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**USE OF ACID EXTRACTED MOLECULAR SIEVE  
CATALYSTS IN OXYGENATE CONVERSION**

**BACKGROUND OF THE INVENTION**

5           This invention relates to a process for enhancing  
ethylene yield in the conversion of oxygenates to  
hydrocarbons or olefins using microporous solid  
catalysts. More particularly, this invention relates  
to a process for enhancing ethylene yields using  
10   silicoaluminophosphate molecular sieve catalysts  
through acid extraction of the catalysts.

          Light olefins have traditionally been produced  
through the process of petroleum cracking. Because of  
the limited availability and high cost of petroleum  
15   sources, the cost of producing light 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  
20   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.  
25   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  
30   hydrocarbon production.

          Molecular sieves, such as the crystalline zeolite  
and silicoaluminophosphate (SAPO) catalysts, are known  
to promote the conversion of oxygenates to hydrocarbon

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mixtures. Numerous patents describe this process for various types of molecular sieve catalysts:

US-A-3,928,483; 4,025,575; 4,252,479 (Chang, et al.); 4,496,786 (Santilly, et al.); 4,677,243 (Kaiser).

5 However, none of these patents teach or suggest that ethylene yield may be enhanced through treatment of the catalyst with acid.

#### SUMMARY OF THE INVENTION

10 In accordance with the present invention, there is provided a process for converting oxygenates to olefins comprising treating an oxygenate feed with a molecular sieve catalyst under effective conversion conditions, characterized in that the catalyst  
15 comprises an acid-extracted molecular sieve catalyst effective to produce olefins with improved ethylene yield. The process preferably employs an acid-extracted molecular sieve catalyst such as acid-extracted silicoaluminophosphate (SAPO), and more  
20 particularly, acid-extracted SAPO-34. Acid extraction with mineral acids alters the crystallinity of the molecular sieve and has been found to enhance ethylene yield.

#### 25 DETAILED DESCRIPTION OF THE INVENTION

The present invention is characterized by use of molecular sieve catalysts which have been extracted with acids, to increase olefin yields and, more particularly, to increase ethylene yields. In one  
30 aspect the invention comprises a process for improving ethylene yields in the conversion of oxygenates to olefins, comprising extracting a molecular sieve catalyst with an acid, then converting an oxygenate

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5 feed to olefins with the acid-extracted molecular sieve catalyst to improve ethylene yields. The molecular sieve catalyst may be a SAPO catalyst, such as, but not limited to, SAPO-34, or a zeolite catalyst.

10 This acid treatment of the catalysts may alter the X-ray diffraction pattern of the catalyst, the inflection of the X-ray peaks and the crystallinity of the molecular sieve. Although the exact mechanism whereby acid treatment improves ethylene yield is not known, it is thought to be related to changes in the crystallinity of the molecular sieve catalyst. In one embodiment the catalyst has a crystallinity which is from 10 to 30% that of the corresponding non-acid-extracted catalyst.

15 Representative acids that can be used include, but are not limited to, hydrochloric, hydrofluoric, sulfuric, phosphoric and acetic acids or any mineral acids or mixtures thereof. Acid strength (concentration) may be for example from 0.1N to 1N, preferably 0.01N to 0.1N and more preferably 0.001N to 0.01N. Extraction times with the acid may be for example up to 100 hours, preferably up to 30 hours, and most preferably from 23 to 26 hours. The appropriate acid, acid strength and concentration, and extraction time will be selected according to the invention to give the desired improvement in olefin or ethylene yield.

30 Any of the large number of molecular sieve catalysts, such as, but not limited to, the zeolite catalysts, can be used in the present invention. Ethylene yield is enhanced by treating the molecular sieve catalyst with an acid. More specifically, this

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invention employs acid extraction of SAPO catalysts to improve ethylene yields.

SAPO catalysts exhibit properties of both aluminosilicate zeolites and aluminophosphates. The SAPO's have a three-dimensional microporous crystal framework structure of  $\text{PO}_2^+$ ,  $\text{AlO}_2^-$  and  $\text{SiO}_2$  tetrahedral units. The chemical composition (anhydrous) is:



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  $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$  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.

The process for producing ethylene employs a feedstock comprising "oxygenates". As used herein, the term "oxygenate feed" is intended to mean not only what might be considered "true" oxygenates, e.g., alcohols, ethers, carbonyl compounds (aldehydes, ketones, carboxylic acids and the like); but also those compounds which behave in a similar fashion to "true" oxygenates in the presence of the specified catalysts, such as substituted paraffins, e.g., halides, mercaptans, sulfides, amines. These oxygenates comprise hydrocarbons containing aliphatic moieties such as, but not limited to, alcohols, halides, mercaptans, sulfides, amines, ethers and carbonyl compounds (aldehydes, ketones, carboxylic

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acids and the like) or 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 alcohols, their unsaturated counterparts and the nitrogen, halogen and sulfur analogues of such. Examples of suitable compounds include, but are not limited to, methanol; isopropanol; n-propanol; ethanol; fuel alcohols; methyl mercaptan; methyl sulfide; methyl amine; dimethyl ether; ethyl mercaptan; ethyl chloride; diethyl ether; methylethyl ether; formaldehyde; dimethyl ketone; acetic acid; n-alkyl amines; n-alkyl halides and n-alkyl sulfides having n-alkyl groups of 3 to 10 carbon atoms; and mixtures thereof. The term "oxygenate feed" 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 ethylene production 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 light olefins, i.e., an effective temperature, pressure, WHSV (Weight Hourly Space Velocity) and, optionally, an effective amount of diluent, correlated to produce light olefins. Alternatively, the process may be carried out in a liquid phase. When the process is carried out in the liquid phase the process necessarily involves the separation of products formed in a liquid reaction medium and can result in

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different conversions and selectivities of feedstock-to-product with respect to the relative ratios of the light olefin products as compared to that formed by the vapor phase process.

5       The temperature which may be employed in the process may vary over a wide range depending, at least in part, on the selected molecular sieve catalyst. In general, the process can be conducted at an effective temperature between 200°C (392°F) and 700°C (1292°F),  
10       preferably between 250°C (482°F) and 600°C (1112°F), and most preferably between 300°C (572°F) and 500°C (932°F). Temperatures outside the stated range are not excluded, although they do not fall within certain desirable embodiments of the present invention. At  
15       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  
20       amount of light olefin products. Notwithstanding these factors, the reaction will still occur and the feedstock, at least in part, can be converted to the desired light olefin products at temperatures outside the range between 200°C (392°F) and 700°C (1292°F).

25       The process is effectively carried out over a wide range of pressures including autogeneous pressures. At pressures between 0.001 atmospheres (0.76 torr) and 1000 atmospheres (760,000 torr), the formation of light olefin products will be effected  
30       although the optimum amount of product will not necessarily form at all pressures. The preferred pressure is between 0.01 atmospheres (7.6 torr) and 100 atmospheres (76,000 torr). The pressures referred

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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.

5 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  
10 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 light olefin  
15 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 molecular  
20 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 between  $0.01 \text{ hr.}^{-1}$  and  $100 \text{ hr.}^{-1}$  and preferably  
25 between  $0.1 \text{ hr.}^{-1}$  and  $40 \text{ hr.}^{-1}$ . Values above  $100 \text{ hr.}^{-1}$  may be employed and are intended to be covered by the instant process, although such are not presently preferred.

The olefin production process may be carried out  
30 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

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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 mixtures of water and aromatic diluents.

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 SAPO molecular sieves in series to provide for a desired product mixture. Owing to the nature of the process, it may be desirable to carry out the process of the present invention by use of the molecular sieve catalysts in a dynamic (e.g. fluidized or moving) 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 of carbonaceous deposits accumulated during reactions.

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It is well known that the catalytic and adsorptive properties of the molecular sieve catalyst may be varied by changing the ions within the catalyst. Appropriate materials that can be used in this ion-exchange process are ammonia and various acids, including hydrochloric acid, having a low molar strength. The use of acids during ion-exchange does not significantly alter the X-ray diffraction pattern, the inflection of the X-ray peaks or the crystallinity of the molecular sieve.

The following example illustrates the invention.

#### Example

SAPO-34 was prepared as described in US-A-4,440,871. SAPO-34 was extracted at room temperature for 24 hours with separately each of the following: water, 0.01N, 0.005N, or 0.001N HCl. After extraction, the solid was washed, dried, and calcined at 500°C (932°F).

Crystallinity was determined using a standard X-ray powder diffraction technique. The radiation source was a high intensity, copper target X-ray tube operated at 40Kv and 40 ma. The diffraction pattern from the copper K $\alpha$  radiation was recorded by an X-ray spectrometer scintillation counter, pulse height analyzer and strip chart recorder. Flat compressed powder samples were scanned at 2 $\theta$  (2 theta) per minute using a two second time constant. Interplanar spacings (d) in Angstrom units were obtained from the position of the diffraction peaks expressed as 2 $\theta$  where  $\theta$  is the Bragg angle as observed on the strip chart. Intensities were determined from the heights of diffraction peaks after subtracting background,

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"I<sub>0</sub>" being the intensity of the strongest line or peak and "I" being the intensity of each of the other peaks. The d-spacings used herein were 44.137 - 1.343 Angstroms. The reference sample (the SAPO-34 not  
5 acid-treated) was arbitrarily set at 100% crystallinity.

The catalytic conversion of methanol/water (1/4 molar ratio) to olefins such as ethylene was carried out in a fixed bed 1/2" diameter (1.27 cm), stainless  
10 steel reactor, equipped with a 1/8" (0.32 cm) coiled preheater. In addition, the reactor was equipped with a 1/8" (0.32 cm) thermocouple well running axially through the reactor. The reactor was inserted into and heated in an Applied Test Systems 3 zone tube  
15 furnace (12", 30.5 cm long; 1 1/4", 3.18 cm I.D.) having one reactor with three spaced "zones." The first reactor zone was used as a preheater zone; the catalyst bed was heated in the second reactor zone. The third reactor zone operates as a quench zone  
20 maintained at a temperature of about 200°C (392°F) to about 300°C (572°F).

Generally, 2 grams (0.07 ounces) of catalyst (-14/+20 mesh) were mixed with 2.5 grams (0.09 ounces) of quartz (-20/+60 mesh); the first and third zones of  
25 the reactor were filled with quartz chips (-10/+20 mesh). To improve the heat transfer between the second reactor zone (containing the catalyst bed) and the furnace heating coils, the second reactor zone was equipped with a cylindrical (1/4", 10.2 cm long; 1  
30 1/4", 3.18 cm O.D.) aluminum or stainless steel block. This block contained a central hole in order to be able to measure the block temperature.

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Gas flows (nitrogen or hydrogen) were controlled by mass flow controllers, while liquid feed rates were controlled by a Beckmann 114M pump or a Sage 3413 syringe pump.

5        The product emerging from the reactor was analyzed on line for ethylene with a Porepack Q column using a thermal conductivity detector. The reaction was conducted at a WHSV = 1.0 hr.<sup>-1</sup>. The reaction was conducted at 450°C (842°F). The results are shown in  
10      the Table.

Table

|    | <u>Treatment</u> | <u>Crystallinity</u> | <u>Ethylene yield<br/>(wt %, excluding H<sub>2</sub>O)</u> |
|----|------------------|----------------------|------------------------------------------------------------|
| 15 | Water            | 100                  | 32                                                         |
|    | 0.01 N HCl       | 28                   | 42                                                         |
|    | 0.005 N HCl      | 10                   | 41                                                         |
|    | 0.001 N HCl      | 12                   | 43                                                         |

20        Thus, in the conversion of oxygenates to olefins, ethylene yield was improved by use of a molecular sieve which had been extracted with acid; in this case the improvement is seen to be at least 25% based on  
25      the yield of the process using the non-acid-extracted catalyst.

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CLAIMS:

1. A process for converting oxygenates to olefins comprising treating an oxygenate feed with a molecular sieve catalyst under effective conversion conditions, characterized in that the catalyst comprises an acid-extracted molecular sieve catalyst effective to produce olefins with improved ethylene yield.
2. A process according to claim 1 wherein the catalyst is an acid extracted silicoaluminophosphate (SAPO) or an acid-extracted zeolite.
3. A process according to claim 2 wherein the catalyst is acid extracted SAPO-34.
4. A process according to any preceding claim wherein the catalyst has been extracted with mineral acid.
5. A process according to claim 1, 2, 3 or 4 wherein the acid comprises hydrochloric, hydrofluoric, acetic, phosphoric or sulfuric acids, or a mixture of any two or more thereof.
6. A process according to any preceding claim wherein the catalyst has been extracted with acid which is from 0.0001N to 1N in concentration, preferably from 0.001N to 0.01N.



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7. A process according to any preceding claim wherein the catalyst has been acid extracted for up to 100 hours, preferably from 23 to 26 hours.

5 8. A process according to any preceding claim wherein the oxygenate feed is treated at a temperature of from 200°C to 700°C, preferably from 250°C to 600°C, more preferably from 300°C to 500°C.

10 9. A process according to any preceding claim wherein the acid-extracted catalyst has a crystallinity which is from 10 to 30% that of the corresponding non-acid-extracted catalyst, as measured by X-ray powder diffraction.

15 10. A process according to any preceding claim wherein the ethylene yield is at least 25% greater than the yield of a corresponding process employing non-acid-extracted catalyst.

20 11. A process according to any preceding claim wherein the oxygenate feed comprises an alcohol, an ether or a carbonyl compound.

25 12. A process according to claim 11 wherein the oxygenate feed comprises methanol, dimethyl ether, diethyl ether, isopropanol, n-propanol, ethanol, a fuel alcohol, or a mixture of any two or more thereof.

30 13. A process according to any preceding claim wherein the oxygenate feed also comprises a diluent.

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14. A process according to claim 13 wherein the diluent comprises water, nitrogen gas ( $N_2$ ), hydrogen gas ( $H_2$ ), a paraffin, an olefin, or an aromatic compound, or a mixture of any two or more thereof.

5

15. The use of an acid-extracted molecular sieve catalyst for converting oxygenate feed to olefins.

10 16. The use according to claim 15 wherein the catalyst is an acid-extracted silicoaluminophosphate (SAPO) or an acid-extracted zeolite.

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