MOLECULAR SIEVE COMPOSITIONS, CATALYST THEREOF, THEIR MAKING AND USE IN CONVERSION PROCESSES

[0001] The present invention relates to molecular sieve compositions and catalysts containing the same, to the synthesis of such compositions and catalysts and to the use of such compositions and catalysts in conversion processes to produce olefin(s).

[0002] Olefins are traditionally produced from petroleum feedstocks 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 feedstocks. Ethylene and propylene are important commodity petrochemicals useful in a variety of processes for making plastics and other chemical compounds.

[0003] The petrochemical industry has known for some time that oxygenates, especially alcohols, are convertible into light olefin(s). The preferred alcohol for light olefin production is methanol and the preferred process for converting a methanol-containing feedstock into light olefin(s), primarily ethylene and/or propylene, involves contacting the feedstock with a molecular sieve catalyst composition.

[0004] There are many different types of molecular sieve known to convert oxygenate containing feedstocks into one or more olefin(s). For example, U.S. Patent No. 5,367,100 describes the use of the 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 aluminophosphate, often designated $AlPO_4$.

[0005] Some of the most useful molecular sieves for converting methanol to olefin(s) are silicoaluminophosphate (SAPO) molecular sieves. Silicoaluminophosphate molecular sieves contain a three-dimensional microporous crystalline framework structure of $[SiO_2]$, $[AlO_2]$ and $[PO_2]$ corner sharing tetrahedral units. Synthesis of a SAPO molecular sieve, its formulation into a catalyst, and its use in converting a feedstock into olefin(s), particularly where the feedstock is methanol, are disclosed 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.

[0006] When used in the conversion of methanol to olefins, most molecular sieves, including SAPO molecular sieves, undergo rapid coking and hence require frequent regeneration, typically involving exposure of the catalyst to high temperatures and steaming environments. As a result, current methanol conversion catalysts tend to have a limited useful lifetime and hence there is a need to provide a molecular sieve catalyst composition which exhibits an enhanced lifetime particularly when used in the conversion of methanol to olefins.

[0007] U.S. Patent No. 4,465,889 describes a catalyst composition comprising a silicalite molecular sieve impregnated with a thorium, zirconium, or titanium metal oxide for use in converting methanol, dimethyl ether, or a mixture thereof into a hydrocarbon product rich in iso-C_4 compounds.

[0008] U.S. Patent No. 6,180,828 discusses the use of a modified molecular sieve to produce methylamines from methanol and ammonia where, for example, a silicoaluminophosphate molecular sieve is combined with one or more modifiers, such as a zirconium oxide, a titanium oxide, an yttrium oxide, montmorillonite or kaolinite.

[0009] U.S. Patent No. 5,417,949 relates to a process for converting noxious nitrogen oxides in an oxygen containing effluent into nitrogen and water using a molecular sieve and a metal oxide binder, where the preferred binder is titania and the molecular sieve is an aluminosilicate.

[0010] EP-A-312981 discloses a process for cracking vanadium-containing hydrocarbon feed streams using a catalyst composition comprising a physical mixture of a zeolite embedded in an inorganic refractory matrix material and at least one oxide of beryllium, magnesium, calcium, strontium, barium or lanthanum, preferably magnesium oxide, on a silica-containing support material.

[0011] Kang and Inui, *Effects of decrease in number of acid sites located on the external surface of Ni-SAPO-34 crystalline catalyst by the mechanochemical method*, Catalysis Letters 53, pages 171-176 (1998) disclose that the shape selectivity can be enhanced and the coke formation mitigated in the conversion of methanol to ethylene over Ni-SAPO-34 by milling the catalyst with MgO, CaO, BaO or Cs_2O on microspherical non-porous silica, with BaO being most preferred.

[0012] International Publication No. WO 98/29370 discloses the conversion of oxygenates to olefins over a small pore non-zeolitic molecular sieve containing a metal selected from the group consisting of a lanthanide, an actinide, scandium, yttrium, a Group 4 metal, a Group 5 metal or combinations thereof.

[0013] In one aspect, the invention resides in a catalyst composition comprising a molecular sieve and at least one oxide of a metal selected from Group 4 of the Periodic Table of Elements, wherein said metal oxide has an uptake of carbon dioxide at 100°C of at least 0.03, and typically at least 0.035, mg/m^2 of the metal oxide.

[0014] Preferably, the catalyst composition also includes at least one of a binder and a matrix material different from said metal oxide.

[0015] The catalyst composition may also include an oxide of a metal selected from Group 2 and Group 3 of the Periodic Table of Elements. In one embodiment, the Group 4 metal oxide comprises zirconium oxide and the Group 2 and/or Group 3 metal oxide comprises one or more oxides selected from calcium oxide, barium oxide, lanthanum oxide, yttrium oxide and scandium oxide.

[0016] Preferably, the molecular sieve conveniently comprises a silicoaluminophosphate.

[0017] In another aspect, the invention resides in a molecular sieve catalyst composition comprising an active Group 4 metal oxide and a Group 2 and/or a Group 3 metal oxide, a binder, a matrix material, and a silicoaluminophosphate molecular sieve.

[0018] In yet another aspect, the invention resides in a method for making a catalyst composition, the method comprising the step of physically mixing first particles comprising a molecular sieve with second particles comprising a Group 4 metal oxide and having an uptake of carbon dioxide at 100°C of at least 0.03 mg/m^2 of the metal oxide particles.

[0019] Preferably, said second particles are produced by causing a hydrated precursor of said Group 4 metal oxide to precipitate from a solution containing ions of said metal, hydrothermally treating the hydrated precursor at a temperature of at least 80°C for up to 10 days and then calcining the hydrated precursor at a temperature in the range of from 400°C to 900°C.

[0020] In a further aspect, the invention is directed to a process for producing olefin(s) by converting a feedstock, such as an oxygenate, conveniently an alcohol, for example methanol, into one or more olefin(s) in the presence of a catalyst composition comprising a molecular sieve and an active Group 4 metal oxide having an uptake of carbon dioxide at 100°C of at least 0.03 mg/m^2 of the metal oxide.

[0021] In still a further aspect, the invention is directed to a process for converting a feedstock into one or more olefin(s) in the presence of a molecular sieve catalyst composition comprising a molecular sieve, a binder, a matrix material and a mixture of metal oxides different from the binder and the matrix material.

[0022] In one embodiment, the catalyst composition has a Lifetime Enhancement Index (LEI) greater than 1, such as greater than 1.5. LEI is defined herein as the ratio of the lifetime of the catalyst composition to that of the same catalyst composition in the absence of an active metal oxide.

[0023] The invention is directed to a molecular sieve catalyst composition and to its use in the conversion of hydrocarbon feedstocks, particularly oxygenated feedstocks, into olefin(s). It has been found that combining a molecular sieve with one or more active metal oxides results in a catalyst composition with a longer lifetime when used in the conversion of feedstocks, such as oxygenates, more particularly methanol, into olefin(s). In addition, the resultant catalyst composition tends to yield larger amounts of the desired lower olefins, especially propylene and lower amounts of unwanted ethane and propane, together with other undesirable compounds, such as aldehydes and ketones, specifically acetaldehyde.

[0024] The preferred active metal oxides are those having a Group 4 metal (for example zirconium and hafnium) from the Periodic Table of Elements using the IUPAC format described in the *CRC Handbook of Chemistry and Physics*, 78th Edition, CRC Press, Boca Raton, Florida (1997). In some cases, it is found that improved results are obtained when the catalyst composition also contains at least one oxide of a metal selected from Group 2 and/or Group 3 of the Periodic Table of Elements.

Molecular Sieves

[0025] Molecular sieves have been classified by the Structure Commission of the International Zeolite Association according to the rules of the IUPAC Commission on Zeolite Nomenclature. According to this classification, 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.

[0026] Non-limiting examples of preferred molecular sieves, particularly for use in converting an oxygenate containing feedstock into olefin(s), include framework types AEL, AFY, AEI, BEA, CHA, EDI, FAU, FER, GIS, LTA, LTL, MER, MFI, MOR, MTT, MWW, TAM and TON. In one preferred embodiment,

the molecular sieve employed in the catalyst composition of the invention has an AEI topology or a CHA topology, or a combination thereof, most preferably a CHA topology.

[0027] Crystalline molecular sieve materials have a 3-dimensional, four-connected framework structure of corner-sharing [TO_4] tetrahedra, where T is any tetrahedrally coordinated cation, such as [SiO_4], [AlO_4] and/or [PO_4] tetrahedral units. The molecular sieves useful herein conveniently comprise a framework including [AlO_4] and [PO_4] tetrahedral units, i.e., an aluminophosphate (AlPO) molecular sieve, or [SiO_4], [AlO_4] and [PO_4]] tetrahedral units, i.e., a silicoaluminophosphate (SAPO) molecular sieve. Most preferably, the molecular sieves useful herein is a silicoaluminophosphate (SAPO) molecular sieve or a substituted, preferably a metal substituted, SAPO molecular sieve. Examples of suitable metal substituents are an alkali metal of Group 1 of the Periodic Table of Elements, an alkaline earth metal of Group 2 of the Periodic Table of Elements, a rare earth metal of Group 3 of the Periodic Table of Elements, including the Lanthanides: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, erbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium; and scandium or yttrium, a transition metal of Groups 4 to 12 of the Periodic Table of Elements, or mixtures of any of these metal species.

[0028] Preferably, the molecular sieve used herein has a pore systenm defined by an 8-membered ring of [TO_4] tetrahedra and has an average pore size less than 5Å, such as in the range of from 3Å to 5Å, for example from 3Å to 4.5Å, and particularly from 3.5Å to 4.2Å.

[0029] Non-limiting examples of SAPO and AlPO molecular sieves useful herein 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. Of these, particularly useful molecular sieves are one or a combination of SAPO-18, SAPO-

34, SAPO-35, SAPO-44, SAPO-56, AlPO-18 and AlPO-34 and metal containing derivatives thereof, such as one or a combination of SAPO-18, SAPO-34, AlPO-34 and AlPO-18, and metal containing derivatives thereof, and especially one or a combination of SAPO-34 and AlPO-18, and metal containing derivatives thereof.

[0030] In an embodiment, the molecular sieve is an intergrowth material having two or more distinct crystalline phases within one molecular sieve composition. In particular, intergrowth molecular sieves are described in the U.S. Patent Application Publication No. 2002-0165089 and International Publication No. 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. Thus the molecular sieve used herein may comprise at least one intergrowth phase of AEI and CHA framework-types, especially where the ratio of CHA framework-type to AEI framework-type, as determined by the DIFFaX method disclosed in U.S. Patent Application Publication No. 2002-0165089, is greater than 1:1.

[0031] Preferably, where the molecular sieve is a silicoaluminophosphate, the molecular sieve has a Si/Al ratio less than or equal to 0.65, such as from 0.65 to 0.10, preferably from 0.40 to 0.10, more preferably from 0.32 to 0.10, and most preferably from 0.32 to 0.15.

Active Metal Oxides

[0032] Active metal oxides useful herein are those metal oxides, different from typical binders and/or matrix materials, that, when used in combination with a molecular sieve, provide benefits in catalytic conversion processes. Preferred active metal oxides are those metal oxides having a Group 4 metal, such as zirconium and/or hafnium, either alone or in combination with a Group 2 (for example magnesium, calcium, strontium and barium) and/or a Group 3 metal (including the Lanthanides and Actinides) oxide, (for example yttrium, scandium and lanthanum). The most preferred active Group 4 metal oxide is a zirconium metal oxide, either alone or in combination with calcium oxide, barium oxide,

lanthanum oxide and/or yttrium oxide.. In general, oxides of silicon, aluminum, and combinations thereof are not preferred.

[0033] In particular, active metal oxides are those metal oxides, different from typical binders and/or matrix materials, that, when used in combination with a molecular sieve in a catalyst composition, are effective in extending of the useful life of the catalyst composition, particularly in the conversion of a feedstock comprising methanol into one or more olefin(s). Quantification of the extension in catalyst life is determined by the Lifetime Enhancement Index (LEI) as defined by the following equation:

$$LEI = \frac{Lifetime\ of\ Catalyst\ in\ Combination\ with\ Active\ Metal\ Oxide}{Lifetime\ of\ Catalyst}$$

where the lifetime of the catalyst or catalyst composition, in the same process under the same conditions, is the cumulative amount of feedstock processed per gram of catalyst composition until the conversion of feedstock by the catalyst composition falls below some defined level, for example 10%. An inactive metal oxide will have little to no effect on the lifetime of the catalyst composition, or will shorten the lifetime of the catalyst composition, and will therefore have a LEI less than or equal to 1. Thus active metal oxides of the invention are those metal oxides, different from typical binders and/or matrix materials, that, when used in combination with a molecular sieve, provide a molecular sieve catalyst composition that has a LEI greater than 1. By definition, a molecular sieve catalyst composition that has not been combined with an active metal oxide will have a LEI equal to 1.0.

[0034] It is found that, by including an active metal oxide in combination with a molecular sieve, a catalyst composition can be produced having an LEI in the range of from greater than 1 to 20, such as from 1.5 to 10. Typically catalyst compositions according to the invention exhibit LEI values greater than 1.1, for example in the range of from 1.2 to 15, and more particularly greater than 1.3, such as greater than 1.5, such as greater than 1.7, such as greater than 2.

[0035] In particular, the metal oxides useful herein have an uptake of carbon dioxide at 100°C of at least 0.03 mg/m^2 of the metal oxide, such as at least 0.035 mg/m^2 of the metal oxide. Although the upper limit on the carbon dioxide uptake of the metal oxide is not critical, in general the metal oxides useful herein will have a carbon dioxide at 100°C of less than 10 mg/m^2 of the metal oxide, such as less than 5 mg/m^2 of the metal oxide. Typically, the metal oxides useful herein have a carbon dioxide uptake of 0.04 to 0.2 mg/m^2 of the metal oxide.

[0036] In order to determine the carbon dioxide uptake of a metal oxide, the following procedure is adopted. A sample of the metal oxide is dehydrated by heating the sample to 200°C to 500°C in flowing air until a constant weight, the "dry weight", is obtained. The temperature of the sample is then reduced to 100°C and carbon dioxide is passed over the sample, either continuously or in pulses, again until constant weight is obtained. The increase in weight of the sample in terms of mg/mg of the sample based on the dry weight of the sample is the amount of adsorbed carbon dioxide.

[0037] In the Examples reported below, the carbon dioxide adsorption is measured using a Mettler TGA/SDTA 851 thermogravimetric analysis system under ambient pressure. The metal oxide sample is dehydrated in flowing air to 500°C for one hour. The temperature of the sample is then reduced in flowing helium to 100°C. After the sample has equilibrated at the desired adsorption temperature in flowing helium, the sample is subjected to 20 separate pulses (about 12 seconds/pulse) of a gaseous mixture comprising 10-weight % carbon dioxide with the remainder being helium. After each pulse of the adsorbing gas the metal oxide sample is flushed with flowing helium for 3 minutes. The increase in weight of the sample in terms of mg/mg adsorbent based on the adsorbent weight after treatment at 500°C is the amount of adsorbed carbon dioxide. The surface area of the sample is measured in accordance with the method of Brunauer, Emmett, and Teller (BET) published as ASTM D 3663 to provide the carbon dioxide uptake in terms of mg carbon dioxide/m^2 of the metal oxide.

[0038] Conveniently, the active metal oxide(s) has a BET surface area of greater than 10 m^2/g, such as greater than 10 m^2/g to 300 m^2/g. Preferably, the active metal oxide(s) has a BET surface area of at least 20 m^2/g, such as from 20 m^2/g to 250 m^2/g. More preferably, the active metal oxide(s) has a BET surface area of at least 25 m^2/g, such as from 25 m^2/g to 200 m^2/g. In a preferred embodiment, the active metal oxide(s) includes a zirconium oxide having a BET surface area greater than 20 m^2/g, such as greater than 25 m^2/g and particularly greater than 30 m^2/g

[0039] The active metal oxide(s) can be prepared using a variety of methods. It is preferable that the active metal oxide is made from an active metal oxide precursor, such as a metal salt, such as a halide, nitrate sulfate or acetate. Other suitable sources of the metal oxide include compounds that form the metal oxide during calcination, such as oxychlorides and nitrates. Alkoxides are also suitable sources of the Group 4 metal oxide, for example zirconium n-propoxide. A preferred source of the Group 4 metal oxide is hydrated zirconia. The expression, hydrated zirconia, is intended to connote a material comprising zirconium atoms covalently linked to other zirconium atoms via bridging oxygen atoms, and further comprising available hydroxyl groups.

[0040] In one embodiment, the hydrated zirconia is hydrothermally treated under conditions that include a temperature of at least 80°C, preferably at least 100°C. The hydrothermal treatment typically takes place in a sealed vessel at greater than atmospheric pressure. However, a preferred mode of treatment involves the use of an open vessel under reflux conditions. Agitation of hydrated Group 4 metal oxide in a liquid medium, for example, by the action of refluxing liquid and/or stirring, promotes the effective interaction of the hydrated oxide with the liquid medium. The duration of the contact of the hydrated oxide with the liquid medium is conveniently at least 1 hour, such as at least 8 hours. The liquid medium for this treatment typically has a pH of about 6 or greater, such as 8 or greater. Non-limiting examples of suitable liquid media include water, hydroxide solutions (including hydroxides of NH_4^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}), carbonate and

bicarbonate solutions (including carbonates and bicarbonates of NH_4^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}), pyridine and its derivatives, and alkyl/hydroxyl amines.

[0041] In another embodiment, the active metal oxide is prepared, for example, by subjecting a liquid solution, such as an aqueous solution, comprising a source of ions of a Group 4 metal to conditions sufficient to cause precipitation of a hydrated precursor of the solid oxide material, such as by the addition of a precipitating reagent to the solution. Conveniently, the precipitation is conducted at a pH above 7. For example, the precipitating agent may be a base such as sodium hydroxide or ammonium hydroxide.

[0042] When a mixture of a Group 4 metal oxide with a Group 2 and/or 3 metal oxide is to be prepared, a first liquid solution comprising a source of ions of a Group 4 metal can be combined with a second liquid solution comprising a source of ions of a Group 2 and/or Group 3 metal. This combination of two solutions can take place under conditions sufficient to cause co-precipitation of a hydrated precursor of the mixed oxide material as a solid from the solution. Alternatively, the source of ions of the Group 4 metal and the source of ions of the Group 2 and/or Group 3 metal may be combined into a single solution. This solution may then be subjected to conditions sufficient to cause co-precipitation of a hydrated precursor to the solid mixed oxide material, such as by the addition of a precipitating reagent to the solution.

[0043] The temperature at which the solution is maintained during the precipitation is generally less than 200°C, for example in the range of from 0°C to less than 200°C. A particular range of temperatures for precipitation is from 20°C to 100°C. The resulting gel is preferably then hydrothermally treated at temperatures of at least 80°C, preferably at least 100°C. The hydrothermal treatment typically takes place at atmospheric pressure. The gel, in one embodiment, is hydrothermally treated for up to 10 days, such as up to 5 days, for example up to 3 days.

[0044] The hydrated precursor to the metal oxide(s) is then recovered, for example by filtration or centrifugation, and washed and dried. The resulting

material can then be calcined, such as in an oxidizing atmosphere, at a temperature of at least 400°C, such as at least 500°C, for example from 600°C to 900°C, and particularly from 650°C to 800°C, to form the active metal oxide or active mixed metal oxide. The calcination time is typically up to 48 hours, such as for 0.5 to 24 hours, for example for 1.0 to 10 hours. In one embodiment, calcination is carried out at about 700°C for 1 to 3 hours.

[0045] In another embodiment, the Group 4 metal oxide and the Group 2 and/or Group 3 metal oxide are made separately and then contacted together to form the mixed metal oxide that is then contacted with the molecular sieve. For example, the Group 4 metal oxide can be contacted with the molecular sieve prior to introducing the Group 2 and/or Group 3 metal oxide or alternatively, the Group 2 and/or Group 3 metal oxide can be contacted with the molecular sieve prior to introducing the Group 4 metal oxide.

[0046] Where the catalyst composition comprises a Group 4 metal oxide and a Group 3 metal oxide, the mole ratio of the Group 4 metal oxide to the Group 3 metal oxide may be in the range of from 1000:1 to 1:1, such as from 500:1 to 2:1, preferably from 100:1 to 3:1, more preferably from 75:1 to 5:1 based on the total moles of the Group 4 and Group 3 metal oxides. In addition, the catalyst composition can contain from 1 to 25 %, preferably from 1 to 20 %, more preferably from 1 to 15 %, by weight of Group 3 metal based on the total weight of the mixed metal oxide, particularly where the Group 3 metal oxide is a lanthanum or yttrium metal oxide and the Group 4 metal oxide is a zirconium metal oxide.

[0047] Where the catalyst composition comprises a Group 4 metal oxide and a Group 2 metal oxide, the mole ratio of the Group 4 metal oxide to the Group 2 metal oxide may be in the range of from 1000:1 to 1:2, such as from 500:1 to 2:3, preferably from 100:1 to 1:1 and more preferably from 50:1 to 2:1, based on the total moles of the Group 4 and Group 2 metal oxides. In addition, the catalyst composition can contain from 1 to 25 %, preferably from 1 to20 % and more preferably from 1 to 15 %, by weight of Group 2 metal based on the total weight

of the mixed metal oxide, particularly where the Group 2 metal oxide is calcium oxide and the Group 4 metal oxide is a zirconium metal oxide.

Catalyst Composition

[0048] The catalyst composition of the invention includes any one of the molecular sieves previously described and one or more of the active metal oxides described above, optionally with a binder and/or matrix material different from the active metal oxide(s). Typically, the weight ratio of the molecular sieve to the active metal oxide in the catalyst composition is in the range of from 5 weight percent to 800 weight percent, preferably from 10 weight percent to 600 weight percent, more preferably from 20 weight percent to 500 weight percent, and most preferably from 30 weight percent to 400 weight percent.

[0049] There are many different binders that are useful in forming the catalyst composition of the invention. Non-limiting examples of binders that are useful alone or in combination include various types of hydrated alumina, silicas, and/or other inorganic oxide sols. One preferred alumina containing sol is aluminum chlorhydrol. 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 binder component. For example, an alumina sol will convert to an aluminum oxide binder following heat treatment.

[0050] Aluminum chlorhydrol, a hydroxylated aluminum based sol containing a chloride counter ion, has the general formula of $Al_mO_n(OH)_oCl_p \cdot x(H_2O)$ 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 $Al_{13}O_4(OH)_{24}Cl_7 \cdot 12(H_2O)$ as is described in G.M. Wolterman, et al., Stud. Surf. Sci. and Catal., 76, pages 105-144 (1993). In another embodiment, one or more binders are combined with one or more other 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.

[0051] 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, Massachussetts.

[0052] Where the catalyst composition contains a matrix material, this is preferably different from the active metal oxide and any binder. Matrix materials are typically effective in reducing overall catalyst cost, acting as thermal sinks during regeneration, densifying the catalyst composition, and increasing catalyst physical properties such as crush strength and attrition resistance.

[0053] Non-limiting examples of matrix materials useful herein include one or more non-active metal oxides including 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 subbentonites 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. The matrix material, such as a clay, may be subjected to well known modification processes such as calcination and/or acid treatment and/or chemical treatment.

[0054] In a preferred embodiment, the matrix material is a clay or a clay-type composition, particularly having a low iron or titania content, and most preferably is kaolin. Kaolin has been found to form a pumpable, high solids content slurry, to have a low fresh surface area, and to pack together easily due to its platelet structure. A preferred average particle size of the matrix material, most preferably kaolin, is from 0.1 μm to 0.6 μm with a D_{90} particle size distribution of less than 1 μm.

[0055] Where the catalyst composition contains a binder or matrix material, the catalyst composition typically contains from 1% to 80%, preferably from

about 5% to 60%, and more preferably from 5% to 50%, by weight of the molecular sieve based on the total weight of the catalyst composition.

[0056] Where the catalyst composition contains a binder and a matrix material, the weight ratio of the binder to the matrix material is typically from 1:15 to 1:5, such as from 1:10 to 1:4, and particularly from 1:6 to 1:5. The amount of binder is typically from about 2% by weight to about 30% by weight, such as from about 5% by weight to about 20% by weight, and particularly from about 7% by weight to about 15% by weight, based on the total weight of the binder, the molecular sieve and matrix material.

[0057] The catalyst composition typically has a density in the range of from 0.5 g/cc to 5 g/cc, such as from from 0.6 g/cc to 5 g/cc, for example from 0.7 g/cc to 4 g/cc, particularly in the range of from 0.8 g/cc to 3 g/cc.

Catalyst Composition Formulation

[0058] In making the catalyst composition, the molecular sieve is first synthesized and is then physically mixed with the active metal oxide, preferably in a substantially dry, dried, or calcined state. Most preferably the molecular sieve and active metal oxide are physically mixed in their calcined state. Intimate physical mixing can be achieved by any method known in the art, such as mixing with a mixer muller, drum mixer, ribbon/paddle blender, kneader, or the like. Chemical reaction between the molecular sieve and the metal oxide(s) is unnecessary and, in general, is not preferred.

[0059] Where the catalyst composition contains a matrix and/or binder, the molecular sieve is conveniently initially formulated into a catalyst precursor with the matrix and/or binder and the active metal oxide is then combined with the formulated precursor. The active metal oxide can be added as unsupported particles or can be added in combination with a support, such as a binder or matrix material. The resultant catalyst composition can then be formed into useful shaped and sized particles by well-known techniques such as spray drying, pelletizing, extrusion, and the like.

[0060] In one embodiment, the molecular sieve composition and the matrix material, optionally with a binder, are combined with a liquid to form a slurry and then mixed to produce a substantially homogeneous mixture containing the molecular sieve composition. Non-limiting examples of suitable liquids include water, alcohol, ketones, aldehydes, and/or esters. The most preferred liquid is water. The slurry of the molecular sieve composition, binder and matrix material is then fed to a forming unit, such as spray drier, that forms the catalyst composition into the required shape, for example microspheres.

[0061] 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 is usually performed. Typical calcination temperatures are in the range from 400°C to 1,000°C, preferably from 500°C to 800°C and more preferably from 550°C to 700°C. Typical calcination environments are air (which may include a small amount of water vapor), nitrogen, helium, flue gas (combustion product lean in oxygen), or any combination thereof.

[0062] In a preferred embodiment, the catalyst composition is heated in nitrogen at a temperature of from 600°C to 700°C for a period of time typically from 30 minutes to 15 hours, preferably from 1 hour to about 10 hours, more preferably from about 1 hour to about 5 hours, and most preferably from about 2 hours to about 4 hours.

Use of Catalyst Composition

[0063] The catalyst composition described above is 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 alkylbenzenes; transalkylation, of for example a combination of aromatic and polyalkylaromatic hydrocarbons; dealkylation; hydrodecylization; disproportionation, of for example toluene to make benzene and xylenes; oligomerization, of for example straight and branched chain olefin(s); and dehydrocyclization.

[0064] Preferred processes include processes for converting naphtha to highly aromatic mixtures; converting light olefin(s) to gasoline, distillates and lubricants; converting oxygenates to olefin(s); converting light paraffins to olefins and/or aromatics; and converting unsaturated hydrocarbons (ethylene and/or acetylene) to aldehydes for conversion into alcohols, acids and esters.

[0065] The most preferred process of the invention is the conversion of a feedstock to one or more olefin(s). Typically, the feedstock contains one or more aliphatic-containing compounds, and preferably one or more oxygenates, such that the aliphatic moiety 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.

[0066] Non-limiting examples of suitable 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, alkylamines such as methylamine, 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. Preferably, the feedstock comprises methanol, ethanol, dimethyl ether, diethyl ether or a combination thereof, more preferably methanol and/or dimethyl ether, and most preferably methanol.

[0067] Using the various feedstocks discussed above, particularly a feedstock containing an oxygenate, such as an alcohol, the catalyst composition of the invention is effective to convert the feedstock primarily into one or more olefin(s). The olefin(s) produced 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 are ethylene and/or propylene.

[0068] Typically, the catalyst composition of the invention is effective to convert a feedstock containing one or more oxygenates into a product containing greater than 50 weight percent, typically greater than 60 weight percent, such as greater than 70 weight percent, and preferably greater than 80 weight percent of olefin(s) based on the total weight of hydrocarbon in the product. Moreover, the amount of ethylene and/or propylene produced based on the total weight of hydrocarbon in the product is typically greater than 40 weight percent, for example greater than 50 weight percent, preferably greater than 65 weight percent, and more preferably greater than 78 weight percent. Typically, the amount ethylene produced in weight percent based on the total weight of hydrocarbon product produced, is greater than 20 weight percent, such as greater than 30 weight percent, for example greater than 40 weight percent. In addition, the amount of propylene produced in weight percent based on the total weight of hydrocarbon product produced is greater than 20 weight percent, such as greater than 25 weight percent, for example greater than 30 weight percent, and preferably greater than 35 weight percent.

[0069] Using the catalyst composition of the invention for the conversion of a feedstock comprising methanol and dimethylether to ethylene and propylene, it

is found that the production of ethane and propane is reduced by greater than 10%, such as greater than 20%, for example greater than 30%, and particularly in the range of from 30% to 40% compared to a similar catalyst composition at the same conversion conditions but without the active metal oxide component(s).

[0070] In addition to the oxygenate component, such as methanol, the feedstock may contain one or more diluents, which are generally non-reactive to the feedstock or molecular sieve catalyst composition and are typically used to reduce the concentration of the feedstock. 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.

[0071] The present process can be conducted over a wide range of temperatures, such as in the range of from 200°C to 1000°C, for example from 250°C to 800°C, including from 250°C to 750 °C, conveniently from 300°C to 650°C, preferably from 350°C to 600°C and more preferably from 350°C to 550°C.

[0072] Similarly, the present process can be conducted over a wide range of pressures including autogenous pressure. Typically the partial pressure of the feedstock exclusive of any diluent therein employed in the process is in the range of from 0.1 kPaa to 5 MPaa, preferably from 5 kPaa to 1 MPaa, and more preferably from 20 kPaa to 500 kPaa.

[0073] The weight hourly space velocity (WHSV), defined as the total weight of feedstock excluding any diluents per hour per weight of molecular sieve in the catalyst composition, can range from 1 hr^{-1} to 5000 hr^{-1}, preferably from 2 hr^{-1} to 3000 hr^{-1}, more preferably from 5 hr^{-1} to 1500 hr^{-1}, and most preferably from 10 hr^{-1} to 1000 hr^{-1}. In one embodiment, the WHSV is at least 20 hr^{-1} and, where the feedstock contains methanol and/or dimethyl ether, is in the range of from 20 hr^{-1} to 300 hr^{-1}.

[0074] The process of the invention is conveniently conducted as a fixed bed process, or more typically as a fluidized bed process (including a turbulent bed process), such as a continuous fluidized bed process, and particularly a continuous high velocity fluidized bed process.

[0075] In one practical embodiment, the process is conducted as a fluidized bed process utilizing a reactor system, a regeneration system and a recovery system. In such a process, fresh feedstock, optionally with one or more diluent(s), is fed together with the molecular sieve catalyst composition into one or more riser reactor(s) in the reactor system. The feedstock is converted in the riser reactor(s) into a gaseous effluent that enters a disengaging vessel in the reactor system along with the coked catalyst composition. The coked catalyst composition is separated from the gaseous effluent within the disengaging vessel, typically with the aid of cyclones, and is then fed to a stripping zone, typically in a lower portion of the disengaging vessel. In the stripping zone the coked catalyst composition is contacted with a gas, such steam, methane, carbon dioxide, carbon monoxide, hydrogen, and/or an inert gas such as argon, preferably steam, to recover adsorbed hydrocarbons from the coked catalyst composition that is then introduced into the regeneration system.

[0076] In the regeneration system the coked catalyst composition is contacted with a regeneration medium, preferably a gas containing oxygen, under regeneration conditions 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. For example, the regeneration conditions may include temperature in the range of from 450°C to 750°C, and preferably from 550°C to 700°C.

[0077] The regenerated catalyst composition withdrawn from the regeneration system is combined with 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).

[0078] The gaseous effluent is withdrawn from the disengaging system and is passed through a recovery system for separating and purifying the light olefin(s), particularly ethylene and propylene, in the gaseous effluent.

[0079] In one practical embodiment, the process of the invention forms part of an integrated process for producing light olefin(s) from a hydrocarbon feedstock, particularly 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 stream, typically comprising carbon dioxide, carbon monoxide and hydrogen. The synthesis gas stream is then converted to an oxygenate containing stream generally by contacting with a heterogeneous catalyst, typically a copper based catalyst, at temperature in the range of from 150°C to 450°C and a pressure in the range of from 5 MPa to 10 MPa. After purification, the oxygenate containing stream can be used as a feedstock in a process as described above for producing light olefin(s), such as ethylene and/or propylene. Non-limiting examples of this integrated process are described in EP-B-0 933 345, which is herein fully incorporated by reference.

[0080] In another more fully integrated process, optionally combined with the integrated processes described above, the olefin(s) produced are directed to one or more polymerization processes for producing various polyolefins.

[0081] In order to provide a better understanding of the present invention including representative advantages thereof, the following Examples are offered.

[0082] In the Examples, LEI is defined as the ratio of the lifetime of a molecular sieve catalyst composition containing an active metal oxide(s) compared to that of the same molecular sieve in the absence of a metal oxide, defined as having an LEI of 1. For the purpose of determining LEI, lifetime is defined as the cumulative amount of oxygenate converted, preferably into one or more olefin(s), per gram of molecular sieve, until the conversion rate drops to about 10% of its initial value. If the conversion has not fallen to 10% of its initial value by the end of the experiment, lifetime is estimated by linear extrapolation

based on the rate of decrease in conversion over the last two data points in the experiment.

[0083] "Prime Olefin" is the sum of the selectivity to ethylene and propylene. The ratio "$C_2^=/C_3^=$" is the ratio of the ethylene to propylene selectivity weighted over the run. The "C_3 Purity" is calculated by dividing the propylene selectivity by the sum of the propylene and propane selectivities. The selectivities for methane, ethylene, ethane, propylene, propane, C_4's and C_5+'s are average selectivities weighted over the run. Note that the C_5+'s consist only of C_5's, C_6's and C_7's. The selectivity values do not sum to 100% in the Tables because they have been corrected for coke as is well known.

Example A

Preparation of Molecular Sieve

[0084] A silicoaluminophosphate molecular sieve, SAPO-34, designated as MSA, was crystallized in the presence of tetraethyl ammonium hydroxide (R1) and dipropylamine (R2) as the organic structure directing agents or templating agents. A mixture of the following mole ratio composition:

$$0.2\ SiO_2 / Al_2O_3 / P_2O_5 / 0.9\ R1 / 1.5\ R2 / 50\ H_2O.$$

was prepared by initially mixing an amount of Condea Pural SB with deionised water, to form a slurry. To this slurry was added an amount of phosphoric acid (85%). These additions were made with stirring to form a homogeneous mixture. To this homogeneous mixture Ludox AS40 (40% of SiO2) was added, followed by the addition of R1 with mixing to form a homogeneous mixture. To this homogeneous mixture R2 was added and the resultant mixture was then crystallized with agitation in a stainless steel autoclave by heating to 170°C for 40 hours. This provided a slurry of the crystalline molecular sieve. The crystals were then separated from the mother liquor by filtration. The molecular sieve crystals were then mixed with a binder and matrix material and formed into particles by spray drying.

Example B

Conversion Process

[0085] All conversion data presented were obtained using a microflow reactor consisting of a stainless steel reactor (1/4 inch (0.64 cm) outer diameter) located in a furnace to which vaporized methanol was fed. The reactor was maintained at a temperature of 475°C and a pressure of 25 psig (172.4 kPag) The flow rate of the methanol was such that the flow rate of methanol on weight basis per gram of molecular sieve, also known as the weight hourly space velocity (WHSV) was 100 h^{-1}. Product gases exiting the reactor were collected and analyzed using gas chromatography. The catalyst load was 50 mg and the catalyst bed was diluted with quartz to minimize hot spots in the reactor.

Example 1

[0086] One thousand grams of $ZrOCl_2 \cdot 8H_2O$ was dissolved with stirring in 3.0 liters of distilled water. Another solution containing 400 grams of concentrated NH_4OH and 3.0 liters of distilled water was prepared. Both solutions were heated to 60°C. These two heated solutions were combined at a rate of 50ml/min using nozzle mixing. The pH of the final composite was adjusted to approximately 9 by the addition of concentrated ammonium hydroxide. This slurry was then put in polypropylene bottles and placed in a steambox (100°C) for 72 hours. The product formed was recovered by filtration, washed with excess water, and dried overnight at 85°C. A portion of this product was calcined to 700°C in flowing air for 3 hours to produce an active zirconium oxide material.

Example 2

[0087] Five hundred grams of $ZrOCl_2 \cdot 8H_2O$ and 84 grams of $La(NO_3)_3 \cdot 6H_2O$ were dissolved with stirring in 3.0 liters of distilled water. Another solution containing 260 grams of concentrated NH_4OH and 3.0 liters of distilled water was prepared. Both solutions were heated to 60°C and then combined at the rate of 50 ml/min using nozzle mixing to form the final mixture, a slurry. The pH of the

final mixture was adjusted to approximately 9 by the addition of concentrated ammonium hydroxide. This slurry was then put in a polypropylene bottle and placed in a steam box (100°C) for 72 hours. The resulting product formed was recovered by filtration, washed with excess water, and dried overnight at 85°C. A portion of this product, was calcined to 700°C in flowing air for 3 hours to produce an active mixed metal oxide containing a nominal 10 weight percent La (lanthanum) based on the final weight of the mixed metal oxide.

Example 3

[0088] Fifty grams of $ZrOCl_2 \cdot 8H_2O$ were dissolved with stirring in 300ml of distilled water. Another solution containing 4.2 grams of $La(NO_3)_3 \cdot 6H_2O$ and 300 ml of distill water was prepared. These two solutions were combined with stirring to form a final mixture. The pH of the final mixture, a slurry, was adjusted to approximately 9 by the addition of concentrated ammonium hydroxide (28.9 grams). This slurry was then put in a polypropylene bottle and placed in a steam box (100°C) for 72 hours. The resulting product formed was recovered by filtration, washed with excess water, and dried overnight at 85°C. A portion of this resulting product was calcined to 700°C in flowing air for 3 hours to produce an active mixed metal oxide containing a nominal 5 weight percent La based on the final weight of the mixed metal oxide.

Example 4

[0089] Five hundred grams of $ZrOCl_2 \cdot 8H_2O$ and 70 grams of $Y(NO_3)_3 \cdot 5H_2O$ were dissolved with stirring in 3.0 liters of distilled water. Another solution containing 260 grams of concentrated NH_4OH and 3.0 liters of distilled water was prepared. Both solutions were heated to 60°C and then combined at the rate of 50 ml/min using nozzle mixing to form a final mixture. The pH of the final mixture, a slurry, was adjusted to approximately 9 by the addition of concentrated ammonium hydroxide. This slurry was then put in a polypropylene bottle and placed in a steam box (100°C) for 72 hours. The resulting product formed was

recovered by filtration, washed with excess water, and dried overnight at 85°C. A portion of the resulting product was calcined to 700°C in flowing air for 3 hours to produce an active mixed metal oxide containing a nominal 10 weight percent Y (yttrium) based on the final weight of the mixed metal oxide.

Example 5

[0090] Five hundred grams of $ZrOCl_2 \cdot 8H_2O$ and 56 grams of $Ca(NO_3)_2 \cdot 4H_2O$ were dissolved with stirring in 3000ml of distilled water. Another solution containing 260 grams of NH_4OH and 3000ml of distilled water was prepared. These two solutions were combined with stirring. The pH of the final composite was adjusted to approximately 9 by the addition of concentrated ammonium hydroxide (160 grams). This slurry was then put in polypropylene bottles and placed in a steambox (100°C) for 72 hours. The resulting product formed was recovered by filtration, washed with excess water, and dried overnight at 85°C. A portion of this product was calcined to 700°C in flowing air for 3 hours to produce an active mixed metal oxide containing a nominal 5 weight percent Ca (calcium) based on the final weight of the mixed metal oxide.

Example 6

[0091] Seventy grams of $TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$ (x=1) were dissolved with stirring in 400 ml of distilled water. Another solution containing 12.8 grams of $CeSO_4$ and 300 ml of distilled water was prepared. These two solutions were combined with stirring. The pH of the final composite was adjusted to approximately 8 by the addition of concentrated ammonium hydroxide (64.3 grams). This slurry was then put in polypropylene bottles and placed in a steambox (100°C) for 72 hours. The product formed was recovered by filtration, washed with excess water, and dried overnight at 85°C. A portion of this product was calcined to 700°C in flowing air for 3 hours to produce an active mixed metal oxide containing a nominal 5 weight percent Ce based on the final weight of the mixed metal oxide.

Example 7

[0092] Five grams of $HfOCl_2 \cdot xH_2O$ was dissolved with stirring in 100ml of distilled water. The pH of the final composite was adjusted to approximately 9 by the addition of concentrated ammonium hydroxide (4.5 grams). This slurry was then put in a polypropylene bottle and placed in a steambox (100°C) for 72 hours. The product formed was recovered by filtration, washed with excess water, and dried overnight at 85°C. A portion of this catalyst was calcined to 700°C in flowing air for 3 hours to produce an active hafnium oxide.

Example 8

[0093] Five grams of $HfOCl_2 \cdot xH_2O$ and 0.62 grams of $La(NO_3)_3 \cdot 6H_2O$ were dissolved with stirring in 100ml of distilled water. The pH of the final composite was adjusted to approximately 9 by the addition of concentrated ammonium hydroxide (3.5 grams). This slurry was then put in a polypropylene bottle and placed in a steambox (100°C) for 72 hours. The product formed was recovered by filtration, washed with excess water, and dried overnight at 85°C. A portion of this catalyst was calcined to 700°C in flowing air for 3 hours to produce an active mixed metal oxide containing a nominal 5 weight % La based on the final weight of the mixed metal oxide.

Example 9

[0094] The carbon dioxide uptake of the oxides of Examples 1 through 8 were measured using a Mettler TGA/SDTA 851 thermogravimetric analysis system under ambient pressure. The metal oxide samples were first dehydrated in flowing air to about 500°C for one hour after which the uptake of carbon dioxide was measured at 100°C. The surface area of the samples were measured in accordance with the method of Brunauer, Emmett, and Teller (BET) to provide the

carbon dioxide uptake in terms of mg carbon dioxide/m^2 of the metal oxide presented in Table 1.

Table 1

Example	Catalyst Dry Weight (mg)	mg of CO_2	Surface Area (m^2/g)	CO_2 Uptake (mg of CO_2/m^2)
1	76	0.0980	29	0.045
2	115	0.7781	80	0.085
3	73	0.4243	89	0.065
4	97	0.3808	100	0.039
5	78	0.5399	85	0.081
6	43	0.1035	50	0.048
7	158	0.3704	25	0.094
8	164	0.7359	60	0.075

Example 10 (Comparative)

[0095] The performance of the control, the molecular sieve of Example A, MSA, using a 50 mg load in the reactor and under the conditions discussed above in Example B is reported in Tables 2 and 3.

Example 11

[0096] In this Example, the catalyst composition consisted of 40 mg MSA of Example A and 10 mg of the active zirconium oxide of Example 1. The catalyst composition and active mixed metal oxide were well mixed, and then diluted with quartz to form the reactor bed. The results of testing this catalyst composition in the process of Example B are shown in Tables 2 and 3. The results indicate that the addition of the active zirconium oxide to the catalyst bed increased the lifetime of the molecular sieve composition significantly, and decreased the amounts of undesired ethane and propane.

Example 12

[0097] In this Example, the catalyst composition consisted of 40 mg MSA of Example A and 10 mg of the active mixed metal oxide containing 10 weight percent La, described in Example 2. The catalyst composition and active mixed metal oxide were well mixed, and then diluted with quartz to form the reactor bed.

The results of testing this catalyst composition in the process of Example B are shown in Tables 2 and 3. The data in Tables 2 and 3 illustrate that by constituting 20% of the catalyst composition load with the active mixed metal oxide containing 10 weight percent La, the lifetime of the molecular sieve doubled, as indicated by its LEI value of 2. In addition, there was a net gain of 1.7% in prime olefins on an absolute basis, with most of this gain being due to an increase in propylene of 2.76%, offsetting a small decrease in ethylene of 1.07%. Selectivity to ethane decreased by 39% and selectivity to propane decreased by 37% suggesting that hydrogen transfer reactions have been significantly reduced.

Example 13

[0098] In this Example, the catalyst consisted of 30 mg MSA of Example A and 20 mg of the active mixed metal oxide containing 10 weight percent La, as described in Example 2. The catalyst composition and active mixed metal oxide were well mixed, and then diluted with quartz to form the reactor bed. The results of testing this catalyst composition in the process of Example B are shown in Tables 2 and 3. The data of Tables 2 and 3 illustrate that by constituting 40% of the catalyst composition load containing 10 weight percent La, the lifetime of the SAPO-34 catalyst composition increased by 440%. Trends in selectivity for this catalyst loading are similar to those seen in Example 8.

Example 14

[0099] In this Example, the catalyst composition consisted of 40 mg MSA from Example A and 10 mg of the active mixed metal oxide containing 10 weight percent Y, as described in Example 4. The catalyst composition and active mixed metal oxide were well mixed, and then diluted with quartz to form the reactor bed. The results of testing this catalyst composition in the process of Example B are shown in Tables 2 and 3. The substitution of yttrium for lanthanum has the effect of increasing the LEI even further. However, the improvements in selectivity are

not as dramatic as seen with the lanthanum, with the gain in prime olefin being 1.2% on an absolute basis.

Example 15

[0100] In this Example, the catalyst consisted of 40 mg MSA of Example A and 10 mg of the active mixed metal oxide containing 5 weight percent La, as described in Example 3. The catalyst composition and active mixed metal oxide were well mixed, and then diluted with quartz to form the reactor bed. The results of testing this catalyst composition in the process of Example B are shown in Tables 2 and 3. It will be seen that the active mixed metal oxide containing 5 weight percent lanthanum oxide seems to have a much stronger effect in increasing the LEI than the active mixed metal oxide of Example 8 containing 10 weight percent La.

Example 16

[0101] In this Example 16, the catalyst consisted of 40 mg MSA of Example A and 10 mg of an active mixed metal oxide containing 5 weight percent Ca, as described in Example 5. The catalyst composition and active mixed metal oxide were well mixed, and then diluted with quartz to form the reactor bed. The results of this experiment in the reactor and conditions discussed above in Example B are shown in Tables 2 and 3. The active mixed metal oxide containing 5 weight percent calcium oxide has increased the lifetime of the molecular sieve composition by 223%.

Example 17 (Comparative)

[0102] In this Comparative Example, the catalyst composition consisted of 40 mg MSA of Example A and 10 mg of an amorphous silica/alumina, an inactive mixed metal oxide. The molecular sieve catalyst composition and the inactive mixed metal oxide catalysts were well mixed, and then diluted with quartz to form the reactor bed. The results of testing this catalyst composition in the process of

Example B are also shown in Tables 2 and 3. This Comparative Example 17 illustrates a reduction in LEI to a value less than 1.0 when an inactive mixed metal oxide is utilized as compared to Example 11 of the invention. In addition, there is a loss of 1.07% in prime olefin selectivity, and no significant reduction in ethane and propane production.

Example 18

[0103] In this Example, the catalyst composition consisted of 40 mg MSA from Example A and 10 mg an active mixed metal oxide containing Ce and titania, as described in Example 6. The catalyst composition and active mixed metal oxide were well mixed, and then diluted with quartz to form the reactor bed. The results of testing this catalyst composition in the process of Example B are shown in Tables 2 and 3. The presence of the active mixed metal oxide increased the lifetime of the molecular sieve composition by 134%.

Example 19

[0104] In this Example, the catalyst composition consisted of 40 mg MSA of Example A and 10 mg of the active hafnium metal oxide described in Example 7. The catalyst composition and active metal oxide were well mixed, and then diluted with quartz to form the reactor bed. The results of testing this catalyst composition in the process of Example B are shown in Tables 2 and 3. The data in Tables 2 and 3 illustrate that by constituting 20% of the catalyst composition load with the active hafnium metal oxide, the lifetime of the molecular sieve has increased by 126%. Selectivity to ethane decreased by 40% and selectivity to propane decreased by 46% suggesting that hydrogen transfer reactions have been significantly reduced.

Example 20

[0105] In this Example, the catalyst composition consisted of 40 mg MSA of Example A and 10 mg of the active mixed metal oxide containing 5 weight

percent La, described in Example 8. The catalyst composition and active mixed metal oxide were well mixed, and then diluted with quartz to form the reactor bed. The results of testing this catalyst composition in the process of Example B are shown in Tables 2 and 3. The data in Tables 2 and 3 illustrate that by constituting 20% of the catalyst composition load with the active mixed metal oxide containing 5 weight percent La, the lifetime of the molecular sieve has increased by 150%. Selectivity to ethane decreased by 51% and selectivity to propane decreased by 51% suggesting that hydrogen transfer reactions have been significantly reduced.

Table 2

Example	Reactor Bed Composition (wt%)	LEI	Prime Olefin (%)	$C_2^=/C_3^=$	C_3 Purity (%)
10 (Comp)	100% MSA	1	74.65	0.92	92.7
11	80% MSA/20%ZrO_2	2.64	74.79	0.82	96.1
12	80% MSA / 20% of 10% La/ZrO_2	2.03	76.34	0.84	95.6
13	60% MSA / 40% of 10% La/ZrO_2	5.41	75.50	0.85	94.6
14	80% MSA / 20% of 10% Y/ZrO_2	2.79	75.81	0.85	94.9
15	80% MSA / 20% of 5% La/ZrO_2	4.85	75.84	0.84	94.8
16	80% MSA / 20% of 5% Ca/ZrO_2	3.23	73.85	0.79	96.7
17 (Comp)	80% MSA / 20% of SiO_2/Al_2O_3	0.79	73.58	0.93	93.3
18	80% MSA / 20% of Ce/TiO_2	2.34	65.65	0.87	95.1
19	80% MSA / 20% of HfO_2	2.26	72.98	0.71	96.2
20	80% MSA / 20% of 5% La/HfO_2	2.50	72.75	0.76	96.5

Table 3

		Product Selectivities (%)						
Example	**Reactor Bed (wt %)**	**CH_4**	**$C_2^=$**	**C_2^o**	**$C_3^=$**	**C_3^o**	**C_4's**	**C_5+**
10 (Comp)	100% MSA	1.51	35.82	0.95	38.83	3.05	14.50	2.12
11	80% MSA / 20% ZrO_2	1.50	33.74	0.53	41.05	1.68	14.79	3.31
12	80% MSA / 20% of 10% La/ZrO_2	1.31	34.75	0.58	41.59	1.93	14.96	2.46
13	60% MSA / 40% of 10% La/ZrO_2	1.47	34.75	0.66	40.75	2.32	14.76	2.52
14	80% MSA/ 20% of 10% Y/ZrO_2	1.32	34.92	0.66	40.88	2.20	14.41	3.07
15	80% MSA / 20% of 5% La/ZrO_2	1.26	34.59	0.64	41.25	2.28	14.96	2.52
16	80% MSA / 20% of 5% Ca/ZrO_2	1.50	32.65	0.42	41.20	1.43	14.84	5.34
17 (Comp)	80% MSA / 20% of SiO_2/Al_2O_3	2.17	35.46	0.89	38.12	2.72	14.21	2.65
18	80% MSA / 20% of Ce/TiO_2	6.79	30.57	0.75	35.09	1.80	12.72	3.97
19	80% MSA / 20% of HfO_2	1.98	31.62	0.52	41.36	1.65	14.64	4.93
20	80% MSA / 20% of 5% La/HfO_2	1.98	31.58	0.47	41.18	1.49	14.53	5.52

CLAIMS

We claim:

1. A catalyst composition comprising a molecular sieve and at least one oxide of a metal selected from Group 4 of the Periodic Table of Elements, wherein said metal oxide has an uptake of carbon dioxide at 100°C of at least 0.03 mg/m^2 of the metal oxide.

2. The catalyst composition of claim 1 wherein said metal oxide has an uptake of carbon dioxide at 100°C of at least 0.035 mg/m^2 of the metal oxide.

3. The catalyst composition of claim 1 wherein said metal oxide has an uptake of carbon dioxide at 100°C of less than 10 mg/m^2 of the metal oxide.

4. The catalyst composition of claim 1 wherein said metal oxide has an uptake of carbon dioxide at 100°C of less than 5 mg/m^2 of the metal oxide.

5. The catalyst composition of claim 1 and also including at least one of a binder and a matrix material different from said metal oxide.

6. The catalyst composition of claim 1 wherein said metal oxide has a surface area greater than 10 m^2/g.

7. The catalyst composition of claim 1 and also including a binder and a matrix material each being different from one another and from said metal oxide.

8. The catalyst composition of claim 7 wherein the binder is an alumina sol and the matrix material is a clay.

9. The catalyst composition of claim 1 wherein said metal oxide is selected from

zirconium oxide and hafnium oxide.

10. The catalyst composition of claim 1 and also including an oxide of a metal selected from Group 2 and Group 3 of the Periodic Table of Elements.

11. The catalyst composition of claim 10 wherein the Group 4 metal oxide comprises zirconium oxide and the Group 2 and/or Group 3 metal oxide comprises one or more oxides selected from the group consisting of calcium oxide, barium oxide, lanthanum oxide, yttrium oxide and scandium oxide.

12. The catalyst composition of claim 1 wherein the molecular sieve comprises a framework inciuding at least two tetrahedral units selected from [SiO_4], [AlO_4] and [PO_4] units.

13. The catalyst composition of claim 12 wherein the molecular sieve comprises a silicoaluminophosphate.

14. The catalyst composition of claim 12 wherein the molecular sieve comprises a CHA framework-type molecular sieve.

15. The catalyst composition of claim 14 wherein the molecular sieve further comprises an AEI framework-type molecular sieve.

16. The catalyst composition of claim 1 wherein the weight ratio of the molecular sieve to metal oxide is in the range of from 5 percent to 800 percent.

17. A molecular sieve catalyst composition comprising an active Group 4 metal oxide and a Group 2 and/or a Group 3 metal oxide, a binder, a matrix material, and a silicoaluminophosphate molecular sieve.

18. A method for making a catalyst composition, the method comprising physically mixing first particles comprising a molecular sieve with second particles comprising a Group 4 metal oxide having an uptake of carbon dioxide at 100°C of at least 0.03 mg/m^2 of the metal oxide particles.

19. The method of claim 18 wherein said second particles have a surface area greater than 10 m^2/g.

20. The method of claim 18 wherein said second particles have a surface area greater than 15 m^2/g.

21. The method of claim 18 wherein said first particles comprise a silicoaluminophosphate molecular sieve and/or an aluminophosphate molecular sieve.

22. The method of claim 18 wherein at least one said first and said second particles also include at least one of a binder and a matrix material.

23. The method of claim 18 wherein said first particles comprise a silicoaluminophosphate molecular sieve, a binder including an alumina sol and a matrix material including a clay.

24. The method of claim 18 wherein said second particles also comprise a Group 2 and/or Group 3 metal oxide.

25. The method of claim 18 wherein said second particles comprise zirconium oxide and at least one of calcium oxide, barium oxide, lanthanum oxide, yttrium oxide and scandium oxide.

26. A method of making a catalyst composition, the method comprising:

(i) synthesizing a molecular sieve from a reaction mixture comprising at least one templating agent and at least two of a silicon source, a phosphorus source and an aluminum source; and

(ii) recovering the molecular sieve synthesized in (i);

(iii) forming a hydrated precursor of a Group 4 metal oxide by precipitation from a solution containing a source of Group 4 metal ions;

(iv) recovering the hydrated precursor formed in (iii);

(v) calcining the hydrated precursor recovered (iv) to form a calcined Group 4 metal oxide that has an uptake of carbon dioxide at 100°C of at least 0.03 mg/m^2 of the metal oxide; and

(vi) physically mixing the molecular sieve recovered in (i) and the calcined metal oxide produced in (v).

27. The method of claim 26 wherein the molecular sieve and/or the Group 4 metal oxide is combined with a binder and/or a matrix material prior to (vi).

28. The method of claim 26 wherein the weight ratio of the molecular sieve to the calcined metal oxide is in the range of from 30 percent to 400 percent.

29. The method of claim 26 wherein the calcined metal oxide has a surface area greater than 10 m^2/g.

30. The method of claim 26 wherein the molecular sieve is spray dried with a matrix material and a binder prior to (vi).

31. The method of claim 30 wherein the molecular sieve is a silicoaluminophosphate, the binder is an alumina sol and the matrix material is a clay.

32. The method of claim 26 wherein a mixed metal oxide is produced in (iii) by precipitation from at least one solution containing a Group 4 metal oxide precursor and at

least one of a Group 2 metal oxide precursor and a Group 3 metal oxide precursor.

33. The method of claim 26 wherein said precipitation is conducted at a pH above 7.

34. The method of claim 26 wherein (iii) also includes hydrothermally treating the precipitate at a temperature of at least 80°C for up to 10 days.

35. The method of claim 26 wherein (v) is conducted at a temperature in the range of from about 400°C to about 900°C.