiment, the synthesis gas stream at a synthesis temperature in the range of from about 150°C to about 450°C and at a synthesis pressure in the range of from about 5 MPa to about 10 MPa is passed through a carbon oxide conversion zone to produce an oxygenate containing stream.

[00112] This oxygenate containing stream, or crude methanol, typically contains the alcohol product and various other components such as ethers, particularly dimethyl ether, ketones, aldehydes, dissolved gases such as hydrogen methane, carbon oxide and nitrogen, and fusel oil. The oxygenate containing stream, crude methanol, in the preferred embodiment is passed through a well known purification processes, distillation, separation and fractionation, resulting in a purified oxygenate containing stream, for example, commercial Grade A and AA methanol. The oxygenate containing stream or purified oxygenate containing stream, optionally with one or more diluents, is contacted with one or more molecular sieve catalyst composition described above in any one of the processes described above to produce a variety of prime products, particularly light olefin(s), ethylene and/or propylene. Non-limiting examples of this integrated process is described in EP-B-0 933 345, which is herein fully incorporated by reference. In another more fully integrated process, optionally with the integrated processes described above, olefin(s) produced are directed to, in one embodiment, one or more polymerization processes for producing various polyolefins. (See for example U.S. Patent Application Serial No. 09/615,376 filed July 13, 2000, which is herein fully incorporated by reference.)

[00113] Polymerization processes 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.

[00114] 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. In this embodiment, the supported metallocene catalyst system comprises a support, a metallocene or metallocene-type compound and an activator, preferably the activator is a non-coordinating anion or alumoxane, or combination thereof, and most preferably the activator is alumoxane.

[00115] In addition to polyolefins, numerous other olefin derived products are formed from the olefin(s) recovered any one of the processes described above, particularly the conversion processes, more particularly the GTO process or MTO process. These include, but are not limited to, aldehydes, alcohols, acetic acid, linear alpha olefins, vinyl acetate, ethylene dicholoride and vinyl chloride, ethylbenzene, ethylene oxide, cumene, isopropyl alcohol, acrolein, allyl chloride, propylene oxide, acrylic acid, ethylene-propylene rubbers, and acrylonitrile, and trimers and dimers of ethylene, propylene or butylenes.

EXAMPLES

[00116] In order to provide a better understanding of the present invention including representative advantages thereof, the following examples are offered. Constituents of a mixture used for formulating catalysts will generally contain volatile components, including, but not limited to, water and, in the case of molecular sieve, organic template. It is common practice to describe the amount or proportion of these constituents as being on a "calcined basis". Calcination involves heating a material in the presence of air at an elevated temperature sufficient to dry and remove any contained volatile content (650°C for one or more hours). On a "calcined basis" is defined, for the purposes of the current invention, as the amount or fraction of each component remaining after it has been mathematically reduced to account for losses in weight expected to occur if the component had been calcined. The term LOI (Loss-On-Ignition) is used herein interchangeably with the fractional loss during calcination, a "calcined basis". Thus, 10 grams of a component containing 25% volatiles would be described as "7.5 g on a calcined basis" with an LOI of 2.5g. Synthesis of a SAPO-34 molecular sieve is well known, and the SAPO-34 used in the Examples below was measured to have a MSA of about 550 m^2/g-molecular sieve.

[00117] MSA is determined using a MICROMERITICS Gemini 2375 from Micromeritics Instrument Corporation, Norcross, Georgia is used. An amount 0.15g to 0.6g of the sample is loaded into the sample cell for degassing at 300°C for a minimum of 2 hours. During the analysis, the Evacuation Time is 1.0 minute, no free space is used, and sample Density of 1.0 g/cc is used. Thirteen (13) adsorption data points are collected with adsorption targets of:

Data Point	Adsorption Target (p/p_o)	Data Point	Adsorption Target (p/p_o)
1	0.00500	8	0.25000
2	0.07500	9	0.30000
3	0.01000	10	0.40000
4	0.05000	11	0.60000
5	0.10000	12	0.75000
6	0.15000	13	0.95000
7	0.20000		

[00118] The correction factor used in the t-plot is 0.975. No de-sorption points are collected. Other analysis parameters include, Analysis Mode: Equilibrate; Equilibration Time: 5 second; Scan Rate: 10 seconds. A t-plot from 0.00000 to 0.90000 is constructed using the ASTM certified form of the Harkins and Jura equation (H-J Model): $t(p) = (13.99/(0.034-\log(p/p_o)))^{0.5}$. It is shown by Cape and Kibby [J.A. Cape and C.L. Kibby, J. Colloids and Interface Science, 138, 516-520 (1990)] that the conventional BET surface area of a microporous material can be decomposed quantitatively into the external area and the micropore volume, as expressed by equation given below: $S_{micro} = S_{tot}-S_{ext} = v_m/d_j$, where v_m is the micropore volume, S_{mciro} is the micropore area calculated from S_{tot} and S_{ext}. S_{tot} is given by the conventional BET method, and S_{ext} is the external area taken from the t-plot. d_j is a nonphysical length the value of which depends on the pressure used in the experiments. The proportionality factor, d_j, is determined quantitatively by the pressures used in the BET fits.

[00119] For purposes of this patent application and appended claims "solids content" is measured by weighing a sample of a slurry, calcining the slurry sample, preferably at 550°C to 750°C, re-weighing the calcined sample; the solids content is equal to the calcined sample weight divided by the weight of the slurry sample multiplied by 100.

Example 1

[00120] A slurry was prepared by mixing 45.8 kg of a SAPO-34 molecular sieve containing a template (Loss-on-Ignition (LOI) of 46.6%) to 25.1 kg of de-ionized water under vigorous stirring conditions using a turbo-blade mixer at 60 to 300 rpm for a period of 2 hours, at which time the solid was totally disintegrated. A high-shear mixing step was applied on this mixture using a Silverson high-shear in-line mixer for two passes depending on the size reduction. Particle size

analysis of a one-pass high-shear treated slurry is given in Table 1.

Example 2

[00121] A slurry of aluminum chlorohydrate (available from Reheis, Berkeley Heights, New Jersey) was prepared by adding 13.4 kg of aluminum chlorohydrate (LOI: 51.6%) into 12.5 kg of de-ionized water using a turbo-blade mixer at 60 to 300 rpm for a period of 0.2 to 12 hours or until a translucent sol was obtained. This aluminum chlorohydrate sol was then added to the slurry of Example 1 using a feed pump and mixed for 0.2 to 5 hours before kaolin clay (ASP grade available from Engelhard Corporation, Macon, Georgia) was added. An amount of 35.1 kg of kaolin clay (LOI: 13.9%) and an additional amount of 4.2 kg of de-ionized water was added to the mixture of SAPO-34 molecular sieve and aluminum chlorohydrate. The resultant mixture was mixed using the turbo-blade mixer at 60 to 300 rpm for a period of 2 hours, then passed through high-shear in-line mixer twice. This slurry was aged at 40°C in a feed tank under constant mixing using a turbo-blade mixer at 60 to 300 rpm for a period of 15 hours. Particle size analysis of the aged slurry is given in Table 1.

Table 1

Example	d_{10} (μm) [a]	D_{50} (μm) [a]	d_{90} (μm) [a]	Solid Content [b]
1	1.08	1.75	2.74	18.7%
2	0.93	1.85	3.24	46.7%

a. d_{10},d_{50}, d_{90}: 10%, 50%, 90% of the particles are at or smaller than the size given.
b. Solid content was determined by calcining the slurry in a microwave muffle furnace to 650°C.

Example 3

[00122] The IEP of the materials used in the formulation of the catalyst composition was determined from the measurements of zeta-potential using a Matec ESA 9800 electrokinetic instrument available from Matec Applied Science, Northboro, MA. Zeta-potentials are calculated

from measurements of an ultrasonic signal originating from distortion of the colloidal particle's double in a high frequency ac field. Conversion of the ultrasonic signal into a zeta-potential value factors in particle size, particle density, and volume fraction of the suspended solid.

Example 4

[00123] Particle size dependence in a very dilute slurry (less than 1 weight percent) of a colloidal silicalite having an average particle size of 60 to 70 nanometers as a function of pH was determined using a Zeta Sizer 3000 (Malvern Instrument as above). At pH's away from the IEP, silicalite particles were in the form of individual particles. However, these individual particles aggregated to 1.45μm (25 to 30 times bigger than the primary particle size) when the pH was adjusted to near the IEP.

Table 2

Example	pH	Viscosity (cP) [b]	d_{10} (μm) [a]	d_{50} (μm) [a]	d_{90} (μm) [a]	Solid Content [d]	Density of Slurry (g/cc)
5	3.6	1840	0.28	1.45	3.54	44.5%	1.44
6	3.7	2940	0.38	0.90	6.48	44.8%	1.46
7	4.2 [c]	720	0.25	1.42	3.80	43.0%	1.42
8	3.7	3920	0.37	0.91	7.94	46.9%	1.48

a. d_{10},d_{50}, d_{90}: 10%, 50%, 90% of the particles are at or smaller this size given.
b. Viscosity was measured using a Brookfield LV viscometer: spindle #3, room temperature, and 30 RPM.
c. Using the procedure of Example 5 except its pH was adjusted from 3.7 to 4.2 using an ammonia solution;
d. Solid content was determined by calcining the slurry in a microwave muffle furnace to 650°C.

Example 5

[00124] A slurry as prepared as in Examples 1 and 2 but added to a slurry of SAPO-34 molecular sieve (B) to give a total solid content of 44.5% while maintained a weight ratio of sieve to aluminum chlorohydrate and kaolin clay at 40/10.6/49.4. Viscosity, pH, and particle size measurements of this Example 5 are given in Table 2.

Example 6

[00125] A slurry was prepared as in Examples 1 and 2 but using a SAPO-34 molecular sieve (C) to give a total solid content of 44.8% while maintained a weight ratio of sieve to aluminum chlorohydrate and kaolin clay at 40/10.6/49.4. Viscosity, pH, and particle size measurements of this Example 6 are given in Table 2.

Example 7

[00126] A slurry was prepared using the same composition and procedure of Example 6 and its pH was increased from 3.7 to 4.2 using a diluted ammonia aqueous solution. Viscosity, pH, and particle size measurements for this Example 7 are given in Table 2.

Example 8

[00127] A slurry as prepared as in Examples 1 and 2 but using a SAPO-34 molecular sieve (D) to give a total solid content of 46.9% while maintaining a weight ratio of molecular sieve to aluminum chlorohydrate and kaolin clay at 40/10.6/49.4. Viscosity, pH, and particle size measurements of this Example 8 are given in Table 2.

Example 9

[00128] Zeta-potential measurement of SAPO-34 molecular sieve (A) used in Example 2 after being calcined in air at 550°C for 5 hours. It was found that the presence of template in SAPO-34 resulted in a substantially lower IEP pH than SAPO-34 free of template.

Example 10

[00129] The slurry made in Example 5 was spray dried using a lab-scale spray dryer (Yamato DL-41 available from Yamato Scientific America, Inc., Orangeburg, N.Y.). Slurry feed rate was at 40 to 50 g/min, inlet temperature of 350°C and product temperature of 80 to 85°C,

atomization pressure of 1 bar. The spray dry product was calcined at 650°C. This catalyst composition of this Example 10 had an ARI of 0.33.

Comparative Example 11

[00130] In contrast to the invention, a typical commercial FCC catalyst, for example, a W. R. Grace Ultima 447 catalyst has an ARI of 7.94.

Comparative Example 12

[00131] A slurry prepared the same as Example 8, its pH was attempted to be increased to 4.5 to 4.6 using a diluted ammonia solution (5-15 wt%). It precipitated and solidified when the pH of the mixture reached of about 4.6. The targeted pH value approached the IEP of the SAPO-34 molecular sieve of Example 9, thus leading to destabilization of the slurry. The resultant material could not be spray dried.

Example 13

[00132] The slurry made in Example 6 was spray dried using a lab-scale spray dryer (Yamato DL-41). Slurry feed rate was at 40 to 50 g/min, inlet temperature of 350°C and product temperature of 80 to 85°C, atomization pressure of 1 bar. The spray dried catalyst composition was calcined at 650°C for 1 hr. This formulated molecular sieve catalyst composition had an ARI of 0.32.

Example 14

[00133] The slurry made in Example 7 was spray dried using a lab-scale spray dryer (Yamato DL-41). Slurry feed rate was at 40 to 50 g/min, inlet temperature of 350°C and product temperature of 80 to 85°C,

atomization pressure of 1 bar. The spray dried catalyst composition was calcined at 650°C. This formulated molecular sieve catalyst composition had an ARI of 0.41.

Example 15

[00134] The slurry made in Example 8 was spray dried using a lab-scale spray dryer (Yamato DL-41). Slurry feed rate was at 40 to 50 g/min, inlet temperature of 350°C and product temperature of 80 to 85°C, atomization pressure of 1 bar. The spray dried catalyst composition was calcined at 650°C. This formulated molecular sieve catalyst composition had an ARI of 0.29.

[00135] While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For example, it is contemplated that the molecular sieve catalyst composition is useful in the inter-conversion of olefin(s), oxygenate to gasoline conversions reactions, malaeic anhydride, phthalic anyhdride and acrylonitrile formulation, vapor phase methanol synthesis, and various Fischer Tropsch reactions. It is further contemplated that a plug flow, fixed bed or fluidized bed process are used in combination, particularly in different reaction zones within a single or multiple reactor system. It is also contemplated the molecular sieve catalyst compositions described herein are useful as absorbents, adsorbents, gas separators, detergents, water purifiers, and other various uses such as agriculture and horticulture. Additionally contemplated the molecular sieve catalyst compositions include one or more other molecular sieves in combination. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

CLAIMS

1. A method for making a molecular sieve catalyst composition, the method comprising the steps of: combining a molecular sieve, a binder, a liquid medium, and optionally a matrix material, to form a slurry, wherein the slurry has a pH above or below the isoelectric point (IEP) of the molecular sieve.

2. The method of claim 1 wherein the molecular sieve is synthesized from the combination from at least two of the group consisting of a silicon source, a phosphorous source and an aluminum source, optionally in the presence of a templating agent.

3. The method of any of the preceding claims wherein the slurry has a pH in the range of from 2.3 to 6.5.

4. The method of any of the preceding claims further comprising the step of spray drying the slurry.

5. The method of any of the preceding claims wherein the pH of the slurry is at least 0.3 above or below the IEP of the molecular sieve.

6. The method of any of the preceding claims wherein the binder has an IEP greater than 9, and the matrix material has an IEP less than about 2.

7. The method of any of the preceding claims wherein the molecular sieve catalyst composition has an ARI less than 2 weight percent per hour after calcination.

8. The method of any of the preceding claims wherein the pH of the slurry is below the IEP of the molecular sieve or the pH of the slurry is below the IEP of the molecular sieve and the IEP of the binder.

9. The method of any of the preceding claims wherein the IEP of the molecular sieve in the range of from about 3 to 7.

10. The method of any of the preceding claims, wherein the molecular sieve, binder and matrix material are combined in the following order: (a) the molecular sieve is introduced in a liquid medium to form a slurry; (b) a binder is added to the slurry; and (c) a matrix material is added to the slurry.

11. The method of any of the preceding claims wherein two of the molecular sieve and the binder have a positive charge at the pH of the slurry.

12. The method of any of the preceding claims wherein the matrix material has a negative charge at the pH of the slurry.

13. The method of any of the preceding claims wherein each of slurry components consisting of the molecular sieve, the binder and the matrix material each have a charge density, and are introduced to each other such that the slurry component with highest charge density per unit mass is added to the slurry components with lower charge density per unit mass.

14. The method of any of the preceding claims wherein the pH of the slurry is below the IEP of the molecular sieve.

15. The method of any of the preceding claims wherein the molecular sieve is a silicoaluminophosphate or aluminophosphate molecular sieve, preferably

selected from the group consisting of one or a combination of SAPO-18, SAPO-34, SAPO-35, SAPO-44, SAPO-56, ALPO-18 and ALPO-34, metal containing forms thereof and intergrown forms thereof.

16. The method of any of the preceding claims wherein the binder is an alumina sol, preferably aluminum chlorohydrate

17. The method of any of the preceding claims wherein the matrix is a clay.

18. The method of any of the preceding claims wherein the liquid medium is water.

19. A process for converting a feedstock into one or more olefin(s) in the presence of a formulated molecular sieve catalyst as obtained by the method of any of claims 1 to 18.

20. The process of claim 19 wherein the feedstock comprises at least one oxygenate.

21. The process of any of claims 19 or 20 wherein conversion of the feedstock into one or more olefin(s) takes place in a reactor system and the process further comprises the steps of withdrawing from the reactor system an effluent stream and passing the effluent gas through a recovery system recovering at least the one or more olefin(s).

22. The process of any of claims 19 to 21 wherein the process further comprises the step of introducing the molecular sieve catalyst composition to a regeneration system to form a regenerated molecular sieve catalyst composition, and introducing the regenerated molecular sieve catalyst composition to the reaction system.

23. The process of any of claims 19 to 22 wherein the feedstock comprises methanol, and the olefin(s) include ethylene and propylene, and the molecular sieve is a silicoaluminophosphate.

24. A process for converting a feedstock into one or more olefin(s)

(i) the feedstock is prepared by passing at least one hydrocarbon tthrough a syngas production zone to produce a synthesis gas stream;

(ii) the synthesis gas stream obtained in step (i) is contacted with a catalyst to form a feedstock comprising at least one oxygenate; and

(c) the feedstock comprising at least one oxygenate obtained in step (ii) is converted into the one or more olefin(s) according to the process of any of claims 19 to 22.

25. The process of any of claims 19 to 24 wherein the process further comprises the step of: (d) polymerizing the one or more olefin(s) in the presence of a polymerization catalyst into a polyolefin.