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(54) Title: METHOD OF SYNTHESIZING MOLECULAR SIEVES

(57) Abstract: The invention is directed to a method of synthesizing a molecular sieve. In particular, the invention is directed to a method for synthesizing a molecular sieve, especially a silicoaluminophosphate molecular sieve, in the presence of a templating agent and a polymeric base. The invention is also directed to formulating the molecular sieve into a catalyst useful in a process for producing olefin(s), preferably ethylene and/or propylene, from a feedstock, preferably an oxygenate containing feedstock.



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## METHOD OF SYNTHESIZING MOLECULAR SIEVES

### Field Of The Invention

5           The present invention relates to a method of synthesizing a molecular sieve. In particular, the invention is directed to a method for synthesizing a molecular sieve, especially a silicoaluminophosphate molecular sieve, and to its formulation into a catalyst composition useful in a process for producing olefin(s), preferably ethylene and/or propylene, from a feedstock, preferably an oxygenate  
10           containing feedstock.

### Background Of The Invention

          Olefins are traditionally produced from petroleum feedstock by catalytic or steam cracking processes. These cracking processes, especially steam  
15           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. Ethylene is used to make various polyethylene plastics, and in making other chemicals such as vinyl chloride, ethylene oxide, ethylbenzene  
20           and alcohol. Propylene is used to make various polypropylene plastics, and in making other chemicals such as acrylonitrile and propylene oxide.

          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  
25           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  
30           are well known, and include conventional steam reforming, autothermal reforming, or a combination thereof.

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.

Molecular sieves are porous solids having pores of different sizes such as zeolites or zeolite-type molecular sieves, carbons and oxides. There are amorphous and crystalline molecular sieves. Molecular sieves include natural, mineral molecular sieves, or chemically formed, synthetic molecular sieves that are typically crystalline materials containing silica, and optionally alumina. The most commercially useful molecular sieves for the petroleum and petrochemical industries are known as zeolites. A zeolite is an aluminosilicate having an open framework structure that usually carries negative charges. This negative charge within portions of the framework is a result of an  $\text{Al}^{3+}$  replacing a  $\text{Si}^{4+}$ . Cations counter-balance these negative charges preserving the electroneutrality of the framework, and these cations are exchangeable with other cations and/or protons. Synthetic molecular sieves, particularly zeolites, are typically synthesized by mixing sources of alumina and silica in a strongly basic aqueous media, often in the presence of a structure directing agent or templating agent. The structure of the molecular sieve formed is determined in part by solubility of the various sources, silica-to-alumina ratio, nature of the cation, synthesis temperature, order of addition, type of templating agent, and the like.

A zeolite is typically formed from corner sharing the oxygen atoms of  $[\text{SiO}_4]$  and  $[\text{AlO}_4]$  tetrahedra or octahedra. 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. The pore size, pore shape,

interstitial spacing or channels, composition, crystal morphology and structure are a few characteristics of molecular sieves that determine their use in various hydrocarbon adsorption and conversion processes.

There are many different types of zeolites well known to convert a feedstock, especially oxygenate containing feedstock, into one or more olefin(s). For example, U.S. Patent No. 5,367,100 describes the use of 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; and U.S. Patent No. 4,079,095 describes the use of ZSM-34 to convert methanol to hydrocarbon products such as ethylene and propylene.

Crystalline aluminophosphates,  $ALPO_4$ , formed from corner sharing  $[AlO_2]$  and  $[PO_2]$  tetrahedra linked by shared oxygen atoms are described in U.S. Patent No. 4,310,440 to produce light olefin(s) from an alcohol. Metal containing aluminophosphate molecular sieves, MeAPO's and ElAPO's, have been also described to convert alcohols into olefin(s). MeAPO's have a  $[MeO_2]$ ,  $[AlO_2]$  and  $[PO_2]$  tetrahedra microporous structure, where Me is a metal source having one or more of the divalent elements Co, Fe, Mg, Mn and Zn, and trivalent Fe from the Periodic Table of Elements. ElAPO's have an  $[ElO_2]$ ,  $[AlO_2]$  and  $[PO_2]$  tetrahedra microporous structure, where El is a metal source having one or more of the elements As, B, Be, Ga, Ge, Li, Ti and Zr. MeAPO's and ElAPO's are typically synthesized by the hydrothermal crystallization of a reaction mixture of a metal source, an aluminum source, a phosphorous source and a templating agent. The preparation of MeAPO's and ElAPO's are found in U.S. Patent Nos. 4,310,440, 4,500,651, 4,554,143, 4,567,029, 4,752,651, 4,853,197, 4,873,390 and 5,191,141.

One of the most useful molecular sieves for converting methanol to olefin(s) are those ELAPO's or MeAPO's where the metal is silicon. These molecular sieves are known as 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  
5 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.

Templating agents are used in the synthesis of molecular sieves, including  
10 SAPO molecular sieves, as crystal structure-directing agents. Furthermore, templating agents are typically nitrogen containing organic bases such as amines or quaternary ammonium species. Additionally, the quantity of the templating agent used is often dictated by the pH of the reaction mixture in which the molecular sieve forms. The templating agent is often used in excess of the  
15 amount required for its incorporation in the intracrystalline structure of the crystalline molecular sieve, in order to control the pH and/or alkaline content in the synthesis of molecular sieves, for example as described in U.S. Patent No. 4,440,871.

The templating agent is oftentimes the most costly ingredient used in  
20 synthesizing molecular sieves. Using a second, less expensive base as a pH controller, in addition to a templating agent, in principle leads to a reduction in the cost of synthesizing a particular molecular sieve, provided that the pH controller does not interfere with the synthesis of the desired molecular sieve. As described in U.S. Patent No. 4,440,871 in a SAPO molecular sieve synthesis,  
25 using an inorganic base to reduce the amount of organic templating agent, often results in the formation of undesirable dense phase products. Some organic bases, for instance, dipropylamine, have been combined with a templating agent, tetraethylammonium hydroxide, for the synthesis of a SAPO molecular sieve. Monomeric organic bases such as dipropylamine are volatile and raise various  
30 environmental and safety concerns. Additionally, higher pressure equipment is

needed for the hydrothermal synthesis of molecular sieves using volatile monomeric organic bases.

Therefore, it would be desirable to have an improved method for reducing the amount of templating agent utilized in synthesizing a molecular sieve.

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#### Summary Of The Invention

This invention provides a method of synthesizing a molecular sieve, to its formulation into a molecular sieve catalyst composition, and to its use in a process, preferably a conversion process, for making one or more olefin(s), particularly light olefin(s).

10

In one embodiment the invention is directed to a method for synthesizing a molecular sieve utilizing a templating agent, preferably an organic templating agent, and a polymeric base. In preferred embodiments, the polymeric base is a polymeric base, or a soluble and/or non-volatile polymeric base or a non-ionic polymeric base, or a combination thereof, and most preferably the polymeric base is a polymeric imine, preferably a polyethylene imine or polyethylenimine.

15

In another embodiment the invention relates to a method for synthesizing a molecular sieve, the method comprising the steps of: (a) forming a reaction mixture of at least one templating agent and at least one of the group consisting of a silicon source, a phosphorous source and an aluminum source; (b) introducing to the reaction mixture a non-ionic polymeric base or a soluble polymeric base; and (c) removing the molecular sieve from the reaction mixture. In one preferred embodiment, the polymeric base is non-volatile and/or has a pH of from about 8 to about 14 in an aqueous solution, and/or has an average molecular weight  $M_w$  greater than 500. In another preferred embodiment of this embodiment, the polymeric base is a polymeric imine.

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In the most preferred embodiment the invention relates to a method of synthesizing a molecular sieve, the method comprising the steps of: (a) combining a silicon source, an aluminum source, and/or a phosphorous source; (b) introducing an organic templating agent; (c) introducing a polymeric base; and (d)

30

removing the molecular sieve. In a preferred embodiment, the mole ratio of the organic templating agent to the monomeric unit of the polymeric base is from about 0.01 to 1, preferably from 0.1 to 0.75, and more preferably 0.25 to 0.5.

5 In another embodiment of the invention the molecular sieve described above is formulated into a molecular sieve catalyst composition. In this embodiment, the molecular sieve removed from step (c) above and step (d) immediately above is combined with a matrix material and optionally a binder to form the molecular sieve catalyst composition of the invention.

10 In yet another embodiment, the invention is directed to a process for producing olefin(s) in the presence of any of the above molecular sieves and catalyst compositions thereof. 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.

## 15 Detailed Description Of The Invention

### Introduction

The invention is directed toward a method for synthesizing a molecular sieve using a templating agent and a polymeric base. It has been found that a  
20 polymeric base is useful in combination with a decreased amount of templating agent to produce a given molecular sieve. Without being bound to any particular theory, it is believed that the soluble or neutral polymeric base, especially a polymeric imine, more specifically a polyethylenimine, is useful to control pH, and therefore, a smaller amount of templating agent can be used to synthesize a  
25 particular molecular sieve.

### Molecular Sieves and Catalysts Thereof

Molecular sieves have various chemical, physical and structural (framework) characteristics. Molecular sieve structures have been classified by  
30 the Structure Commission of the International Zeolite Association according to

framework-types. A framework-type describes the connectivity or topology of the tetrahedrally coordinated atoms constituting the molecular sieve framework. Molecular sieve for which the framework-type has been elucidated are assigned a three letter code and are described in the *Atlas of Zeolite Framework Types*, 5th  
5 edition, Elsevier, London, England (2001).

In one embodiment of the invention, the molecular sieve is represented by the empirical formula, on an anhydrous basis:



wherein R represents at least one templating agent, preferably an organic  
10 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 from 0 to 0.5, and most preferably from 0 to 0.3; x, y, and z represent the mole fraction of M, Al and P, respectively, where M is a metal selected from the group consisting of Group IA, IIA, IB, IIIB, IVB, VB, VIB, VIIB, VIIIB and Lanthanide metals, M being preferably being a metal  
15 selected from the group consisting of Co, Cr, Cu, Fe, Ga, Ge, Mg, Mn, Ni, Si, Sn, Ti, Zn and Zr, M being most preferably Si. 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 in the range between 0.1 to 1, x is in the range between 0 and 0.25, y is in the range between 0.4 and 0.5, and z is in the  
20 range between 0.25 and 0.5, more preferably m is in the range between 0.15 and 0.7, x is in the range between 0.01 and 0.2, y is in the range between 0.4 and 0.5, and z is in the range between 0.3 and 0.5.

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-  
25 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 forms thereof. The more preferred zeolite-type molecular sieves include one or a combination of  
30 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 forms thereof.

5           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 a preferred embodiment, the molecular sieve comprises at least one intergrown phase of AEI and CHA framework-types.

#### 10       Molecular Sieve Synthesis

          Generally, molecular sieves are synthesized by the hydrothermal crystallization of a reaction mixture comprising a templating agent and at least two of the groups consisting of a source of aluminum, a source of phosphorous and a source of silicon. Typically, the reaction mixture is placed in a sealed  
15       pressure vessel, optionally lined with an inert plastic such as polytetrafluoroethylene, and heated, under a crystallization pressure and temperature, until a crystalline molecular sieve is formed. The crystalline molecular sieve is then recovered by filtration, centrifugation and/or decanting.

          In a preferred embodiment the molecular sieve is synthesized by forming a  
20       reaction mixture comprising a source of silicon, a source of aluminum, a source of phosphorous, an organic templating agent, preferably a nitrogen containing organic templating agent, and one or more polymeric bases. This particularly preferred embodiment results in the synthesis of a silicoaluminophosphate crystalline material that is then isolated by filtration, centrifugation and/or  
25       decanting.

          Non-limiting examples of silicon sources include 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)),  
30       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.

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.

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  $\text{ALPO}_4$ , phosphorous salts, or combinations thereof. The preferred source of phosphorous is phosphoric acid, particularly when producing a silicoaluminophosphate.

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-butylamine, ethylenediamine, pyrrolidine, and 2-imidazolidone.

The preferred templating agent 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, particularly when producing a silicoaluminophosphate molecular sieve having the CHA framework-type. 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, and at least one polymeric base.

In the context of the present invention, polymeric base means an organic molecular containing at least 3, preferably at least 5, more preferably at least 10 basic sites. In a preferred embodiment, the basic sites are nitrogen atoms, and the polymeric base is a polyamine or polyimine. Preferably, the polymeric base is miscible with water and non-ionic. More preferably, the polymeric base has chemical properties such that aqueous phases containing the polymeric base have a pH sufficient to control the pH desired for synthesizing a given molecular sieve, especially a SAPO molecular sieve. In a preferred embodiment, the polymeric base is a polymeric imine. In one embodiment, the polymeric base of the invention has chemical properties such that aqueous phases, preferably aqueous solutions, containing them have a pH from greater than 7 to about 14, more preferably from about 8 to about 14, most preferably from about 9 to 14.

In another embodiment, the polymeric base is represented by the formula:  $(R-NH)_x$ , where R-NH is a monomeric unit in which R is a hydrocarbon group having from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms, more preferably from 1 to 6 carbon atoms, and most preferably from 1 to 4 carbon atoms; x is an integer from 3 to 500,000, preferably from 5 to 250,000, most preferably from 50 to 50,000. In one embodiment, R is a linear, branched, or cyclic hydrocarbon group, preferably a linear hydrocarbon group having from 1 to 20 carbon atoms, more preferably a hydrocarbon group having from 1 to 10 carbon atoms.

In another embodiment, the polymeric base is a polyethylenimine that is represented by the following general formula:

$(-\text{NHCH}_2\text{CH}_2-)_m[-\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)\text{CH}_2\text{CH}_2-]_n$ , wherein  $m$  is from 10 to 20,000, preferably from 5 to 15,000 and  $n$  is from 0 to 2,000, preferably from 5 to 2,000.

5 In another embodiment, the polymeric base of the invention has a weight average molecular weight from about 500 to about 1,000,000, preferably from about 700 to about 800,000, more preferably from about 750 to about 750,000, and most preferably from about 800 to about 750,000.

10 In another embodiment, the mole ratio of the monomeric unit R-NH of the polymeric base of the invention to the templating agent(s) is less than 20, preferably less than 12, more preferably less than 10, even more preferably less than 8, still even more preferably less than 5, and most preferably less than 4.

15 Non-limiting examples of polymeric bases include: polyethylenimine, epichlorohydrin modified polyethylenimine, ethoxylated polyethylenimine, polypropylenimine diamine dendrimers (DAB-Am- $n$ ), poly(allylamine)  $[\text{CH}_2\text{CH}(\text{CH}_2\text{NH}_2)]_n$ , poly(1,2-dihydro-2,2,4-trimethylquinoline), and poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine).

20 In another embodiment the invention is directed to a method for synthesizing a molecular sieve utilizing a templating agent, preferably an organic templating agent such as an organic amine, an ammonium salt and/or an ammonium hydroxide, in combination with a polymeric base such as polyethylenimine.

25 In a typical synthesis of a molecular sieve according to the invention, a reaction mixture is formed, comprising: at least one templating agent, at least one polymeric base containing at least three basic sites, in combination with at least two of the group consisting of a silicon source, a phosphorus source and an aluminum source. The reaction mixture is then maintained at a temperature and for a period of time sufficient for forming the crystalline molecular sieve.

30 Generally, the reaction mixture described above 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, preferably from about 100°C to about 250°C, more preferably from about 125°C to about 225°C, even more preferably from about 150°C to about 180°C. In another embodiment, the hydrothermal crystallization temperature is less than 225°C, preferably less than 200°C to about 80°C, and more preferably less than 195°C to about 100°C.

In yet another embodiment, the crystallization temperature is increased gradually or stepwise during synthesis, preferably the crystallization temperature is maintained constant, for a period of time effective to form a crystalline product. 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. In one embodiment, the crystalline product is formed under heating from about 30 minutes to around 2 weeks, preferably from about 45 minutes to about 240 hours, and more preferably from about 1 hour to about 120 hours.

In one embodiment, the synthesis of a molecular sieve is aided by seeds from another or the same framework type molecular sieve.

The hydrothermal crystallization is carried out with or without agitation, stirring and/or tumbling. Stirring, agitation or tumbling may be continuous or intermittent during the crystallization period. Typically, the crystalline molecular sieve product forms, usually as an aqueous slurry, and is recovered by any standard technique well known in the art, for example centrifugation, filtration or decantation. Once isolated from the crystallization mixture, the crystalline molecular sieve is washed, typically with water or a water miscible solvent, once or several times. The washed crystalline product is then optionally dried, preferably in air.

The templating agent, still present in the molecular sieve, can be 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 oxygen, at an elevated temperature sufficient to either partially or completely decompose, oxidize and remove the templating agent.

Molecular sieves may have a wide range of silicon (Si) to aluminum (Al) atomic ratios. In the case of SAPO molecular sieves, low Si/Al ratios are preferred. In one embodiment, the SAPO 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 the case of aluminosilicate (zeolite) molecular sieves, high silicon to aluminum ratios are preferred. 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.

The pH of the reaction mixture should be 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. Optionally, the pH can be controlled by the addition of basic or acidic compounds as necessary to maintain the pH during the synthesis in the preferred range of from 4 to 9. In a preferred embodiment, the templating agent and/or polymeric base are added to the reaction mixture in quantities such that the pH of the reaction mixture does not exceed 10.

#### Method for Making Molecular Sieve Catalyst Compositions

Once the molecular sieve is synthesized, and depending on the requirements of the particular conversion process, the molecular sieve is then formulated into a molecular sieve catalyst composition. The molecular sieve synthesized according to the invention is made or formulated into catalysts by combining the synthesized molecular sieve with a binder and/or 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.

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 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 matrix component. For example, an alumina sol will convert to an aluminum oxide matrix following heat treatment.

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), 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,  $\gamma$ -alumina, boehmite, diaspor, and transitional aluminas such as  $\alpha$ -alumina,  $\beta$ -alumina,  $\gamma$ -alumina,  $\delta$ -alumina,  $\epsilon$ -alumina,  $\kappa$ -alumina, and  $\rho$ -alumina, aluminum trihydroxide, such as gibbsite, bayerite, nordstrandite, doyleite, and mixtures thereof.

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 pseudoboehmite, 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 available from The PQ Corporation, Valley Forge, Pennsylvania.

The molecular sieve synthesized 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.

Non-limiting examples of matrix materials include one or more of: rare earth metals, 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: halloysite, 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.

In one embodiment, the binder, the molecular sieve and the matrix material are combined in the presence of a liquid to form a molecular sieve catalyst composition. The molecular sieve and matrix material, and the optional binder, 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 optional binder, are combined in a liquid as solids, substantially dry or in a dried form, or as slurries, together or separately. If solids are added together as dry or substantially dried solids, it is preferable to add a limited and/or controlled amount of liquid.

In another embodiment, the slurry of the molecular sieve, binder and 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 spray dryer.

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 15 minutes to about 2 hours.

In a preferred embodiment, the molecular sieve catalyst composition is heated in nitrogen at a temperature of from about 600°C to about 700°C. Heating is carried out 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.

#### Process For Using the Molecular Sieve Catalyst Compositions

The molecular sieve catalysts and 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 cumene or with long chain olefins; transalkylation, of for example a combination of aromatic and polyalkylaromatic hydrocarbons; dealkylation; hydrodecyclization; disproportionation, of for example toluene to make benzene and paraxylene; oligomerization, of for example straight and branched chain olefin(s); and dehydrocyclization.

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).

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.

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.

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.

5           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  
10       of moles of the feedstock and diluent, preferably from about 1 to 80 mole percent, more preferably from about 5 to about 50, most preferably from about 5 to about 25. 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,  
15       preferably propylene, butylene, pentylene, and other hydrocarbons having 4 or more carbon atoms, or mixtures thereof.

          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  
20       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.

          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  
25       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  
30       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.

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.

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.

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.

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.

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

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.

After reaction, 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.

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, olefin(s) produced are directed to one or more polymerization processes for producing various polyolefins. 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.

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, acids, linear alpha olefins, vinyl acetate, ethylene dichloride 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

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

#### COMPARATIVE EXAMPLE 1

##### Preparation of Molecular Sieve Two mole TEAOH per mole of $P_2O_5$

Following a typical SAPO-34 synthesis, the a silicon source, a phosphorous source and an aluminum source and a templating agent were mixed according to the following molar ratio:

2.0TEAOH:1.0Al<sub>2</sub>O<sub>3</sub>:0.3SiO<sub>2</sub>:1.0P<sub>2</sub>O<sub>5</sub>:50H<sub>2</sub>O to form a reaction mixture. The sources of the ingredients were pseudo-boehmite (an aluminum source), 85% phosphoric acid (a phosphorous source), LUDOX HS-40 (a silicon source), and 40% aqueous solution of TEAOH (an organic templating agent). The order of mixing was first adding H<sub>3</sub>PO<sub>4</sub>, then H<sub>2</sub>O, followed by Ludox, then Pseudo-boehmite, and finally TEAOH in the molar proportions described above. The reaction mixture was then blended into a uniform gel using a microhomogenizer. The gel was then placed into a Parr bomb with a Teflon liner, and was heated to 180°C for six days. The solid product formed was centrifuged and washed several times with deionized water, and was then dried in a 60°C vacuum oven

overnight. The XRD, X-ray powder pattern, of the product confirms that the product is a pure SAPO-34 and having an elemental analysis of the following molar composition:  $\text{Al}_{1.0}\text{Si}_{0.173}\text{P}_{0.834}$ .

## EXAMPLE 2

### Preparation of Molecular Sieve using Polyethylenimine (PEI) replacing some TEAOH

Polyethylenimine (available from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin) described as  $(-\text{NHCH}_2\text{CH}_2-)_x[-\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)\text{CH}_2\text{CH}_2-]_y$  in a 50 weight percent (wt%) aqueous solution, and having average molecular weight ( $M_w$ ) of 750,000, was diluted with water to a 25 wt% solution. The sources of phosphorous, silicon, aluminum, polymeric base, and templating agent were added according to the following order: first the phosphorous source,  $\text{H}_3\text{PO}_4$ , then  $\text{H}_2\text{O}$ , then the silicon source, Ludox, followed by the aluminum source, pseudo-boehmite, then the polymeric base, PEI, and lastly the templating agent, TEAOH. The reaction mixture was blended using a microhomogenizer. When higher amount of the polymeric base, PEI, was used, the gel had the consistency of a soft gum coexisting with a clear liquid. The molar ratios of ingredients for three preparations were as follows:

(1) 2.0 PEI monomeric unit

$(\text{CH}_2\text{CH}_2\text{NH}):1.5\text{TEAOH}:1.0\text{Al}_2\text{O}_3:0.3\text{SiO}_2:1.0\text{P}_2\text{O}_5:50\text{H}_2\text{O}$

(2) 4.0 PEI monomeric unit

$(\text{CH}_2\text{CH}_2\text{NH}):1.0\text{TEAOH}:1.0\text{Al}_2\text{O}_3:0.3\text{SiO}_2:1.0\text{P}_2\text{O}_5:50\text{H}_2\text{O}$

(3) 6.0 PEI monomeric unit

$(\text{CH}_2\text{CH}_2\text{NH}):0.5\text{TEAOH}:1.0\text{Al}_2\text{O}_3:0.3\text{SiO}_2:1.0\text{P}_2\text{O}_5:50\text{H}_2\text{O}$

Each reaction mixture, individually, were sealed in a Teflon lined Parr bomb and were heated to  $180^\circ\text{C}$  for seven days. The solid product formed were centrifuged and washed several times with deionized water, and then dried in a  $60^\circ\text{C}$  vacuum oven. The X-ray powder diffraction patterns of the three molecular sieves synthesized, preparations 1 and 2 produced pure a SAPO-34 phase, while

preparation 3 produced a SAPO-34 molecular sieve plus an unidentified phase having two broad peaks at around 15Å and 7.5Å d-spacings.

### EXAMPLE 3

#### 5     Preparation of a Molecular Sieve with One mole equivalent of Polyethylenimine (PEI) replacing One mole of TEOAH.

The same procedure as described in Example 1 was used except the mole ratio of the sources of silicon, aluminum, and phosphorous, the templating agent, and polymeric base, were as follows:

10     (4) 1.0 PEI monomeric unit

(CH<sub>2</sub>CH<sub>2</sub>NH):1.0TEAOH:1.0Al<sub>2</sub>O<sub>3</sub>:0.3SiO<sub>2</sub>:1.0P<sub>2</sub>O<sub>5</sub>:50H<sub>2</sub>O

The reaction mixture was homogenized, sealed in a Teflon lined Parr bomb and then heated to 180°C (hydrothermal reaction temperature) for thirteen days. The solid product formed was centrifuged and washed several times with deionized water, and was dried in a 60°C vacuum oven. The X-ray powder diffraction pattern indicated pure SAPO-34 was obtained. The SAPO-34 yield was 17.5 wt%, based on the total weight of the starting materials. Elemental analysis showed:

Al, 16.5%; Si, 2.76%; P, 16.0% corresponding to the composition:

Al<sub>1.0</sub>Si<sub>0.161</sub>P<sub>0.845</sub>.

20

### EXAMPLE 4

#### Preparation of Molecular Sieve using One mole equivalent of Polyethylenimine (PEI) replacing One mole of TEOAH, at 200 °C

The same synthesis procedure as described in Example 3 above was used except that the hydrothermal reaction temperature was set at 200°C .

Crystallization proceeded for 5 days. The XRD of the molecular sieve product showed a highly crystalline SAPO-34 with a minor amount of an unidentified crystalline impurity. The molecular sieve solid yield was 17.0 wt%, based on the total weight of the starting materials. This Example 4 illustrates that



crystallization time is dramatically reduced by increasing the hydrothermal synthesis reaction temperature.

#### EXAMPLE 5

Preparation of Molecular Sieve using Three mole equivalent of Polyethylenimine (PEI) and One mole of N,N,N-trimethyladamantylammonium iodide, at 180 °C

2.07g H<sub>3</sub>PO<sub>4</sub>(75%), 3.17g H<sub>2</sub>O, 1.08g pseudo-boehmite, 0.16g fumed silica, 4.03g polyethylenimine (PEI), and 2.50g N,N,N-

trimethyladamantylammonium iodide was added, in sequence with vigorous blending. The molar ratios of the ingredients are the following:

(5) 3.0(CH<sub>2</sub>CH<sub>2</sub>NH):1.0R<sup>+</sup>T:1.0Al<sub>2</sub>O<sub>3</sub>:0.3SiO<sub>2</sub>:1.0P<sub>2</sub>O<sub>5</sub>:50H<sub>2</sub>O, where R<sup>+</sup>T is N,N,N-trimethyladamantylammonium iodide.

In one embodiment, a molecular sieve, most preferably a SAPO molecular sieve, even more particularly a SAPO-34 molecular sieve, is formed using the templating agent, N,N,N-trimethyladamantylammonium iodide.

The mixture was sealed, and crystallization carried out, as described above in Example 4. After 4 days of crystallization the crystalline molecular sieve was isolated by centrifugation and was washed with deionized water. The XRD of the solid product indicated that pure SAPO-34 (CHA structure-type) was obtained.

The molecular sieve solid yield was 19.3wt% based on the total weight of the starting materials. This example illustrates the use of a quaternary ammonium iodide salt as the templating agent, instead of the more expensive quaternary ammonium hydroxide, when a polymeric base is used to control the pH.

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, maleic anhydride, phthalic anhydride and acrylonitrile formulation, vapor phase methanol synthesis, and various Fischer Tropsch reactions. It is further

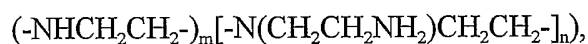
contemplated that a plug flow, fixed bed or fluidized bed process are used in combination, particularly in different reaction zones within a single or multiple reactor system. It is also contemplated the molecular sieves described herein are useful as absorbents, adsorbents, gas separators, detergents, water purifiers, and other various uses such as agriculture and horticulture. 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 synthesizing a crystalline molecular sieve, the method comprising: (a) forming a reaction mixture comprising: at least one  
5 templating agent, a polymeric base containing at least three basic sites, and at least two of the group consisting of a silicon source, a phosphorous source and an aluminum source; (b) treating the reaction mixture for a period of time and at a temperature sufficient for forming the crystalline molecular sieve.  
10
2. The method of claim 1 wherein the polymeric base is miscible with water.
3. The method of any one of claims 1 or 2 wherein the polymeric base is selected from the group consisting of: polyethylenimine, epichlorohydrin  
15 modified polyethylenimine, ethoxylated polyethylenimine, polypropylenimine diamine dendrimers, poly(allylamine), poly(1,2-dihydro-2,2,4-trimethylquinoline), and poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine).
- 20 4. The method of any one of claims 1 to 3 wherein the polymeric base has a weight average molecular weight of from 500 to 1,000,000.
5. The method of any one of claims 1 to 4, wherein the polymeric base is represented by the formula  $(R-NH)_x$  in which R-NH is a monomeric unit,  
25 R is a hydrocarbon group containing from 1 to 10 carbon atoms and x is an integer from 10 to 250,000.
6. The method of claim 5, wherein R is a hydrocarbon group containing from 1 to 6 carbon atoms.

7. The method of any one of claims 5 or 6, wherein x is an integer from 15 to 100,000.

8. The method of any of claims 5 to 7 wherein the polymeric base is represented by the formula:



wherein m is from 10 to 20,000, and n is from 1 to 2,000.

9. The method of claim 8, wherein m is from 5 to 15,000.

10. The method any of claims 4 to 8 wherein the mole ratio of the monomeric unit R-NH of the polymeric base to the templating agent is less than 20.

11. The method of claim 9, wherein the mole ratio of the monomeric unit R-NH of the polymeric base to the templating agent is less than 10.

12. The method of any of the preceding claims wherein the reaction mixture is maintained at a pH in the range of from 3 to 10.

13. The method of any of the preceding claims wherein the templating agent is a quaternary ammonium hydroxide or a quaternary ammonium salt.

14. The method of any of claim 13, wherein the reaction mixture comprises a phosphorous source and an aluminum source.

15. The method of any of the preceding claims wherein the reaction mixture further comprises a silicon source.

16. A crystalline molecular sieve comprising a polymeric base represented by the formula  $(R-NH)_x$  in which R is a hydrocarbon group containing from 1 to 10 carbon atoms and x is an integer from 10 to 250,000.
- 5 17. A molecular sieve catalyst composition comprising a crystalline molecular sieve according to claim 16 or a crystalline molecular sieve prepared according to the method of any of claims 1 to 15.
- 10 18. A process for producing one or more olefin(s), the process comprising the steps of:
- (a) introducing a feedstock to a reactor system in the presence of a molecular sieve catalyst composition according to claim 17;
  - (b) withdrawing from the reactor system an effluent stream;
  - 15 and
  - (c) passing the effluent gas through a recovery system recovering at least the one or more olefin(s) .
- 20 19. The process of claim 18 further comprising the step of (e) polymerizing the one or more olefin(s) in the presence of a polymerization catalyst into a polyolefin.

## INTERNATIONAL SEARCH REPORT

Intel onal Application No

PCT/US 02/28788

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B37/08 C01B37/04 C01B39/54 C01B39/04 B01J29/04  
C10G3/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B B01J C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 065 401 A (ICI PLC) 24 November 1982 (1982-11-24) claims 4,12-14 page 5, line 32 -page 8, line 21 page 10, line 1-15 page 10, line 28-31 page 12, line 22-25 page 13, line 18-26	16-18
A	examples 1,3,6-12,17-19 ---	1-15,19
A	EP 0 463 793 A (MOBIL OIL CORP) 2 January 1992 (1992-01-02) claims 1-4,10-12 page 5, line 5 -page 6, line 15 examples 1,3; table 1 ---	1-19
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/28788

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