Use of Alkaline Earth Metal Containing Small Pore Non-Zeolitic Molecular Sieve Catalysts in Oxygenate Conversion

Background of the Invention

Field of Invention

This invention relates to a process for the conversion of oxygenates to hydrocarbons using small pore non-zeolitic molecular sieve catalysts. More particularly, this invention relates to a catalyst composition, a method to prepare such a catalyst, and a process to use such a catalyst in a process for conversion of oxygenates to olefins using silicoaluminophosphate molecular sieve catalysts which have been incorporated with certain alkaline earth metals either during or after the synthesis of the molecular sieve.

Background Art of the Invention

Olefins have traditionally been produced through the process of petroleum cracking. Because of the potential limited availability and high cost of petroleum sources, the cost of producing olefins from such petroleum sources has been steadily increasing. Light olefins such as ethylene serve as feeds for the production of numerous chemicals.

The search for alternative materials for the production of light olefins such as ethylene has led to the use of oxygenates such as alcohols, and more particularly to methanol and ethanol or their derivatives as feedstocks. These and other alcohols may be produced by fermentation or from synthesis gas. Synthesis gas can be produced from natural gas,

petroleum liquids, carbonaceous materials including coal, recycled plastics, municipal wastes, or any organic material. Thus, alcohol and alcohol derivatives may provide non-petroleum based routes for hydrocarbon production.

It is well known in the prior art to convert oxygenates to olefins by contacting the oxygenate with various types of catalysts. Large, medium, and small pore, zeolitic and non-zeolitic, molecular sieve catalysts may be used.

It is also well known in the prior art that molecular sieves of various pore diameters and compositions have been treated by addition of alkaline earth metals to improve catalyst performance for use in various applications. It is also well known that when comparing the performance of two catalysts, even if every physical parameter of each of the catalysts is the same, that if the two catalysts have a different composition, then one cannot predict based on the performance of one catalyst, how the second catalyst will perform, USA-4752651, col. 2, lines 31 - 68. So even if a particular alkaline earth metal has been added to one type of catalyst for a particular use, it does not mean that the same metal will have the same beneficial effect on the performance of the second catalyst.

Even though the art teaches the use of some of the alkaline earth metals to improve the performance of large, medium and small pore zeolites, it fails to teach the use of all such alkaline earth metals, including strontium, calcium, and barium, to improve the performance of non-zeolitic molecular sieve catalysts with diameters of less than 5 Angstroms for the use in oxygenate conversion.

USA-4752651 teaches the modification of small pore non-zeolitic molecular sieve catalysts using the alkaline earth metals of beryllium and magnesium. However, the prior art fails to teach and/or enable either the incorporation of the alkaline earth metals of strontium, calcium, and barium into small pore molecular sieves or the in situ process of such metals into such a catalyst for the use in oxygenate conversion.

This failure to teach may be due to larger ionic radii of the cations with the higher atomic numbers in Group IIA. For example, beryllium and magnesium each have a size of 0.31 and 0.65 Angstroms, respectively. This is to be contrasted with the larger sizes of calcium, strontium, and barium with ionic radii of 0.99, 1.13, and 1.35 Angstroms, respectively. Based on this size difference, one of ordinary skill in the art would not think that these larger radii ions could be used as effectively in modifying a small pore catalyst. Even though all of these radii are less than 5 Angstroms, it is well known that the ions exist in the solvated form with the solvent molecules attached. Therefore, even though the metal ion has a radius of less than 5 Angstroms, that in the solvated form, the effective radius will be much larger.

Meanwhile, JP94074134 (JP01051316) discloses an in-situ process which appears to be a method to make a small pore aluminophosphosilicate containing any one of the alkaline earth metals which is useful in an oxygenate conversion process. However, upon a close reading of the disclosure, this patent actually teaches the use of a medium pore catalyst, such as ZSM5, and not a small pore catalyst, such as SAPO-34, for oxygenate conversion. The disclosure focuses on how their catalyst is unique compared to a conventional ZSM-5. For example, their catalyst has a pore diameter of 5 to 6 Angstroms and an adsorption volume that is

similar to that of common ZSM-5 type zeolites. The x-ray pattern of their material is similar to medium pore sized ZSM-5 and not similar to that of small pore sized SAPO-34. Their catalyst is described as a novel zeolite that has a pore diameter that is between large diameter zeolites, such as faujasite X and Y types, and small diameter zeolites, such as erionite and offretite which further distinguishes their catalyst from a small pore molecular sieve.

Therefore, based on the teachings of the prior art, it is surprising to learn that the alkaline earth metals of strontium, calcium, or barium can be successfully added to a small pore non-zeolitic molecular sieve for enhancement of the performance for such a catalyst for use in the oxygenate conversion process.

Summary of Invention

This invention provides a catalyst, a method to prepare the catalyst, and a method for converting a starting material to olefins, comprising contacting the starting material with a small pore non-zeolitic molecular sieve catalyst under effective conversion conditions to provide olefins wherein the molecular sieve has been prepared in-situ or modified after synthesis by incorporation of one or more of the alkaline earth metals of strontium, calcium, or barium, originating from a corresponding metal compound.

One embodiment of the invention provides a catalyst composition, comprising a non-zeolitic molecular sieve and one or more alkaline earth metals selected from the group consisting of strontium, calcium, barium, and mixtures thereof, wherein the non-zeolitic molecular sieve has a pore diameter size of less than 5 Angstroms. One embodiment includes

wherein the non-zeolitic molecular sieve further comprises a third metal oxide in addition to the alumina and silica components and the silicon to aluminum atomic ratio is less than 0.8.

Another embodiment includes a method for converting starting material to olefins comprising contacting the starting material with a non-zeolitic molecular sieve catalyst under effective conditions to produce olefins, wherein the non-zeolitic molecular sieve comprises a catalyst composition of claims 1 or 2 and has been prepared in-situ or modified after molecular sieve synthesis by incorporation of an alkaline earth metal selected from the group consisting of strontium, calcium, barium, and mixtures thereof, using an alkaline earth metal compound, wherein the alkaline earth metal ion is selected from the group consisting of strontium, calcium, barium, and mixtures thereof.

Additionally, the method of the invention includes the embodiments wherein the molecular sieve catalyst is selected from the group consisting of a silicoaluminophosphate (SAPO), aluminophosphate (ALPO), and mixtures thereof, preferably is selected from the group consisting of SAPO-17, SAPO-18, SAPO-34, SAPO-44, and SAPO-56, and most preferably is SAPO-34.

Yet another embodiment includes wherein the molecular sieve catalyst pore size is greater than 3.5 Angstroms and less than 5.0 Angstroms, preferably greater than 4.0 Angstroms and less than 5.0 Angstroms, and most preferably is in the range of from 4.3 to 5.0 Angstroms.

Also, embodiments of the invention include wherein the alkaline earth metal is strontium or calcium and preferably is strontium.

In one embodiment, the alkaline earth metal compound is selected from the group comprising halides, sulfates, formates, acetates, alkoxides, carbonyls, nitrates, or mixtures thereof and preferably is a carbonyl.

In yet another additional embodiment, the modified non-zeolitic molecular sieve has a metal to silicon atomic ratio in the range of from 0.01:1 to 2:1, preferably in the range of from 0.05:1 to 1.5:1, and most preferably in the range of from 0.01:1 to 1:1.

The invention additionally includes those embodiments wherein the process for converting the starting material to olefins is conducted at a temperature of from 200°C to 700°C, preferably at a temperature of from 250°C to 600°C, and most preferably at a temperature of from 300°C to 500°C.

The invention additionally includes those embodiments wherein the starting material feed is selected from the group consisting of methanol, ethanol, n-propanol, isopropanol, $C_4 - C_{20}$ alcohols, methyl ethyl ether, di-methyl ether, di-ethyl ether, di-isopropyl ether, di-methyl carbonate, carbonyl compounds, and mixtures thereof, and preferably comprises methanol or dimethyl ether.

The invention additionally includes those embodiments wherein the starting material also includes a diluent., and preferably wherein the diluent is selected from the group consisting of water, nitrogen, hydrogen, paraffins, olefins, aromatics, and mixtures thereof, and most preferably the diluent is water or nitrogen.

The invention additionally includes those embodiments wherein the starting material comprises a halide, a mercaptan, a sulfide, or an amine.

The invention additionally includes those embodiments wherein the process for converting the starting material to olefins is conducted at a pressure of from 0.1 kPa to 100 MPa, preferably at a pressure in the range of from 6.9 kPa to 34 MPa, and most preferably at a pressure of from 48kPa to 0.34MPa.

The invention additionally includes those embodiments wherein the process for converting the starting material to olefins using the treated molecular sieve is conducted at a WHSV in the range of from 0.01 to 500 hr^{-1}, preferably at a WHSV in the range of from 0.1 to 200 hr^{-1}, and most preferably in the range of from 0.5 to 100 hr^{-1}.

The invention additionally includes those embodiments wherein process for preparing a catalyst post-synthesis, which comprises forming a mixture containing one or more sources of alkaline earth metals selected from the group consisting of strontium, calcium, barium, and mixtures thereof, in a solvent and treating the non-zeolitic molecular sieve with the mixture under conditions sufficient to incorporate a desired amount of the metal.

The invention additionally includes those embodiments wherein the process for preparing a catalyst in-situ, which comprises forming a reaction mixture containing one or more sources of alkaline earth metals selected from the group consisting of strontium, calcium, barium, and mixtures thereof, and precursors required for producing the non-zeolitic molecular sieve and subjecting the mixture to conditions sufficient to form the catalyst.

Brief Description of the Drawings

Figure 1 is the X-ray diffraction pattern for the strontium silicoaluminophosphate (Sr-SAPO) sample which was prepared per Example III as defined below.

Detailed Description of the Invention

The present invention is characterized by use of a small pore non-zeolitic molecular sieve catalyst, which has one or more of the alkaline earth metals, selected from the group consisting of strontium, calcium, barium, incorporated onto the molecular sieve either during or after synthesis, in a process for the conversion of starting material to olefins.

For this application, the non-zeolitic molecular sieve may be a silicoaluminophosphate (SAPO), an aluminophosphate (ALPO), and mixtures thereof, preferably, but not limited to, a SAPO catalyst. In the present invention, small pore non-zeolitic molecular sieves are defined as having a pore size of less than 5.0 Angstrom units. Generally, suitable catalysts have a pore size ranging from 3.5 to 5.0 Angstroms units, preferably from 4.0 to 5.0 Angstroms, and most preferably from 4.3 to 5.0 Angstroms.

Non-zeolitic materials have been demonstrated to have catalytic properties for various types of hydrocarbon conversion processes. In addition, non-zeolitic materials have been used as adsorbents, catalyst carriers for various types of hydrocarbon conversion processes, and other applications. Non-zeolitic molecular sieves are complex three

dimensional crystalline structures which include either AlO_2 or SiO_2 or both AlO_2^- and SiO_2 and a third metal oxide. The interstitial spaces or channels formed by the crystalline network enable non-zeolites to be used as molecular sieves in separation processes and catalysts for chemical reactions and catalyst carriers in a wide variety of hydrocarbon conversion processes.

SAPO's have a three-dimensional microporous crystal framework structure of PO_2^+, AlO_2^-, and SiO_2 tetrahedral units. The chemical composition (anhydrous) is:

$$mR:(Si_xAl_yP_z)O_2$$

wherein "R" represents at least one organic templating agent present in the intracrystalline pore system: "m" represents the moles of "R" present per mole of $(Si_xAl_yP_z)O_2$ and has a value of from zero to 0.3, the maximum value in each case depending upon the molecular dimensions of the templating agent and the available void volume of the pore system of the particular SAPO species involved, and "x", "y", and "z" represent the mole fractions of silicon, aluminum and phosphorus, respectively. Typical small pore SAPO's are SAPO-17, SAPO-18, SAPO-34, SAPO-44, SAPO-56, and others. "R" may be removed at elevated temperatures.

ALPO's have a three-dimensional microporous crystal framework structure of PO_2^+ and AlO_2^- tetrahedral units. The chemical composition (anhydrous) is:

$$mR:(Al_yP_z)O_2$$

wherein "R" represents at least one organic templating agent present in the intracrystalline pore system: "m" represents the moles of "R" present per mole of $(Al_yP_z)O_2$ and has a value of from zero to 0.3, the maximum value in each case depending upon the molecular dimensions of the templating agent and the available void volume of the pore system of the particular SAPO species involved, and "y" and "z" represent the mole fractions of aluminum and phosphorus, respectively. "R" may be removed at elevated temperatures.

The metal which may be employed in either the in-situ or incorporation process is an alkaline earth metal selected from group consisting of strontium, calcium, barium, and mixtures thereof. Preferably, the metal is either strontium or calcium, and most preferably, the metal is strontium.

The metal containing compounds which may be used in the present invention may be of various compositions, i.e. in the form of the corresponding halide, sulfate, formate, acetate, alkoxide, carbonyl, nitrate, or mixtures thereof. When the desired catalyst comprises SAPO-34 and the metal is strontium, it is preferable to use the hydrated form of strontium acetate as the metal containing compound.

The process of making the catalyst in-situ may be accomplished through any one of the standard methods well known to those skilled in the art including, but not limited to, hydrothermal synthesis under autogenic pressure at elevated temperatures. Typical precursors include, but are not limited to, aluminum oxide, aluminum trimethoxide, and aluminum triethoxide as the source of aluminum. Orthophosphoric acid, trimethyl phosphate, and triethyl phosphate are examples of typically used precursors for phosphorus. Colloidal silica, silica sol, silicon

tetramethoxide, and silicon tetraethoxide are examples of typically used precursors for silica. Templates which are often used in the synthesis process, include, but are to limited to, tetramethylammonium hydroxide and tetraethylammonium hydroxide.

In one embodiment, a reaction mixture is first prepared by mixing the desired amounts of the selected aluminum oxide and selected phosphoric acid with vigorous stirring. Next, de-ionized water and the desired amount of silica sol is added and the entire mixture is continued to be stirred to achieve complete mixing. Then, the selected organic template is added to this mixture and the resultant catalyst mixture is completely mixed by additional stirring. An aqueous solution containing the desired metal is then added to the mixture.

The aqueous solution of the desired metal is made by dissolving the desired amount of the metal containing compound in water under mild conditions. Preferably the water is de-ionized. The temperature of mixing is dependent upon the solubility of the metal compound in water. Alternatively, a medium other than water may be selected. The process may be conducted under pressure or at atmospheric pressure.

The resultant catalyst mixture is stirred as required. In some cases, stirring is not required and the mixture may be left undisturbed for a time adequate to permit the desired level of incorporation. The catalyst product is finally filtered, optionally washed, dried, and calcined by methods well known to those skilled in the art.

The process of taking the molecular sieve and incorporating the selected alkaline earth metal post synthesis may be accomplished through any one

of the standard methods well known to those skilled in the art including, but not limited to, incipient wetness methods, ion-exchange, and mechanical mixing. In one embodiment, a solution of the desired metal is first made by dissolving the desired amount of the metal containing compound in water under mild conditions. Preferably the water is de-ionized. The temperature of mixing is dependent upon the solubility of the metal compound in water, or whatever other medium is selected. The process may be conducted under pressure or at atmospheric pressure.

After adequate mixing, the solution is then added to the selected amount of the molecular sieve. The resulting mixture is stirred as required. In some cases, stirring is not required and the mixture may be left undisturbed for a time adequate to permit the desired level of incorporation. The catalyst product is then filtered, optionally washed, dried, and calcined by methods well known to those skilled in the art.

For either method of preparation, either in-situ or post-synthesis, the amount of metal which is incorporated into the molecular sieve may vary over a wide range depending, at least in part, on the method of preparation, the selected molecular sieve catalyst, and the incorporation method.

The resulting composition of the prepared Sr-, Ca-, and Ba-SAPO's may be expressed as follows:

$$M_aSi_bAl_cP_dO_x \cdot mH_2O$$

wherein, the ratio of a to b = 0.01 to 2,
b = 0.01 to 0.3,

c = at least 0.05,

d = at least 0.05,

b + c + d = 1.0,

the ratio of b to c is less than 0.8,

x = to balance the charge,

m = 0 to 100, and

M = the alkaline earth metal of Sr, Ca, or Ba.

The amount of metal incorporated is measured on an atomic metal basis in terms of metal to silicon ratio. The metal to silicon atomic ratios are in the range from 0.01:1 to 2:1, preferably from 0.05:1 to 1.5:1, and most preferably from 0.1:1 to 1:1.

The conversion process employs a starting material (feedstock) comprising "oxygenates". As used herein, the term "oxygenates" is intended to comprise aliphatic alcohols, ethers, carbonyl compounds (aldehydes, ketones, carboxylic acids, carbonates, and the like) along with also those compounds containing hetero-atoms, e.g., halides, mercaptans, sulfides, amines, and mixtures thereof. The aliphatic moiety preferably contains from 1 to 10 carbon atoms and more preferably contains 1 to 4 carbon atoms. Representative oxygenates include, but are not limited to, lower straight or branched chain aliphatic alcohols, their unsaturated counterparts and the nitrogen, halogen and sulfur analogues of such. Examples of suitable compounds include, but are not limited to: methanol; ethanol; n-propanol; isopropanol; C_4 – C_{20} alcohols; methyl ethyl ether; dimethyl ether; diethyl ether; di-isopropyl ether; methyl mercaptan; methyl sulfide; methyl amine; ethyl mercaptan; di-ethyl sulfide; di-ethyl amine; ethyl chloride; formaldehyde; di-methyl carbonate; di-methyl ketone; acetic acid; and n-alkyl amines, n-alkyl halides, n-alkyl

sulfides, each having n-alkyl groups of 3 to 10 carbon atoms; and mixtures thereof. The term "oxygenate" as employed herein designates only the organic material used as the feed. The total charge of feed to the reaction zone may contain additional compounds such as diluents.

The conversion process is preferably carried out in the vapor phase such that the feedstock is contacted in a vapor phase in a reaction zone with the defined molecular sieve catalyst at effective process conditions so as to produce the desired olefins, i.e., an effective temperature, pressure, WHSV (Weight Hourly Space Velocity) and, optionally, an effective amount of diluent, correlated to produce olefins. Alternatively, the process may be carried out in a liquid phase. When the process is carried out in the liquid phase, different conversions and selectivities of feedstock-to-product may result with respect to the relative ratios of the light olefin products as compared to that formed by the vapor phase process.

The temperature which may be employed in the conversion process may vary over a wide range depending, at least in part, on the selected molecular sieve catalyst. The process is conducted at an effective temperature range from 200°C to 700°C, preferably from 250°C to 600°C, and most preferably from 300°C to 500°C. Temperatures outside the stated preferred ranges are not excluded, although they do not fall within certain desirable embodiments of the present invention. At the lower end of the temperature range, and thus, generally, at a lower rate of reaction, the formation of the desired light olefin products may become markedly slow. At the upper end of the temperature range and beyond, the process may not form an optimum amount of light olefin products.

The process is effectively carried out over a wide range of pressures including autogeneous pressures. At pressures in the range from 0.1 kPa to 100 MPa, the formation of light olefin products will be effected although the optimum amount of product will not necessarily form at all pressures. The preferred pressure is in the range from 6.9 kPa to 34 Mpa, with the most preferred range being from 48 kPa to 0.34 MPa. The pressures referred to herein for the process are exclusive of the inert diluent, if any, that is present, and refer to the partial pressure of the feedstock as it relates to oxygenate compounds and / or mixtures thereof. Pressures outside the stated range are not excluded from the scope of this invention, although such do not fall within certain desirable embodiments of the invention. At the lower and upper end of the pressure range, and beyond, the selectivities, conversions and / or rates to light olefin products may not occur at the optimum, although light olefins such as ethylene may still be formed.

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

The process is effectively carried out over a wide range of WHSV for the feedstock and is generally in the range from 0.01 hr^{-1} to 500 hr^{-1}, preferably from 0.1 hr^{-1} to 200 hr^{-1}, and most preferably from 0.5 hr^{-1} and 100 hr^{-1}. As the catalyst may contain other materials which act as inerts,

the WHSV is calculated on the weight basis of methanol and small pore molecular sieve used.

The conversion process may optionally be carried out in the presence of one or more inert diluents which may be present in the feedstock for example in an amount between 1 and 99 molar percent, based on the total number of moles of all feed and diluent components fed to the reaction zone (or catalyst). Typical of diluents which may be employed in the instant process are helium, argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, paraffins, hydrocarbons (such as methane), aromatic compounds, and mixtures thereof. The preferred diluents are water and nitrogen.

The olefin production process may be carried out in a batch, semi-continuous or continuous fashion. The process can be conducted in a single reaction zone or a number of reaction zones arranged in series or in parallel, or it may be conducted intermittently or continuously in an elongated tubular zone or a number of such zones. When multiple reaction zones are employed, it may be advantageous to employ one or more of the defined small pore molecular sieves in series to provide for a desired product mixture.

Owing to the nature of the process, it may be desirous to carry out the process of the present invention by use of the molecular sieve catalysts in a dynamic bed system or any system of a variety of transport beds rather than in a fixed bed system. Such systems would readily provide for any regeneration (if required) of the molecular sieve catalyst after a given period of time. If regeneration is required, the molecular sieve catalyst can be continuously introduced as a moving bed to a regeneration zone

where it can be regenerated, such as for example by removing carbonaceous materials or by oxidation in an oxygen-containing atmosphere. In the preferred practice of the invention, the catalyst will be subject to a regeneration step by burning off carbonaceous deposits accumulated during the conversion reactions.

The following examples illustrate, but do not limit, the present invention.

Examples

Catalysts were prepared and then tested for methanol conversion.

Catalyst Preparation Examples

Comparative Example

SAPO-34 was prepared according to US-A-4440871 to provide a basis for comparison with the examples of alkaline earth metal incorporated small pore molecular sieve catalysts as prepared by the methods as described above.

Example I - The invention

Sr-SAPO-34 was prepared as follows. A strontium containing solution was prepared by dissolving 0.22 grams of strontium acetate in 20 ml of de-ionized water at room temperature. This solution was added to 3.12 grams of SAPO-34 and the mixture was stirred for two hours, also at room temperature. The solid catalyst product was filtered, and then washed two times, each with 20 ml of de-ionized water. The finished catalyst product was then dried at 110°C for two hours, followed by calcination at 650°C

for sixteen hours. The resulting catalyst had a metal loading of 3.55 wt.% strontium.

Example II - The invention

Ca-SAPO-34, was prepared as follows. A calcium containing solution was prepared by dissolving 0.184 grams of calcium acetate in 20 ml of de-ionized water at room temperature. This solution was added to 3.014 grams of SAPO-34 and the mixture was left to stand at room temperature for twenty four hours. The finished catalyst was filtered, and then dried at 110°C for two hours. The resulting dried catalyst was then calcined at 650°C for 16 hours. The resulting catalyst had 1.4 wt.% calcium.

Example III - The Invention

Ba-SAPO-34, was prepared as follows. A barium containing solution was prepared by dissolving 0.266 grams of barium acetate in 20 ml of de-ionized water at room temperature. This solution was added to 3.136 grams of SAPO-34 and the mixture was left to stand at room temperature for twenty four hours. The finished catalyst was filtered, and then dried at 110°C for two hours. The resulting dried catalyst was then calcined at 650°C for 16 hours. The resulting catalyst had 4.56 wt.% barium.

Example IV - The Invention

A reaction mixture is prepared by mixing 40.2 grams of aluminum isopropoxide, $Al[O\text{-}CH(CH)_2]_3$ and 72.6 grams of 25.1% orthophosphoric acid with vigorous stirring. Next, 3 ml of de-ionized water and 7.2 grams of 25 wt% silica sol are added and the entire mixture is stirred for one

hour in a closed container. 15 grams of 40 wt% tetraethylammonium hydroxide are then added to this mixture and the resultant mixture is stirred for another hour in the same closed container. Once this mixture is stirred, an aqueous solution containing 1.1 grams of strontium acetate $Sr[OOCCH_3]_2$ and 11 ml of water is added. The entire mixture is stirred for thirty minutes and transferred to a teflon™ lined autoclave and heated to 195°C under autogenic pressure for 168 hours. The recovered product is recovered by centrifugation and filtration, followed by washing with de-ionized water. The solid is dried at 110°C for two hours, followed by calcination at 550°C for sixteen hours to give a strontium silicoaluminophosphate product with the following composition:

$$Sr_{0.01}Si_{0.072}Al_{0.282}P_{0.159}O \cdot mH_2O$$

The structure is similar to SAPO-34. The resulting strontium to silicon atomic ratio measured in terms of an atomic weight basis will be 0.14 to 1.

Conversion Examples

Each of the prepared catalysts, the comparative and the two metal treated catalysts, was then tested using the following procedure. 5.0 cc (approximately 2.8 grams) of the selected SAPO-34 catalyst, were mixed with 15 cc of quartz beads and loaded into a 3/4" outer diameter 316 stainless steel tubular reactor which was heated by a three-zone electric furnace. The first zone, acting as the preheating zone, vaporized the feed. The temperature of the center zone of the furnace was adjusted to give the desired reaction temperature of 450°C. The reactor was purged first with nitrogen at 50 cc/min. flow rate for 30 minutes. The feed, containing 30.8 wt.% methanol, equivalent to a 4:1(molar ratio) of water

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and methanol, was pumped into the reactor and calibrated to give a flow rate of 0.7 hr^{-1} WHSV at a pressure of 3 psig. In each case, the methanol conversion was 100%. The effluent was analyzed at pre-determined intervals by an on-line gas chromatograph fitted with both a thermal conductivity detector and a flame ionization detector.

The results are shown in the following table.

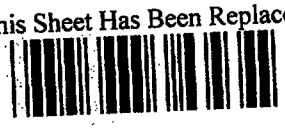
Olefins Yield	Comparative SAPO-34	Invention Sr-SAPO-34	Invention Ca-SAPO-34	Invention Ba-SAPO-34
Ethylene, wt.%	49.2	67.1	52.3	50.3
Propylene, wt.%	34.0	22.4	34.7	35.3
Total of $C_2^=$ and $C_3^=$, wt.%	83.2	89.5	87.0	85.6
Ethylene to propylene ratio	1.3	2.3	1.5	1.4

The examples illustrate an increase of over 36% in the ethylene yield using the Sr-SAPO-34 catalyst, as compared to the untreated SAPO-34 catalyst. The examples illustrate an increase of over 7% in the combined ethylene and propylene yield using the Sr-SAPO-34 catalyst, as compared to the untreated SAPO-34 catalyst. The Ca-SAPO-34 and Ba-SAPO catalysts achieved a respective 6% and 2% increase in ethylene yield as compared to the untreated SAPO-34 catalyst. The combined ethylene and propylene yield also increased by 5% and 3% respectively.

Thus, in the conversion of a starting material to olefins, the use of a small pore non-zeolitic molecular sieve is enhanced by the addition of one or

more of the alkaline earth metals of strontium, calcium, and barium, either during or post catalyst synthesis.

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What is Claimed is:

1. A catalyst composition, comprising a non-zeolitic molecular sieve and one or more alkaline earth metals selected from the group consisting of strontium, calcium, barium, and mixtures thereof, wherein the non-zeolitic molecular sieve has a pore diameter size of less than 5 Angstroms.

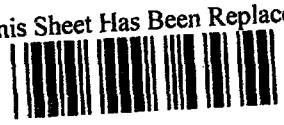
2. The catalyst composition of claim 1, wherein the non-zeolitic molecular sieve comprises a third metal oxide in addition to the alumina and silica components and the silicon to aluminum atomic ratio is less than 0.8.

3. A method for converting starting material to olefins comprising contacting the starting material with a non-zeolitic molecular sieve catalyst under effective conditions to produce olefins, wherein the non-zeolitic molecular sieve comprises a catalyst composition of claims 1 or 2 and has been prepared in-situ or modified after molecular sieve synthesis by incorporation of an alkaline earth metal selected from the group consisting of strontium, calcium, barium, and mixtures thereof, using an alkaline earth metal compound, wherein the alkaline earth metal ion is selected from the group consisting of strontium, calcium, barium, and mixtures thereof.

4. The method of any of the preceding claims wherein the molecular sieve catalyst is selected from the group consisting of a silicoaluminophosphate (SAPO), aluminophosphate (ALPO), and mixtures thereof, preferably is selected from the group consisting of



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SAPO-17, SAPO-18, SAPO-34, SAPO-44, and SAPO-56, and most preferably is SAPO-34.

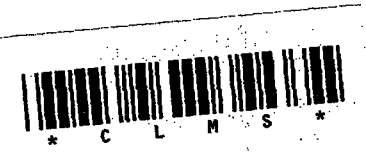
5. The method of any of the preceding claims wherein the molecular sieve catalyst pore size is greater than 3.5 Angstroms and less than 5.0 Angstroms, preferably greater than 4.0 Angstroms and less than 5.0 Angstroms, and most preferably in the range of from 4.3 to 5.0 Angstroms.

6. The method of any of the preceding claims wherein the alkaline earth metal is strontium or calcium and preferably is strontium.

7. A method of any of the preceding claims wherein the alkaline earth metal compound is selected from the group comprising halides, sulfates, formates, acetates, alkoxides, carbonyls, nitrates, or mixtures thereof and preferably is a carbonyl.

8. A method of any of the preceding claims wherein the modified non-zeolitic molecular sieve has a metal to silicon atomic ratio in the range of from 0.01:1 to 2:1, preferably in the range of from 0.05:1 to 1.5:1, and most preferably in the range of from 0.01:1 to 1:1.

9. A method of any of the preceding claims wherein the process for converting the starting material to olefins is conducted at a temperature of from 200°C to 700°C, preferably at a temperature of from 250°C to 600°C, and most preferably at a temperature of from 300°C to 500°C.



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THIS SHEET HAS BEEN REPLACED

10. The process of any of the preceding claims wherein the starting material feed is selected from the group consisting of methanol, ethanol, n-propanol, isopropanol, C_4 – C_{20} alcohols, methyl ethyl ether, di-methyl ether, di-ethyl ether, di-isopropyl ether, di-methyl carbonate, carbonyl compounds, and mixtures thereof, and preferably comprises methanol or dimethyl ether.

11. The process of any of the preceding claims wherein the starting material also includes a diluent.

12. The process of any of the preceding claims wherein the diluent is selected from the group consisting of water, nitrogen, hydrogen, paraffins, olefins, aromatics, and mixtures thereof, and preferably the diluent is water or nitrogen.

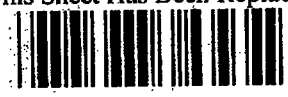
13. The method of any of the preceding claims wherein the starting material comprises a halide, a mercaptan, a sulfide, or an amine.

14. The process of any of the preceding claims wherein the process for converting the starting material to olefins is conducted at a pressure of from 0.1 kPa to 100 MPa, preferably at a pressure in the range of from 6.9 kPa to 34 MPa, and most preferably at a pressure of from 48kPa to 0.34MPa.

15. The method of any of the preceding claims wherein the process for converting the starting material to olefins using the treated molecular sieve is conducted at a WHSV in the range of from 0.01 to 500 hr^{-1}, preferably at a WHSV in the range of from 0.1 to 200 hr^{-1}, and most preferably in the range of from 0.5 to 100 hr^{-1}.



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16. The process for preparing a catalyst post-synthesis according to Claims 1 or 2, which comprises forming a mixture containing one or more sources of alkaline earth metals selected from the group consisting of strontium, calcium, barium, and mixtures thereof, in a solvent and treating the non-zeolitic molecular sieve with the mixture under conditions sufficient to incorporate a desired amount of the metal.

17. The process for preparing a catalyst in-situ according to Claim 1 or 2, which comprises forming a reaction mixture containing one or more sources of alkaline earth metals selected from the group consisting of strontium, calcium, barium, and mixtures thereof, and precursors required for producing the non-zeolitic molecular sieve and subjecting the mixture to conditions sufficient to form the catalyst.



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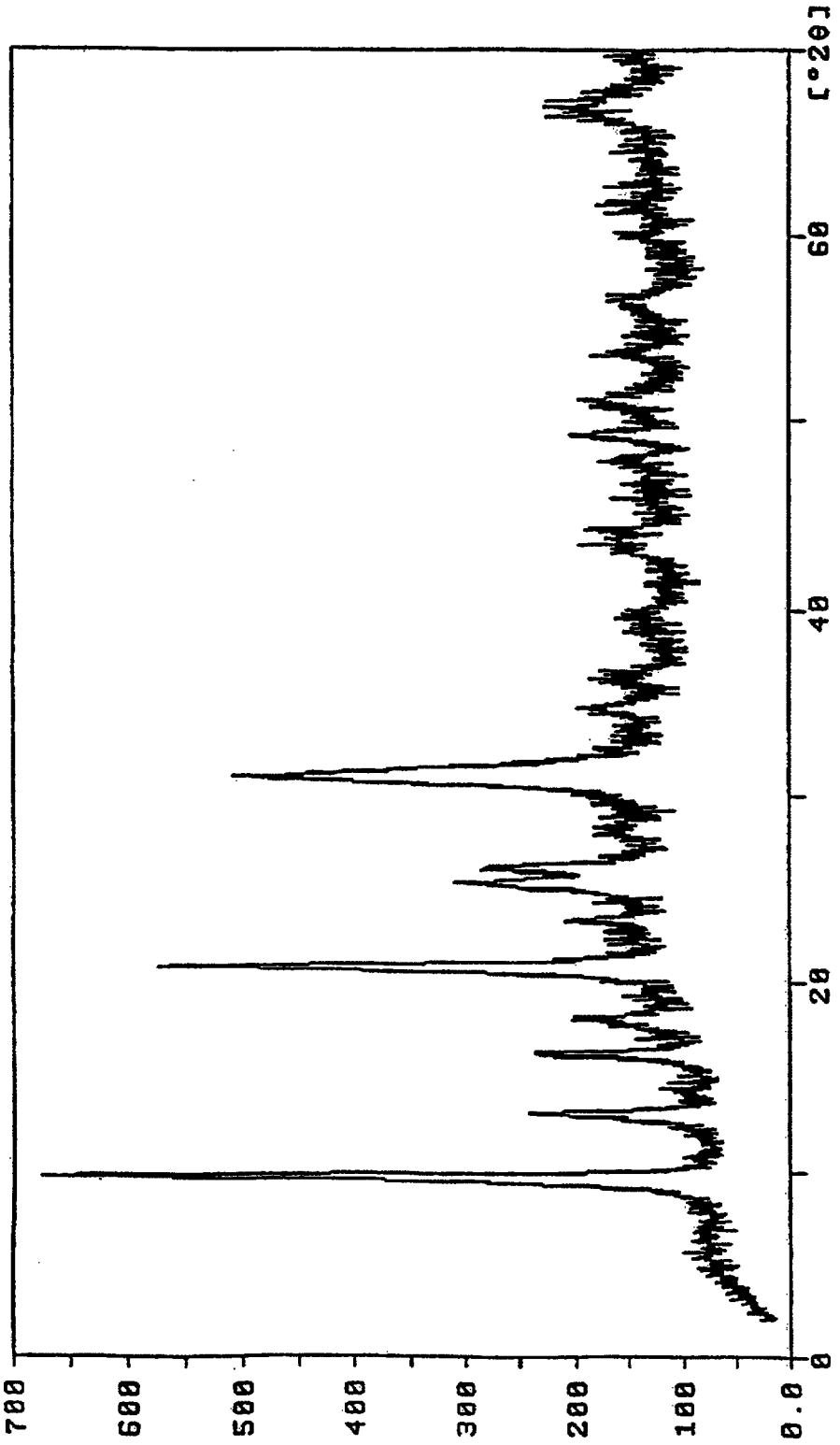


FIG. 1

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IPOS.

PATENT COOPERATION TREATY

REC'D 26 MAY 1998

WIPO PCT

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

15

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (PCT/IPEA/416)
BT-96B012		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US97/05670	04/04/1997	04/04/1996
International Patent Classification (IPC) or national classification and IPC		
B01J29/04		
Applicant		
EXXON CHEMICAL PATENTS INC.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:

I	☒	Basis of the report
II	☐	Priority
III	☐	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	☐	Lack of unity of invention
V	☒	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	☐	Certain documents cited
VII	☐	Certain defects in the international application
VIII	☒	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
03/11/1997	
Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Jourdan, A Telephone No. (+49-89) 2399-8349

Form PCT/IPEA/409 (Cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US97/05670

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-18,20,21	as originally filed			
19	as received on	14/04/1998	with letter of	08/04/1998

Claims, No.:

1-17	as received on	14/04/1998	with letter of	08/04/1998

Drawings, sheets:

1/1	as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-17
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-17
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-17
	No:	Claims	

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

V.

1. The subject-matter of claims 1-17 seems to be novel over the prior art, since none of the documents of the Search report discloses a catalyst composition comprising a molecular sieve having a pore diameter size of less than 5 Angstroms and an alkaline earth metal selected from the group of calcium, barium and/or strontium.

   Closest prior art is WO95/05342 which discloses acidic crystalline silicoaluminophosphate having a pore diameter of between 4 and 5 Angstroms.

2. The silicoaluminophosphate of WO95/05342 is useful in the conversion of methanol into light olefins C_2-C_4. However, none of the prior art documents give a hint that the conversion towards ethylene and propylene can be improved by incorporation of calcium, strontium or barium into silicoaluminophosphates. Therefore, the subject-matter of claims 1-17 also seems to involve an inventive step.

3. There is no doubt concerning the industrial applicability.

VIII.

1. According to claim 1 the non-zeolitic molecular sieve shall comprise a metal oxide and either AlO2- or SiO2. The alternative disclosed in the description on page 8, last line to page 9, line 2 that the non-zeolitic molecular sieve shall comprise a metal oxide and both AlO2- and SiO2 has been omitted from the claim 1. Due to this there is a discrepancy between claim 2 and claim 1 leading to a lack of clarity according to Article 6 PCT.

2. The wording of claim 16 is not clear contrary to the requirements of Article 6 PCT. Presumably, it could read "A post-synthesis process for preparing a catalyst according to claims 1 or 2...." or "A process for preparing a catalyst according to claims 1 or 2 by post-synthesis..."

3. The term "starting material" used in claim 15 is broader than the term "oxygenates" used in the preceding claims to which claim 15 refers back. This discrepancy leads to a lack of clarity according to Article 6 PCT.

AMENDED SHEET

hour in a closed container. 15 grams of 40 wt% tetraethylammonium hydroxide are then added to this mixture and the resultant mixture is stirred for another hour in the same closed container. Once this mixture is stirred, an aqueous solution containing 1.1 grams of strontium acetate $Sr[OOCCH_3]_2$ and 11 ml of water is added. The entire mixture is stirred for thirty minutes and transferred to a teflon™ lined autoclave and heated to 195°C under autogenic pressure for 168 hours. The recovered product is recovered by centrifugation and filtration, followed by washing with de-ionized water. The solid is dried at 110°C for two hours, followed by calcination at 550°C for sixteen hours to give a strontium silicoaluminophosphate product with the following composition:

$$Sr_{0.01}Si_{0.072}Al_{0.292}P_{0.159}O \cdot mH_2O$$

The structure is similar to SAPO-34. The resulting strontium to silicon atomic ratio measured in terms of an atomic weight basis will be 0.14 to 1.

Conversion Examples

Each of the prepared catalysts, the comparative and the two metal treated catalysts, was then tested using the following procedure. 5.0 cc (approximately 2.8 grams) of the selected SAPO-34 catalyst, were mixed with 15 cc of quartz beads and loaded into a 1.9 cm (3/4") outer diameter 316 stainless steel tubular reactor which was heated by a three-zone electric furnace. The first zone, acting as the preheating zone, vaporized the feed. The temperature of the center zone of the furnace was adjusted to give the desired reaction temperature of 450°C. The reactor was purged first with nitrogen at 50 cc/min. flow rate for 30 minutes. The feed, containing 30.8 wt.% methanol, equivalent to a 4:1 (molar ratio) of water

What is Claimed is:

1. A catalyst composition, comprising a non-zeolitic molecular sieve and one or more alkaline earth metals selected from the group consisting of strontium, calcium, barium, and mixtures thereof, wherein the non-zeolitic molecular sieve comprises a metal oxide and either AlO_2 or SiO_2 and the non-zeolite molecular sieve has a pore diameter size of less than 5 Angstroms.

2. The catalyst composition of claim 1, wherein the non-zeolitic molecular sieve comprises a third metal oxide in addition to the alumina and silica components and the silicon to aluminum atomic ratio is less than 0.8.

3. A method for converting oxygenates to olefins comprising contacting the oxygenate with a non-zeolitic molecular sieve catalyst under effective conditions to produce olefins, wherein the non-zeolitic molecular sieve comprises a catalyst composition of claims 1 or 2 and has been prepared in-situ or modified after molecular sieve synthesis by incorporation of an alkaline earth metal selected from the group consisting of strontium, calcium, barium, and mixtures thereof, using an alkaline earth metal compound, wherein the alkaline earth metal ion is selected from the group consisting of strontium, calcium, barium, and mixtures thereof.

4. The method of any of the preceding claims wherein the molecular sieve catalyst is selected from the group consisting of a silicoaluminophosphate (SAPO), aluminophosphate (ALPO), and mixtures thereof, preferably is selected from the group consisting of

SAPO-17, SAPO-18, SAPO-34, SAPO-44, and SAPO-56, and most preferably is SAPO-34.

5. The method of any of the preceding claims wherein the molecular sieve catalyst pore size is greater than 3.5 Angstroms and less than 5.0 Angstroms, preferably greater than 4.0 Angstroms and less than 5.0 Angstroms, and most preferably in the range of from 4.3 to 5.0 Angstroms.

6. The method of any of the preceding claims wherein the alkaline earth metal is strontium or calcium and preferably is strontium.

7. A method of any of the preceding claims wherein the alkaline earth metal compound is selected from the group comprising halides, sulfates, formates, acetates, alkoxides, carbonyls, nitrates, or mixtures thereof and preferably is a carbonyl.

8. A method of any of the preceding claims wherein the modified non-zeolitic molecular sieve has a metal to silicon atomic ratio in the range of from 0.01:1 to 2:1, preferably in the range of from 0.05:1 to 1.5:1, and most preferably in the range of from 0.1:1 to 1:1.

9. A method of any of the preceding claims wherein the process for converting the oxygenates to olefins is conducted at a temperature of from 200°C to 700°C, preferably at a temperature of from 250°C to 600°C, and most preferably at a temperature of from 300°C to 500°C.

10. The method of any of the preceding claims wherein the oxygenate is selected from the group consisting of methanol, ethanol, n-

propanol, isopropanol, C_4 – C_{20} alcohols, methyl ethyl ether, di-methyl ether, di-ethyl ether, di-isopropyl ether, di-methyl carbonate, carbonyl compounds, and mixtures thereof, and preferably comprises methanol or dimethyl ether.

11. The method of any of the preceding claims wherein the oxygenate feed also includes a diluent.

12. The method of any of the preceding claims wherein the diluent is selected from the group consisting of water, nitrogen, hydrogen, paraffins, olefins, aromatics, and mixtures thereof, and preferably the diluent is water or nitrogen.

13. The method of any of the preceding claims wherein the oxygenate comprises a halide, a mercaptan, a sulfide, or an amine.

14. The method of any of the preceding claims wherein the process for converting oxygenate to olefins is conducted at a pressure of from 0.1 kPa to 100 MPa, preferably at a pressure in the range of from 6.9 kPa to 34 MPa, and most preferably at a pressure of from 48kPa to 0.34MPa.

15. The method of any of the preceding claims wherein the process for converting the starting material to olefins using the treated molecular sieve is conducted at a WHSV in the range of from 0.01 to 500 hr^{-1}, preferably at a WHSV in the range of from 0.1 to 200 hr^{-1}, and most preferably in the range of from 0.5 to 100 hr^{-1}.

16. A process for preparing post-synthesis according to Claims 1 or 2, which comprises forming a mixture containing one or more sources

of alkaline earth metals selected from the group consisting of strontium, calcium, barium, and mixtures thereof, in a solvent and treating the non-zeolitic molecular sieve with the mixture under conditions sufficient to incorporate a desired amount of the metal.

17. An in-situ process for preparing a catalyst according to Claim 1 or 2, which comprises forming a reaction mixture containing one or more sources of alkaline earth metals selected from the group consisting of strontium, calcium, barium, and mixtures thereof, and precursors required for producing the non-zeolitic molecular sieve and subjecting the mixture to conditions sufficient to form the catalyst.

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PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
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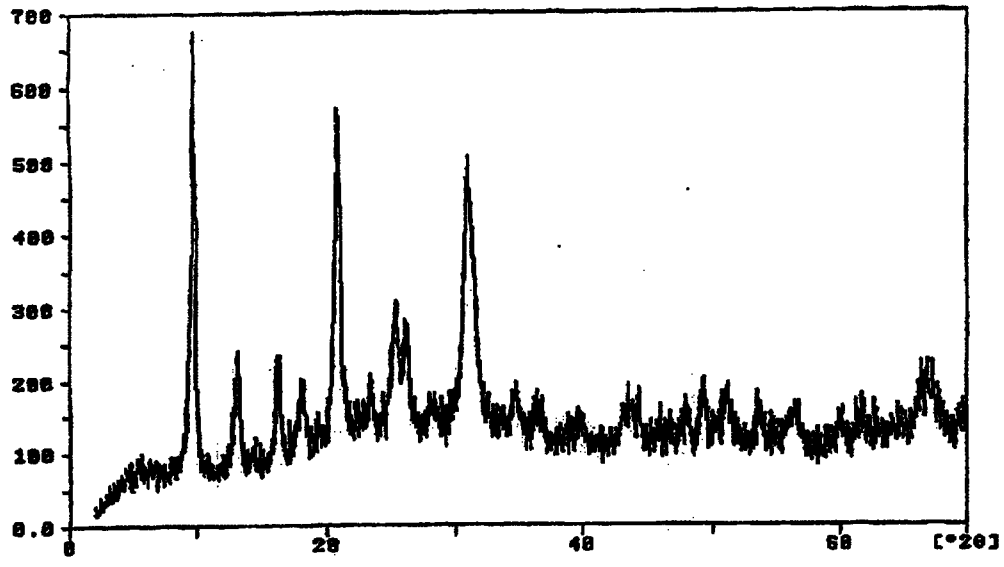
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(54) Title: USE OF ALKALINE EARTH METAL CONTAINING SMALL PORE NON-ZEOLITIC MOLECULAR SIEVE CATALYSTS IN OXYGENATE CONVERSION



(57) Abstract

A method for converting starting material to olefins comprising contacting the starting material with a small pore non-zeolitic molecular sieve catalyst under effective conditions to produce olefins, wherein the non-zeolitic molecular sieve has been prepared in-situ or modified after synthesis by incorporation using an alkaline earth metal compound, wherein the alkaline earth metal ion is selected from the group consisting of strontium, calcium, barium, and mixtures thereof.