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(54) Title: OXYGENATE CONVERSIONS USING SMALL PORE NON–ZEOLITIC MOLECULAR SIEVE CATALYSTS

(57) Abstract

The present invention provides a method for converting an organic starting material to olefins comprising contacting a feed comprising said organic starting material with a small pore non–zeolitic catalyst at a temperature, a pressure, and a weight hourly space velocity effective to produce olefins; wherein said molecular sieve catalyst comprises at least one metal selected from the group consisting of a lanthanide metal, an actinide metal, scandium, yttrium, Group IVB metals, Group VB metals, and combinations thereof.

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Oxygenate Conversions Using Small Pore Non-Zeolitic Molecular Sieve Catalysts

This application claims priority to U.S. Provisional Patent Application No. 60/034,054, filed December 31, 1996.

Field of the Invention

The invention relates to a process for converting oxygenated organic material, such as methanol and dimethyl ether, to olefins using small pore non-zeolitic catalysts comprising a metal selected from the group consisting of lanthanide metals, actinide metals, scandium, yttrium, Group IVB metals, and Group VB metals.

Background of the Invention

Light olefins, such as ethylene, serve as feeds for the production of numerous chemicals. Olefins traditionally are produced by petroleum cracking. Because of the limited supply and/or the high cost of petroleum sources, the cost of producing olefins from petroleum sources has increased steadily.

Alternative feedstocks for the production of light olefins are oxygenates, such as alcohols, particularly methanol, dimethyl ether, and ethanol. Alcohols may be produced by fermentation, or from synthesis gas derived from natural gas, petroleum liquids, carbonaceous materials, including coal, recycled plastics, municipal wastes, or any organic material. Because of the wide variety of sources, alcohol, alcohol derivatives, and other oxygenates have promise as an economical, non-petroleum source for olefin production.

Small pore catalysts, such as SAPO-34, have been used to convert methanol and dimethyl ether to olefins. However, the conversion stability

has been better using medium pore molecular sieves which have been ion-exchanged with metal ions.

Small pore catalysts which will convert oxygenates to olefins with a high conversion stability are needed.

SUMMARY OF THE INVENTION

The present invention provides a method for converting an organic starting material to olefins comprising contacting a feed comprising said organic starting material with a small pore non-zeolitic catalyst at a temperature, a pressure, and a weight hourly space velocity effective to produce olefins; wherein said molecular sieve catalyst comprises at least one metal selected from the group consisting of a lanthanide metal, an actinide metal, scandium, yttrium, Group IVB metals, and Group VB metals, and combinations thereof.

DETAILED DESCRIPTION OF THE INVENTION

The invention involves the conversion of oxygenates to olefins using small pore non-zeolitic molecular sieve catalysts comprising certain metals. Suitable small pore non-zeolitic molecular sieve catalysts include, but are not necessarily limited to, small pore silicoaluminophosphates (SAPOs) and small pore aluminophospho oxides (ALPO's). Examples of suitable small pore ALPO's include, but are not necessarily limited to ALPO-20 and ALPO-25. Preferred molecular sieve catalysts are SAPOs, such as SAPO-34, SAPO 17, SAPO-18, SAPO-43, and SAPO-44, and others which may be synthesized according to US-A-4,440,871, incorporated herein by reference, and *Zeolites*, Vol. 17, pp. 512-522 (1996), incorporated herein by reference. Most preferred catalysts are SAPO-17, SAPO-18, and SAPO-34.

"Small pore" molecular sieve catalysts are defined as catalysts with pores having a diameter or pore size of less than about 5.0 Angstroms. Suitable catalysts have a pore size ranging from about 3.5 to about 5.0

Angstroms, preferably from about 4.0 to about 5.0 Angstroms, and most preferably from about 4.3 to about 5.0 Angstroms.

SAPO's have a three-dimensional microporous crystal framework of PO^+, 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 ARE present per mole of $(Si_xAl_yPz)O_2$ 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 in the pore system of the particular SAPO species involved, and "x", "y", and "z" represent the mole fractions of silicon, aluminum and phosphorus, respectively. "R" may be removed at elevated temperatures.

Preferred metals for incorporation into the molecular sieve catalysts are selected from the group consisting of the lanthanide series, the actinide series, scandium, yttrium, Group IVB metals, Group VB metals (referring to Group IVB and VB of the Periodic Table of the Elements, as defined by the CAS Version, inside front cover, *CRC Handbook of Chemistry and Physics*, 76th Ed., CRC Press, 1995-96), and combinations thereof. Such metals include, but are not necessarily limited to lanthanum, actinium, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, thorium, protactinium, uranium, scandium, yttrium, titanium, zirconium, hafnium, vanadium, niobium, tantalum, and combinations thereof.

The metals may be derived from various compounds, i.e. in the form of the corresponding halide, sulfate, acetate, formate, propionate, oxalate, maleate, fumarate, other carboxylate, alkoxide, carbonyl, nitrate, or mixtures thereof. When the desired catalyst comprises SAPO-34 and

the metal is ytterbium, it is preferable to use ytterbium (III) acetate tetrahydrate as the metal containing compound. When the desired catalyst comprises SAPO-34 and the metal is titanium, it is preferable to use titanium tetrabutoxide as the metal containing compound.

The process of incorporating the metal into the non-zeolitic catalyst may be accomplished using any of the standard methods well known to those skilled in the art. Examples are the incipient wetness method, mechanical mixing, and others. Ion exchange also is a suitable method for metals having a valence of less than about three. It is very difficult, if not impossible, to use ion exchange methods to incorporate ions having valences of three or higher.

In one embodiment, a solution of the desired metal is first made by dissolving a 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 solvent is selected. Suitable solvents are organic, inorganic, and aqueous. The process may be conducted under pressure, at reduced pressure, or at atmospheric pressure.

After adequate mixing, the solution is added to a predetermined amount of the non-zeolitic catalyst. 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 metal incorporation. The catalyst product then is filtered, optionally washed, dried, and calcined by methods well known to those skilled in the art.

The amount of metal incorporated into the catalyst may vary over a wide range depending, at least in part, on the selected catalyst and the incorporation method. Preferably, the amount of metal incorporated should be at least about 0.0001 wt%, more preferably in the range of from about 0.0001 wt% and about 10 wt%.

The conversion process employs a starting material (feedstock) preferably comprising "oxygenates". As used herein, the term "oxygenates" is defined to include, but is not necessarily limited to aliphatic alcohols, ethers, carbonyl compounds (aldehydes, ketones, carboxylic acids, carbonates, and the like), and also compounds containing hetero-atoms, such as, halides, mercaptans, sulfides, amines, and mixtures thereof. The aliphatic moiety preferably should contain in the range of from about 1 - 10 carbon atoms and more preferably in the range of from about 1 - 4 carbon atoms. Representative oxygenates include, but are not necessarily limited to, lower straight chain or branched aliphatic alcohols, their unsaturated counterparts, and their nitrogen, halogen and sulfur analogues. Examples of suitable compounds include, but are not necessarily limited to: methanol; ethanol; n-propanol; isopropanol; C_4 - C_{10} alcohols; methyl ethyl ether; dimethyl ether; diethyl ether; di-isopropyl ether; methyl mercaptan; methyl sulfide; methyl amine; ethyl mercaptan; diethyl sulfide; diethyl amine; ethyl chloride; formaldehyde; dimethyl carbonate; dimethyl ketone; acetic acid; n-alkyl amines, n-alkyl halides, n-alkyl sulfides having n-alkyl groups of in the range of from about 3 - 10 carbon atoms; and mixtures thereof. As used herein, the term "oxygenate" 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 of feed to olefins preferably should be carried out in the vapor phase. Preferably, the feedstock should be contacted in the 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. Alternately, the process may be carried out in a liquid phase. When the process is carried out in the liquid phase, different

conversion rates and selectivities of feedstock-to-product may result depending upon the composition of the liquid.

The temperature employed in the conversion process may vary over a wide range depending, at least in part, on the selected catalyst. Although not limited to a particular temperature, best results will be obtained if the process is conducted at temperatures in the range of from about 200 - 700 °C, preferably in the range of from about 250 -600 °C, and most preferably in the range of from about 300 - 500 °C. Lower temperatures generally result in lower rates of reaction, and the formation of the desired light olefin products may become markedly slow. However, at higher temperatures, the process may not form an optimum amount of light olefin products, and the coking rate may become too high.

Light olefin products will form--although not necessarily in optimum amounts--at a wide range of pressures, including but not limited to autogeneous pressures and pressures in the range of from about 0.1 kPa to about 100 MPa,. A preferred pressure is in the range of from about 6.9 kPa to about 34 Mpa, most preferably in the range of from about 48 kPa to about 0.34 MPa. The foregoing pressures are exclusive of diluent, if any is present, and refer to the partial pressure of the feedstock as it relates to oxygenate compounds and/or mixtures thereof. Pressures outside of the stated ranges may operate and are not excluded from the scope of the invention. Lower and upper extremes of pressure may adversely affect selectivity, conversion, coking rate, and/or reaction rate; however, light olefins such as ethylene still may form.

The process should be continued for a period of time sufficient to produce the desired olefin products. The reaction time may vary from tenths of seconds to a number of hours. The reaction time is largely determined by the reaction temperature, the pressure, the catalyst selected, the weight hourly space velocity, the phase (liquid or vapor), and the selected process design characteristics.

A wide range of weight hourly space velocity (WHSV) for the feedstock will function in the present invention. The WHSV generally should be in the range of from about 0.01 hr^{-1} to about 500 hr^{-1}, preferably in the range of from about 0.1 hr^{-1} to about 200 hr^{-1}, and most preferably in the range of from about 0.5 hr^{-1} to about 100 hr^{-1}. The catalyst may contain other materials which act as inerts, fillers, or binders; therefore, the WHSV is calculated on the weight basis of methanol or dimethyl ether and non-zeolitic catalyst.

The feed may contain one or more diluents in an amount in the range of from about 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). Diluents which may be employed in the process include, but are not necessarily limited to, helium, argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, paraffins, other hydrocarbons (such as methane), aromatic compounds, and mixtures thereof. Preferred diluents are water and nitrogen.

The process may be carried out in a batch, semi-continuous, or continuous fashion. The process may use a single reaction zone or a number of reaction zones arranged in series or in parallel. The process may be intermittent or continuous in an elongated tubular zone or a number of such zones. When multiple reaction zones are used, one or more of the non-zeolitic catalysts advantageously may be used in series to provide for a desired product mixture.

A dynamic bed system, or any system that includes a variety of transport beds rather than fixed beds, may be desirable. If regeneration of the catalyst is required, such a system would permit introduction of the catalyst as a moving bed to a regeneration zone where, e.g., carbonaceous material could be removed or oxidized. Preferably, the catalyst should be regenerated by burning off carbonaceous deposits that accumulate during the process.

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

Example I

A sample of SAPO-34, received from UOP, Des Plaines, Illinois, as disclosed in US-A-4,440,871, incorporated herein by reference, was used to act as a control for each experiment.

Example II

An ytterbium-containing solution was prepared by dissolving 0.42g of ytterbium (III) acetate tetrahydrate in 6ml of de-ionized water at room temperature. This solution was added to 3.5 grams of SAPO-34 calcined for 16 hours at 550°C and the mixture was allowed to stand at room temperature for one hour, and then dried at 110[1]°C for 2 hours. The resulting dried catalyst was then calcined at 5001°C for 16 hours, to result in ytterbium-SAPO-34.

Example III

The control and the ytterbium-modified catalysts were tested using the following procedure. 5.0 cc (approximately 2.7 grams) of each catalyst was mixed with 15 cc of quartz beads and loaded into a 3/4 inch 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 4501°C and the pressure was maintained at 1 atm. The reactor was purged first with nitrogen at 50 cc/min flow rate for 30 minutes. The feed, a 4:1(molar ratio) of water and methanol, was pumped into the reactor and calibrated to give a flow rate of about 0.7 hr^{-1} WHSV. 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	Control SAPO-34	Invention Yb-SAPO-34
Conversion (wt%)	99.4	99.8
Methane	3.1	3.4
Ethylene	45.8	50.4
Ethane	1.7	1.5
$C_3^=/C_3°$	36.5	34.0

An increase of approximately 10% in the ethylene yield is seen using the Yb-SAPO-34 catalyst, as compared to the untreated SAPO-34 catalyst.

Example IV

A titanium-containing solution was prepared by dissolving 0.449 g of titanium tetrabutoxide in 5cc of cyclohexane at room temperature. This solution was added to 3.0 grams of calcined SAPO-34 and the mixture was allowed to stand at room temperature overnight. The mixture was then dried at 110 °C for 2 hours, and calcined at 6501°C overnight, to result in titanium-SAPO-34.

Example V

The control and the titanium-modified catalysts were tested using the following procedure. 5.0 cc (approximately 2.7 grams) of each catalyst was diluted with 15 cc of glass beads and loaded into a 3/4 inch 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 a reaction temperature of 4501°C and the pressure

was maintained at 1 atm. The reactor was purged first with nitrogen at 50 cc/min flow rate for 30 minutes. The feed, a 4:1(molar ratio) of water and methanol, was pumped into the reactor and calibrated to give a flow rate of about 0.7 hr^{-1} WHSV calculated on the basis of methanol and catalyst only. 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 demonstrated a reduction in methane and ethane production, as shown in the following table.

Yield	Control SAPO-34	Invention Ti-SAPO-34
Methane	3.0	2.6
Methane + Ethane	5.2	4.1

Persons of ordinary skill in the art will recognize that many modifications may be made to the present invention without departing from the spirit and scope of the present invention. The embodiments described herein are meant to be illustrative only and should not be taken as limiting the invention, which is defined in the following claims.

Claims:

1. A method for converting an organic starting material to olefins comprising:

contacting a feed comprising the organic starting material with a small pore non-zeolitic molecular sieve catalyst at a temperature, a pressure, and a weight hourly space velocity effective to produce olefins;

wherein the catalyst comprises a non-zeolitic framework and a metal consisting of a lanthanide metal, an actinide metal, scandium, yttrium, a Group IVB metal, a Group VB metal, or combinations thereof.

2. A catalyst for converting an organic starting material to olefins comprising a non-zeolitic framework; and at least 0.0001 wt% of a metal consisting of lanthanide metals, actinide metals, scandium, yttrium, Group IVB metals, Group VB metals, or combinations thereof.

3. The method of Claim 1 or the catalyst of Claim 2 wherein the metal consists of a lanthanide metal, an actinide metal, scandium, yttrium, or combinations thereof, and preferably consists of lanthanum, actinium, cerium praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, thorium, protactinium, uranium, scandium, yttrium, or combinations thereof.

4. The method of Claim 1 or the catalyst of Claim 2 wherein the metal is a Group IVB metal, a Group VB metal, or combinations thereof.

5. The method or the catalyst of any of the preceeding claims wherein the catalyst is a silicoaluminophosphate catalyst, and preferably is SAPO-17, SAPO-18, SAPO-34, and SAPO-44.

6. The method or the catalyst of any of the preceeding claims wherein the catalyst comprises pores having a diameter greater than 3.5 Angstroms and less than 5.0 Angstroms.

7. The method or the catalyst of any of the preceeding claims wherein the metal is derived from a compound consisting of halides, sulfates, acetates, formates, propionates, oxalates, maleates, fumarates, carboxylates, alkoxides, carbonyls, nitrates, or mixtures thereof.

8. The method or the catalyst of any of the preceeding claims wherein the catalyst comprises at least 0.0001 wt% of the metal, and preferably comprises in the range of from 0.0001 wt% to 10 wt%.

9. The method of any of the preceeding claims wherein the temperature is in the range of from 200°C to 600°C, preferably in the range of 250° to 600°C, and most preferably in the range of 300° to 500°C.

10. The method of any of the preceeding claims wherein the organic starting material consists of a halide, a mercaptan, a sulfide, or an amine, methanol, ethanol, n-propanol, isopropanol, C_4 - C_{10} alcohols, methyl ethyl ether, dimethyl ether, diethyl ether, di-isopropyl ether, dimethyl carbonate, carbonyl compounds, or

11. The method of any of the preceeding claims wherein the organic starting material further comprises a diluent wherein the diluent consists of water, nitrogen, hydrogen, paraffins, olefins, aromatics, or mixtures thereof, and preferably is water and/or nitrogen.

12. The method of any of the preceeding claims wherein said pressure is in the range of from 0.1 kPa to 100 Mpa, preferably in the range of from 6.9 kPa to 34 Mpa, and most preferably in the range of from 48 kPa to 0.34 MPa.

13. The method of any of the preceeding claims wherein the weight hourly space velocity is in the range of from 0.01 to about 500 hr^{-1}, preferably in the range of 0.1 hr^{-1} to 200 hr^{-1}, and most preferably in the range of 0.5 hr^{-1} to 100 hr^{-1}.

INTERNATIONAL SEARCH REPORT

In tional Application No
PCT/US 97/24125

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C11/02 C07C1/26 C07C1/32 C07C1/20 C07C1/36
C07C1/207

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 6 C07C

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 249 915 A (UNION CARBIDE CORP) 23 December 1987 see claims -----	1,2, 4-12,21

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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2

Date of the actual completion of the international search	Date of mailing of the international search report
26 March 1998	07.04.98
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Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 97/24125

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 13-20; 10-12 and 21 only partially
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

Claims 13 to 20 are missing; propably claim 21 should have been numbered as 13. Claim 10 is incomplete: at least one word is missing at the end of this claim. Claims 10 - 12 and 21 could thus only be searched partially.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/US 97/24125

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0249915 A	23-12-87	US 4752651 A	21-06-88
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