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USE OF ZEOLITES IN THE CONVERSION
OF OXYGENATES TO HYDROCARBONS

BACKGROUND OF THE INVENTION

5 This invention relates to a process for using
microporous solid catalysts to convert oxygenates and
substituted paraffins into olefinic hydrocarbons and,
more particularly, relates to a process for converting
alcohols into light olefins using ECR-1, mazmorite, or
10 ECR-18 catalysts.

Light olefins have traditionally been produced
through the process of steam or catalytic cracking.
Because of the limited availability and high cost of
petroleum sources, the cost of producing light olefins
15 from such petroleum sources has been steadily
increasing.

The search for alternative materials for light
olefin production has led to the use of oxygenates
such as alcohols, and more particularly to methanol,
20 ethanol, and higher alcohols or their derivatives.
These 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,
25 municipal wastes, or any organic material. Thus,
alcohol and alcohol derivatives may provide non-
petroleum based routes for the production of olefin
and other related hydrocarbons.

Molecular sieves such as the microporous
30 crystalline zeolite catalysts are known to promote the
conversion of oxygenates to hydrocarbon mixtures.
Numerous patents describe this process for various
types of zeolite catalysts: US-A-3,928,483,
4,025,575, 4,252,479 (Chang et al.); 4,496,786
35 (Santilli et al.); 4,547,616 (Avidan et al.);



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4,677,243 (Kaiser); 4,843,183 (Inui); 4,499,314
(Seddon et al.); and 4,447,669 (Harmon et al.).

However, none of these patents teach the conversion of
oxygenates to hydrocarbons using the type of zeolite
catalysts described herein.

US-A-4,467,133 (Chang, et al.) discloses the
conversion of alcohols and ethers to hydrocarbons,
wherein the zeolite can be paulingite. However,
inclusion of paulingite is incidental, and not
intended to suggest that paulingite can be used to
convert oxygenate feeds to olefins or to hydrocarbons
containing substantially only light olefins. Most of
the zeolites listed by Chang, et al., are well known
to have no hydrocarbon porosity (such as analcite,
noselite, phillipsite, datolite, leucite, scapolite,
and kaolin). From this list, only faujisite, L,
gmelenite, and mordenite have pores greater than 6
angstroms, fitting the constraint index qualification
of column 2, lines 43 to 53. From a catalytic
perspective, Chang's list of zeolites has no
significance. Rather, the list apparently refers to
aluminosilicates in general, and contains no
indication of the olefin forming effect of the
zeolites which are employed in the instant invention.

According to one aspect of the present invention
there is provided a process for producing olefins
which comprises: contacting an oxygenate starting
material (as herein defined) with a microporous
zeolite catalyst comprising ECR-1, a mazmorite or a
synthetic paulingite-type zeolite, to produce the
desired olefin product.

Another aspect of the invention provides the use
of ECR-1, a mazmorite or a synthetic paulingite-type
zeolite such as ECR-18, for converting an oxygenate
starting material (as herein defined) to an olefin.



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In a preferred embodiment the oxygenate starting material, also termed "feed" herein, is converted to a hydrocarbon mixture containing light olefins, i.e., enriched in light olefins compared with the starting material. Preferably the product mixture contains substantially only light olefins.

As used herein, the term "oxygenate starting material" 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 zeolites, such as substituted paraffins, e.g., halides, mercaptans, sulfides, amines.

In a preferred embodiment, methanol is employed as an oxygenate feed for conversion to hydrocarbons rich in light olefins by contacting this feed with ECR-1, mazmorites, and/or paulingite-type zeolites such as ECR-18. Other oxygenate feeds may be for example, but are not limited to, dimethyl ether, ethanol, isopropanol, n-propanol or mixtures thereof. Further, a diluent may be part of the feed and may comprise water, nitrogen (N₂), hydrogen (H₂), or other hydrocarbons, including but not limited to paraffins, olefins and aromatics.

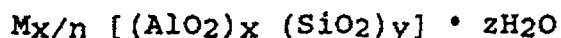
DETAILED DESCRIPTION OF THE INVENTION

The present invention employs ECR-1, mazmorite and/or synthetic paulingite-type (such as ECR-18) microporous zeolite catalysts to convert oxygenate feeds to hydrocarbons. Zeolites are microporous, crystalline-hydrated aluminosilicates of Group I and II elements interconnected through shared oxygen atoms. The rigid three-dimensional framework of



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silica and alumina creates a tetrahedral-shaped block which forms the primary building unit of the zeolites. Because the oxygen atoms in zeolites are shared between tetrahedra, the framework possesses a net negative charge. The net negative charge is balanced by exchangeable cations in the crystalline structure, leading to the representation:



where M is the cation, n is the cation charge, and z represents the water of hydration. The silica-to-alumina ratio is governed by the amounts of alumina "x" and silica "y" comprising the zeolite. When M is a proton, the zeolite acquires the characteristics of a Brønsted acid.

The zeolites generally have ordered, porous crystalline structures containing a small number of cavities that are interconnected by a number of still smaller channels. The cavities and channels are uniform in size within a certain type of zeolitic material. The dimensions of the pores or cavities allow for adsorption of molecules of certain dimensions while excluding molecules of larger dimensions. The crystal structure of zeolites provides a selective, constrained access to and egress from the intracrystalline free space. This phenomenon, also called "shape-selective catalysis," derives from zeolite geometry.

An important component of zeolite geometry derives from the proportions of silicon and aluminum atoms comprising the tetrahedra. The molar ratio of silica-to-alumina may be determined by conventional analysis such as wet chemical analysis (e.g., atomic absorption spectrometry or inductively coupled plasma emission spectroscopy) or by the stoichiometry of silica and alumina used in zeolite synthesis. This



ratio is meant to represent, as closely as possible, the silica-to-alumina ratio in the rigid anionic framework of the zeolite crystal. Aluminum in the binder or in cationic or other form within the porous channels is not considered in calculating the silica-to-alumina ratio.

The catalytic and adsorptive properties of the zeolite may also be varied by changing the ions within the catalyst. Conventional ion exchange techniques may be used to change the cations. There are a large number of both natural and synthetic zeolitic structures. The enormity of zeolite structural permutations can be understood by considering the book Atlas of Zeolite Structures by W. M. Meier and D. H. Olson.

ECR-1 is a 12-ring synthetic zeolite. It may be formed by using bis (2-hydroxyethyl) dimethylammonium or bis (2-hydroxypropyl) dimethylammonium as an organic template. ECR-1 is described more fully in US-A-4,657,748. ECR-1 has a silica-to-alumina (Si/Al₂) molar ratio of about 5-20, and usually about 7, comparable to naturally occurring mazzite. ECR-1 has a recurrent twin structure comprising component sheets structurally characteristic of naturally occurring mordenite (which normally has a silica-to-alumina molar ratio of greater than 10) and mazzite. Thus ECR-1 represents a complex synthetic zeolite having structural similarities to both these existing natural zeolites.

Mazmorites are materials similar and related to ECR-1 and are described in US-A-4,892,721. The mazmorites are complex intergrown synthetic permutations of ECR-1.

Paulingite is a very rare mineral classified as a member of the faujasite group. Synthetic paulingite-



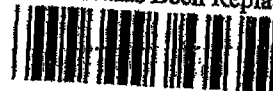
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type zeolites may be used according to the invention, for example ECR-18 which is structurally similar to the natural mineral paulingite. ECR-18 may be produced using a tetraethylammonium template. It is described in more detail in US-A-4,661,332 and 5,013,536. Like ECR-1, ECR-18 is a complex synthetic zeolite having structural similarities to naturally occurring zeolites. The pore size and adsorptive capacities of these synthetic ECR zeolites are nevertheless different from the natural zeolites.

In accordance with the process of the present invention, an oxygenate feed is catalytically converted to hydrocarbons containing aliphatic moieties such as, but not limited to, methane, ethane, ethylene, propane, propylene and other higher aliphatics and aromatics, by contacting the oxygenate feed with a preselected zeolite catalyst. The oxygenate feed comprises hydrocarbons containing aliphatic moieties such as, but not limited to, alcohols, halides, mercaptans, sulfides, amines, ethers and carbonyl compounds or mixtures thereof. The aliphatic moiety preferably contains from 1 to 10 carbon atoms, and more preferably 1 to 4 carbon atoms. Representative oxygenate starting materials include, but are not limited to methanol, isopropanol, n-propanol, ethanol, fuel alcohols, dimethyl ether, diethyl ether, methyl mercaptan, methyl sulfide, methyl amine, ethyl mercaptan, ethylchloride, formaldehyde, dimethylketone, acetic acid, n-alkylamines, n-alkylhalides, and n-alkylsulfides preferably having alkyl groups of 1 to 10 carbon atoms or mixtures thereof. In a preferred embodiment, methanol is used as the oxygenate feed.

The total charge of starting material to the reaction zone may contain additional compounds such as

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diluents. Thus the process may be generally conducted in the presence of one or more diluents which may be present in the oxygenate starting material in an amount between about 1 and about 99 molar percent, based on the total number of moles of all feed and diluent components fed to the reaction zone (or catalyst). Diluents include, but are not limited to, helium, argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, paraffins, hydrocarbons (such as methane and the like), aromatic compounds, or mixtures thereof. Use of an aqueous diluent as part of the feed imparts as a non-limiting example a hydrocarbon fraction particularly rich in light olefins. In a particularly preferred embodiment of the invention, the starting material comprises an oxygenate/water feed, preferably having a molar ratio of starting material:water of from 1:3 to 1:5, more preferably having an approximate 1:4 molar ratio. Most preferably a methanol:water feed is used, especially one having an approximate 1:4 molar ratio. Even though the process described herein may employ a diluent, computable quantities of the starting material (i.e., composition and weight hourly space velocity (WHSV) are to be computed as an essentially diluent-free feed unless otherwise stated.

The feedstock flow rate affects olefin production. Increasing the feedstock flow rate (expressed as weight hourly space velocity, or WHSV) enhances the formation of olefin production relative to paraffin production. However, the enhanced olefin production relative to paraffin production is offset by a diminished conversion of oxygenate to hydrocarbons.

The process of the invention is conducted such that the oxygenate feed is contacted in a reaction



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zone with the zeolite catalyst at effective process conditions to produce olefinic hydrocarbons, i.e., an effective temperature, pressure, WHSV and, optionally, an effective amount of diluent, correlated to produce hydrocarbons rich in olefins. Preferably the process is conducted in the vapor phase. Alternatively, the process may be conducted 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 media and can result in 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.

The process is effectively carried out over a wide range of pressures, including autogenous pressures. At pressures between about 0.001 atmospheres (0.76 torr) and about 1000 atmospheres (760,000 torr), 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 between about 0.01 atmospheres (7.6 torr) and about 100 atmospheres (76,000 torr). 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 starting material 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,



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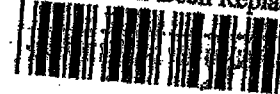
although light olefin such as ethylene may still be formed.

The process is effected for a period of time sufficient to produce the desired light 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 molecular sieve selected, the WHSV, the phase (liquid or vapor) and process design characteristics selected.

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 of for example from 200°C (392°F) to 700°C (1292°F). Temperatures outside the stated range 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. 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 about 200°C (392°F) and about 700°C (1292°F).

The processes employing ECR-1, Mazmorite, a synthetic paulingite-type zeolite such as ECR-18, or mixtures of any two or more thereof, for conversion of an oxygenate feed to hydrocarbons are preferably conducted at temperatures of from 350°C to 550°C, more

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preferably 400°C to 500°C, and most preferably 440°C to 460°C. The WHSV of these processes is preferably from 0.01 hr.⁻¹ to 100 hr.⁻¹, more preferably 0.1 hr.⁻¹ to 10 hr.⁻¹, and most preferably 0.8 hr.⁻¹ to 1.2 hr.⁻¹.
5 At 0.8 hr.⁻¹ to 1.2 hr.⁻¹ WHSV, approximately 95% to 100% conversion of oxygenate feed to light olefin hydrocarbons occurs.

The following examples illustrate the invention:

10 Example 1

A synthetic ECR-1 zeolite catalyst was produced as described in US-A-4,657,748. The ECR-1 described in this example had a silica-to-alumina molar ratio of 7:1, determined by chemical analysis. ECR-1 was
15 calcined at 510°C (950°F) to remove the template and the calcined material was ion-exchanged with an ammonium-nitrate solution (85°C, 185°F; 12 hrs.). Generally, the ion exchange was repeated two or three times, with a calcination at 510°C (950°F) between
20 each ion exchange step. The catalytic conversion of oxygenate to hydrocarbons was conducted at 450°C (842°F) and at a WHSV of 1.0 hr.⁻¹. The feed consisted of a mixture of methanol:water (approximately 1:4 molar ratio).

25 The catalytic conversion of methanol to hydrocarbons was carried out in a fixed bed (1/2", 1.27 cm diameter), stainless steel reactor having three spaced zones and equipped with a 1/8" (0.32 cm) coiled preheater. In addition, the reactor was
30 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 furnace (12", 30.5 cm long; 1 1/4", 3.18 cm I.D.). The first reactor zone is used as a preheater
35 zone; the catalyst bed is heated in the second reactor



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zone. The third zone operates as a quench zone maintained at a temperature of about 200°C (392°F) to about 300°C (572°F).

Generally, 2 grams (0.07 ounces) catalyst
5 (-14/+20 mesh) were mixed with 2.5 grams (0.09 ounces)
of quartz (-20/+60 mesh); the first and third zones of
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
10 the furnace heating coils, the second reactor zone was
equipped with a cylindrical (4", 10.2 cm long; 1
1/4", 3.18 cm O.D.) aluminum or stainless steel block.
This block contained a central hole for a thermocouple
well in order to be able to measure the block
15 temperature.

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 341B
syringe pump.

20 The product emerging from the bottom of the
reactor was analyzed on line for (i) carbon monoxide;
carbon dioxide; water; dimethyl ether; methanol; C₁-C₃
hydrocarbons, including ethylene (C₂=), propylene
(C₃=), and other products (such as C₄ and higher
25 hydrocarbons) with a Porepack Q (capillary column gas
chromatography) column using a thermal conductivity
detector and (ii) C₁-A₁₀ hydrocarbons with a DB-1
(capillary column gas chromatography) column using a
flame ionization detector. Product distribution was:



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Hydrocarbon distribution	
<u>Hydrocarbon</u>	<u>(Wt%, Excluding H₂O)</u>
CH ₄	33
C ₂ =	27
C ₃ =	11
C ₂ + C ₃	24
Other	5

10 Example 2

A synthetic paulingite-type zeolite catalyst (ECR-18) was produced as described in US-A-5,013,536. The ECR-18 described in this example had a silica-to-alumina molar ratio of 6.4 as determined by wet chemical analysis. ECR-18 was calcined at 510°C (950°F) and the calcined material was ion-exchanged with an ammonium-nitrate solution (85°C, 185°F; 12 hrs.). Generally, the ion exchange was repeated two or three times, with a calcination at 510°C (950°F) between each ion exchange step. The catalytic conversion of oxygenate to hydrocarbons was conducted at 450°C (842°F) and at a WHSV of 1.0 hr.⁻¹, in the same equipment, using the same catalyst loadings, the same reaction conditions, and the same measurement techniques as described for Example 1. Again, the feed consisted of a mixture of methanol:water (approximately 1:4 molar ratio).

Product distribution:



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		Hydrocarbon distribution	
		<u>(Wt%, Excluding H₂O)</u>	
<u>Hydrocarbon</u>			
5	CH ₄	7	
	C ₂ =	38	
	C ₃ =	30	
	C ₂ + C ₃	7	
	Other	18	
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CLAIMS:

1. A process for producing olefins which comprises contacting an oxygenate starting material (as herein defined) with a microporous zeolite catalyst comprising ECR-1, a mazmorite or a synthetic paulingite-type zeolite, to produce the desired olefin product.
2. A process according to claim 1 wherein the olefin product comprises a hydrocarbon mixture containing light olefins, preferably a hydrocarbon mixture containing substantially only light olefins.
3. A process according to claim 1 or 2 wherein the olefin or light olefin comprises ethylene or propylene.
4. A process according to any preceding claim wherein the synthetic paulingite-type zeolite comprises ECR-18.
5. A process according to any preceding claim wherein the oxygenate starting material comprises an alcohol, an ether or a carbonyl compound, or a substituted paraffin comprising a halide, a mercaptan, a sulfide or an amine.
6. A process according to claim 5 wherein the oxygenate starting material comprises methanol, dimethyl ether, diethyl ether, isopropanol, n-propanol, ethanol, a fuel alcohol, or a mixture of any two or more thereof.



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7. A process according to any preceding claim wherein the oxygenate starting material additionally includes a diluent.

5 8. A process according to claim 7 wherein the diluent comprises helium, argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, a hydrocarbon (preferably paraffinic or aromatic), or a mixture of any two or more thereof.

10 9. A process according to claim 8 wherein the diluent is water and the molar ratio of oxygenate starting material to water is from 1:3 to 1:5, preferably approximately 1:4.

15 10. A process according to any preceding claim wherein the catalyst and starting material are contacted at a temperature of from 350°C (662°F) to 550°C (1022°F), preferably from 400°C (752°F) to 500°C (932°F), more preferably from 440°C (824°F) to 460°C (860°F).

25 11. A process according to any preceding claim when performed at a weight hourly space velocity (WHSV) of from 0.01 hr.⁻¹ to 100 hr.⁻¹, preferably from 0.8 hr.⁻¹ to 10 hr.⁻¹, more preferably from 0.8 hr.⁻¹ to 1.2 hr.⁻¹.

30 12. A process according to any preceding claim when performed at a pressure of from 0.001 atmospheres (0.76 torr), to 1000 atmospheres (760,000 torr), preferably from 0.01 atmospheres (7.6 torr) to 100 atmospheres (76,000 torr).

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13. A process according to claim 1 comprising:
contacting a methanol/water starting material
(preferably in approximately 1/4 molar ratio) with
ECR-1 or a synthetic paulingite-type zeolite
5 comprising ECR-18, at a temperature of from 440°C to
460°C, a WHSV of 0.8 hr.⁻¹ to 1.2 hr.⁻¹ and a pressure
of between 0.01 atmospheres (7.6 torr) and 100
atmospheres (76,000 torr) to produce the light olefin
enriched hydrocarbon mixture.

10 14. The use of ECR-1, a mazmorite or a synthetic
paulingite-type zeolite such as ECR-18, for converting
an oxygenate starting material (as herein defined) to
an olefin.

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