

**“METALLO ALUMINOPHOSPHATE MOLECULAR
SIEVE WITH CUBIC CRYSTAL MORPHOLOGY
AND METHANOL TO OLEFIN PROCESS USING THE SIEVE”**

BACKGROUND OF THE INVENTION

The limited supply and increasing cost of crude oil has prompted the search for alternative processes for producing hydrocarbon products. One such process is the conversion of methanol to hydrocarbons and especially light olefins (by light olefins is meant C₂ to C₄ olefins). The interest in the methanol to olefin (MTO) process is based on the fact that methanol can be obtained from coal or natural gas by the production of synthesis gas which is then processed to produce methanol.

Processes for converting methanol to light olefins are well known in the art. Initially aluminosilicates or zeolites were used as the catalysts necessary to carry out the conversion. For example, see US-A-4,238,631; US-A-4,328,384, US-A-4,423,274. These patents further disclose the deposition of coke onto the zeolites in order to increase selectivity to light olefins and minimize the formation of C₅+ byproducts. The effect of the coke is to reduce the pore diameter of the zeolite.

The prior art also discloses that silico aluminophosphates (SAPOs) can be used to catalyze the methanol to olefin process. Thus, US-A-4,499,327 discloses that many of the SAPO family of molecular sieves can be used to convert methanol to olefins. The '327 patent also discloses that preferred SAPOs are those that have pores large enough to adsorb xenon (kinetic diameter of 4.0 Å) but small enough to exclude isobutane (kinetic diameter of 5.0 Å). A particularly preferred SAPO is SAPO-34.

US-A-4,752,651 discloses the use of nonzeolitic molecular sieves (NZMS) including ELAPOs and MeAPO molecular sieves to catalyze the methanol to olefin reaction.

The effect of the particle size of the molecular sieve on activity has also been documented in US-A-5,126,308. In the '308 patent it is disclosed that molecular sieves in which 50% of the molecular sieve particles have a particle size less than 1.0 μm and no more than 10% of the particles have a particle size greater than 2.0 μm have increased activity and/or durability. The '308 patent also discloses that restricting the silicon content to about 0.005 to about 0.05 mole fraction also improves catalytic performance.

In contrast to this art, applicants have found that molecular sieves having the empirical formula $(EL_xAl_yP_z)O_2$ (hereinafter ELAPO) where EL is a metal selected from the group consisting of silicon, magnesium, zinc, iron, cobalt, nickel, manganese, chromium and mixtures thereof and x, y and z are the mole fractions of EL, Al and P respectively and having a predominantly plate crystal morphology wherein the average smallest crystal dimension is at least 0.1 micron and has an aspect ratio of less than or equal to 5. These molecular sieves produce a higher amount of ethylene versus propylene. This increased selectivity is a very desirable feature of a MTO catalyst. This morphology is obtained by controlling the metal (EL) content of the molecular sieve and the crystallization time during synthesis of the molecular sieve.

SUMMARY OF THE INVENTION

As stated, this invention relates to an ELAPO containing catalyst and a process for converting methanol to light olefins using the catalyst. Accordingly, one embodiment of the invention is a process for converting methanol to light olefins comprising contacting the methanol with a catalyst at conversion conditions, the catalyst comprising a crystalline metal aluminophosphate molecular sieve having a chemical composition on an anhydrous basis expressed by an empirical formula of:



where EL is a metal selected from the group consisting of silicon, magnesium, zinc, iron, cobalt, nickel, manganese, chromium and mixtures thereof, "x" is the mole fraction of EL and has a value of at least 0.005, "y" is the mole fraction of Al and has a value of at least 0.01, "z" is the mole fraction of P and has a value of at least 0.01 and $x + y + z = 1$, the molecular sieve characterized in that it has predominantly a plate crystal morphology, wherein the average smallest crystal dimension is at least 0.1 micron and has an aspect of less than or equal to 5.

Another embodiment of the invention is a catalyst for converting methanol to light olefins comprising a crystalline metallo aluminophosphate molecular sieve having an empirical chemical composition on an anhydrous basis expressed by the formula:



where EL is a metal selected from the group consisting of silicon, magnesium, zinc, iron, cobalt, nickel, manganese, chromium and mixtures thereof, "x" is the mole fraction

of EL and has a value of at least 0.005, "y" is the mole fraction of Al and has a value of at least 0.01, "z" is the mole fraction of P and has a value of at least 0.01 and $x + y + z = 1$, the molecular sieve characterized in that it has a crystal morphology wherein the average smallest crystal dimension is at least 0.1 micron.

5 These and other objects and embodiments of the invention will become more apparent after the detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

An essential feature of the process of the instant invention is an ELAPO molecular sieve. ELAPOs are molecular sieves which have a three-dimensional microporous framework structure of AlO_2 , PO_2 and ELO_2 tetrahedral units. Generally the ELAPOs have the empirical formula



where EL is a metal selected from the group consisting of silicon, magnesium, zinc, iron, cobalt, nickel, manganese, chromium and mixtures thereof, "x" is the mole fraction of EL and has a value of at least 0.005, "y" is the mole fraction of Al and has a value of at least 0.01, "z" is the mole fraction of P and has a value of at least 0.01 and $x + y + z = 1$. When EL is a mixture of metals, "x" represents the total amount of the metal mixture present. Preferred metals (EL) are silicon, magnesium and cobalt with silicon being especially preferred.

20 The preparation of various ELAPOs are well known in the art and may be found in US-A-: 4,554,143 (FeAPO); 4,440,871 (SAPO); 4,853,197 (MAPO, MnAPO, ZnAPO, CoAPO); 4,793,984 (CAPO), 4,752,651 and 4,310,440. Generally, the ELAPO molecular sieves are synthesized by hydrothermal crystallization from a reaction mixture containing reactive sources of EL, aluminum, phosphorus and a templating agent. Reactive sources of EL are the metal salts such as the chloride and nitrate salts. When EL is silicon a preferred source is fumed, colloidal or precipitated silica. Preferred reactive sources of aluminum and phosphorus are pseudo-boehmite alumina and phosphoric acid. Preferred templating agents are amines and quaternary ammonium compounds. An especially preferred templating agent is tetraethylammonium hydroxide (TEAOH).

30 The reaction mixture is placed in a sealed pressure vessel, optionally lined with

an inert plastic material such as polytetrafluoroethylene and heated preferably under autogenous pressure at a temperature between 50°C and 250°C and preferably between 100°C and 200°C for a time sufficient to produce crystals of the ELAPO molecular sieve. Typically the time varies from 1 hour to 120 hours and preferably from 24 hours to 48 hours. The desired product is recovered by any convenient method such as centrifugation or filtration.

The ELAPO molecular sieves of this invention have predominantly a plate crystal morphology. By predominantly is meant greater than 50% of the crystals. Preferably at least 70% of the crystals have a plate morphology and most preferably at least 90% of the crystals have a plate morphology. Especially good selectivity (C_2^- versus C_3^-) is obtained when at least 95% of the crystals have a plate morphology. By plate morphology is meant that the crystals have the appearance of rectangular slabs. More importantly, the aspect ratio is less than or equal to 5. The aspect ratio is defined as the ratio of the largest crystalline dimension divided by the smallest crystalline dimension. A preferred morphology which is encompassed within the definition of plate is cubic morphology. By cubic is meant not only crystals in which all the dimensions are the same, but also those in which the aspect ratio is less than or equal to 2. It is also necessary that the average smallest crystal dimension be at least 0.1 microns and preferably at least 0.2 microns.

As is shown in the examples, the morphology of the crystals and the average smallest crystal dimension is determined by examining the ELAPO molecular sieve using Scanning Electron Microscopy (SEM) and measuring the crystals in order to obtain an average value for the smallest dimension.

Without wishing to be bound by any one particular theory, it appears that a minimum thickness is required so that the diffusion path for the desorption of ethylene and propylene is sufficiently long to allow differentiation of the two molecules. Since ethylene is a more valuable product, by controlling the crystal dimensions one can maximize the formation of ethylene. As will be shown in the examples, when the smallest dimension is less than 0.1, the ratio of ethylene to propylene (C_2^-/C_3^-) is about 1.2, whereas when the smallest dimension is greater than 0.1 microns, the ratio of C_2^-/C_3^- is 1.4. This provides a greater production of ethylene.

The ELAPOs which are synthesized using the process described above will usually contain some of the organic templating agent in its pores. In order for the

ELAPOs to be active catalysts, the templating agent in the pores must be removed by heating the ELAPO powder in an oxygen containing atmosphere at a temperature of about 200° to about 700°C until the template is removed, usually a few hours.

A preferred embodiment of the invention is one in which the metal (EL) content varies from 0.005 to 0.05 mole fraction. If EL is more than one metal then the total concentration of all the metals is between 0.005 and 0.05 mole fraction. An especially preferred embodiment is one in which EL is silicon (usually referred to as SAPO). The SAPOs which can be used in the instant invention are any of those described in U.S. Patent 4,440,871. Of the specific crystallographic structures described in the '871 patent, the SAPO-34, i.e., structure type 34, is preferred. The SAPO-34 structure is characterized in that it adsorbs xenon but does not adsorb isobutane, indicating that it has a pore opening of about 4.2 Å.

The ELAPO molecular sieve of this invention may be used alone or they may be mixed with a binder and formed into shapes such as extrudates, pills, spheres, etc. Any inorganic oxide well known in the art may be used as a binder. Examples of the binders which can be used include alumina, silica, aluminum-phosphate, silica-alumina, etc. When a binder is used, the amount of ELAPO which is contained in the final product ranges from 10 to 90 weight percent and preferably from 30 to 70 weight percent.

The conversion of methanol to light olefins is effected by contacting the methanol with the ELAPO catalyst at conversion conditions, thereby forming the desired light olefins. The methanol can be in the liquid or vapor phase with the vapor phase being preferred. Contacting the methanol with the ELAPO catalyst can be done in a continuous mode or a batch mode with a continuous mode being preferred. The amount of time that the methanol is in contact with the ELAPO catalyst must be sufficient to convert the methanol to the desired light olefin products. When the process is carried out in a batch process, the contact time varies from about 0.001 hr. to about 1 hr. and preferably from about 0.01 hr. to about 1.0 hr. The longer contact times are used at lower temperatures while shorter times are used at higher temperatures. Further, when the process is carried out in a continuous mode, the Weight Hourly Space Velocity (WHSV) based on methanol can vary from about 1 hr⁻¹ to about 1000 hr⁻¹ and preferably from about 1 hr⁻¹ to about 100 hr⁻¹.

Generally, the process must be carried out at elevated temperatures in order to form light olefins at a fast enough rate. Thus, the process should be carried out at a

Optionally, the methanol feedstock may be diluted with an inert diluent in order to more efficiently convert the methanol to olefins. Examples of the diluents which may be used are helium, argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen, steam, paraffinic hydrocarbons, e.g., methane, aromatic hydrocarbons, e.g., benzene, toluene and mixtures thereof. The amount of diluent used can vary considerably and is usually from 5 to 90 mole percent of the feedstock and preferably from 25 to 75 mole percent.

The actual configuration of the reaction zone may be any well known catalyst reaction apparatus known in the art. Thus, a single reaction zone or a number of zones arranged in series or parallel may be used. In such reaction zones the methanol feedstock is flowed through a bed containing the ELAPO catalyst. When multiple reaction zones are used, one or more ELAPO catalyst may be used in series to produce the desired product mixture. Instead of a fixed bed, a dynamic bed system, e.g., fluidized or moving, may be used. Such a dynamic system would facilitate any regeneration of the ELAPO catalyst that may be required. If regeneration is required, the ELAPO catalyst can be continuously introduced as a moving bed to a regeneration zone where it can be regenerated by means such as oxidation in an oxygen containing atmosphere to remove carbonaceous materials.

The following examples are presented in illustration of this invention and are not intended as undue limitations on the generally broad scope of the invention as set out in the appended claims

EXAMPLE 1

A series of molecular sieves (SAPOs) were prepared by the following procedure. In a container orthophosphoric acid (85%) was combined with water. To this there was added a silica sol and a 35 wt.% aqueous solution of tetraethylammonium hydroxide (TEAOH). Finally, alumina in the form of pseudo-boehmite along with water and SAPO-34 seed material were added and blended in. The resulting mixtures had compositions in molar oxide ratios as set forth in Table 1 below.

TABLE 1

Reaction Mixture Compositions For SAPOs						
Sample I.D.	Reaction Time	TEAOH	SiO ₂	Al ₂ O ₃	P ₂ O ₅	H ₂ O
A	48	1.0	0.10	1.0	1.0	35
B	48	1.0	0.10	1.0	1.0	35
C	48	1.0	0.10	1.0	1.0	45
D	24	1.0	0.10	1.0	1.0	45
E	36	1.0	0.15	1.0	1.0	40
F	48	1.0	0.20	1.0	1.0	45

The mixture was now placed in a steel pressure reactor equipped with a turbine stirrer. The mixture was now stirred and heated to 100°C over a 6 hour period, held at 100°C for 6 hours, then heated to 175°C over a period of 3 hours and held there for the reaction time of 24, 36 or 48 hours. Finally, the reaction mixture was cooled to ambient temperature and the solid product recovered by centrifugation and washed with water. All the products were analyzed and found to be SAPO-34 molecular sieves.

EXAMPLE 2

The catalysts prepared in Example 1 were evaluated for the conversion of methanol to light olefins in a fixed bed pilot plant. A 4 gram sample in the form of 20-40 mesh agglomerates was used for the testing. Before testing, each sample was calcined in air in a muffle oven at 650°C for 2 hours and then pre-treated *in situ* by heating to 400°C for 1 hour under nitrogen. The pretreated sample was now contacted with a feed consisting of methanol and H₂O in a 1/0.44 molar ratio at 435°C, 5 psig and 2.5 hr⁻¹ MeOH WHSV. The composition of the effluent was measured by an on-line GC after 30 minutes on stream to determine initial conversion and selectivities. Complete conversion was obtained initially with all catalysts but it fell with time on stream as the catalysts deactivated. Table 2 presents the selectivity to ethylene and propylene and the ethylene/propylene product ratio at the point where conversion was 99% for each catalyst.

TABLE 2Effect of Crystal Dimension on Ethylene/Propylene Production

Catalyst I.D.	Average Smallest Dimension (Microns)	Crystal Morphology	$C_2^=+C_3^=$ Selectivity (%)	$C_2^=/C_3^=$
A	0.07	Thin plates	82.4	1.17
B	0.08	Plates	79.2	1.18
C	0.09	Thin Plates	82.2	1.25
D	0.13	Plates	80.8	1.40
E	0.17	Plates	81.2	1.41
F	0.58	Cubic	78.7	1.48

The average smallest crystallite dimension was determined by measuring 20 representative crystallites in one or more micrographs obtained using a Scanning Electron Microscope at 30,000x magnification. The data indicate that when the smallest crystal dimension is greater than 0.1 micron and the crystal morphology is plates, a greater amount of ethylene is produced. It is also observed that when the crystal morphology is cubic and the smallest dimension is greater than 0.2 microns, one obtains the highest production of ethylene. Note that when the smallest dimension is less than 0.1, one obtains poor results (greater propylene production) even though the crystal morphology is plates.

CLAIMS:

1. A catalyst for converting methanol to light olefins comprising a crystalline metallo aluminophosphate molecular sieve having an empirical chemical composition on an anhydrous basis expressed by the formula:



where EL is a metal selected from the group consisting of silicon, magnesium, zinc, iron, cobalt, nickel, manganese, chromium and mixtures thereof, "x" is the mole fraction of EL and has a value of at least 0.005, "y" is the mole fraction of Al and has a value of at least 0.01, "z" is the mole fraction of P and has a value of at least 0.01 and $x + y + z = 1$, the molecular sieve characterized in that it has predominantly a plate crystal morphology, wherein the average smallest crystal dimension is at least 0.1 micron and has an aspect ratio no greater than 5.

2. The catalyst of Claim 1 where the EL metal is selected from the group consisting of silicon, magnesium, cobalt and mixtures thereof.
3. The catalyst of Claim 2 where the EL metal is silicon and the molecular sieve has the crystal structure of SAPO-34.
4. The catalyst of any one of claims 1 to 3 where catalyst comprises a metal aluminophosphate molecular sieve and an inorganic oxide binder selected from the group consisting of alumina, silica, aluminum phosphate, silica-alumina and mixtures thereof.
5. The catalyst of any one of claims 1 to 4 where the molecular sieve is present in an amount from about 10 to about 90 weight percent of the catalyst.
6. The catalyst of any one of claims 1 to 5 where the aluminophosphate has a metal (EL) content from about 0.005 to about 0.05 mole fraction.
7. A process for converting methanol to light olefin comprising contacting the methanol with the catalyst of any one of claims 1 to 6 at conversion conditions.

8. The process of claim 7 where the conversion conditions are a temperature of about 300°C to about 600°C, a pressure of about 0 kPa to about 17224 kPa and a weight hourly space velocity of about 1 to about 100 hr⁻¹.