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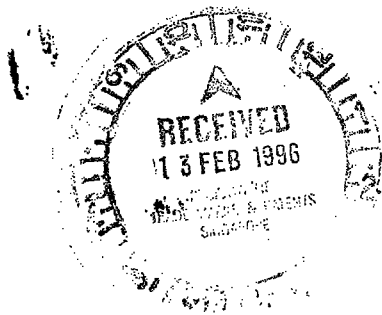
OLIGOMERIZATION OF OLEFINS

This invention relates to oligomerization of olefins.

Conversion of olefins to gasoline and/or
5 distillate products is disclosed in U.S. Patents
3,960,978 and 4,021,502 wherein gaseous olefins in
the range of ethylene to pentene, either alone or in
admixture with paraffins, are converted into an
olefinic gasoline blending stock by contacting the
10 olefins with a catalyst bed made up of ZSM-5 zeolite.

Shape-selective oligomerization, as it applies
to the conversion of C_2 - C_{10} olefins over ZSM-5, may
produce higher olefins up to C_{30} and higher. As
reported by Garwood in "Intrazeolite Chemistry 23",
15 (Amer. Chem. Soc., 1983), reaction conditions
favoring higher molecular weight product are low
temperature (200°-260°C.), elevated pressure (about
2000 kPa or greater), and long contact time (less
than 1 WHSV). The reaction under these conditions
20 proceeds through the acid-catalyzed steps of
(1) oligomerization, (2) isomerization-
cracking to a mixture of intermediate carbon number
olefins, and (3) interpolymerization to give a
continuous boiling product containing all carbon
25 numbers.

The final molecular configuration of the
oligomerization-polymerization product is influenced
by the pore structure of the catalyst. For the
higher carbon numbers, the structure is primarily a
methyl-branched straight olefinic chain, with the
30 maximum cross-section of the chain limited by the
dimension of the largest zeolite pore. Although
emphasis is placed on the normal 1-alkenes as
feedstocks, other lower olefins, such as 2-butene or
isobutylene, are readily employed as starting
35 materials due to rapid isomerization over the acidic



zeolite catalysts. At conditions chosen to maximize heavy distillate and lubricant range products (C_{20}^{+}), the raw aliphatic product is essentially mono-olefinic. Overall branching is not extensive and may occur at spaced positions within the molecule.

The viscosity index of a hydrocarbon lube oil is related to its molecular configuration. Extensive branching in a molecule usually results in a low viscosity index. It is believed that two modes of oligomerization/polymerization of olefins can take place over acidic zeolites, such as HZSM-5. One reaction sequence takes place at Brönsted acid sites inside the channels or pores, producing essentially linear materials. The other reaction sequence occurs on the outer surface, producing more branched material. By decreasing the surface acid activity of such zeolites, fewer highly branched products with low VI are obtained.

Several techniques may be used to increase the relative ratio of intra-crystalline acid sites to surface active sites. This ratio tends to increase with crystal size due to geometric relationship between volume and superficial surface area. Deposition of carbonaceous materials by coke formation can also shift the effective ratio, as disclosed in U.S. Patent 4,547,613. Dealumination of zeolite surfaces can also reduce surface activity. Conventional techniques for zeolite dealumination include hydrothermal treatment, mineral acid treatment with HCl , HNO_3 , and H_2SO_4 , and chemical treatment with $SiCl_4$ or EDTA. The treatments are limited, in many cases, in the extent of dealumination by the onset of crystal degradation and loss of sorption capacity. U.S. Patent 4,419,220 discloses that dealumination of zeolite beta via

treatment with HCl solutions is limited to $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 200 to 300 beyond which significant losses to zeolite crystallinity are observed.

U.S. Patent 3,442,795 describes a process for
5 preparing highly siliceous zeolite-type materials from crystalline aluminosilicates by means of a solvolysis, e.g. hydrolysis, followed by a chelation. In this process, the acid form of a zeolite is subjected to hydrolysis, to remove aluminum from the
10 aluminosilicate. The aluminum can then be physically separated from the aluminosilicate by the use of complexing or chelating agents such as ethylenediaminetetraacetic acid or carboxylic acid, to form aluminum complexes that are readily removable
15 from the aluminosilicate. The examples are directed to the use of EDTA to remove alumina.

EP-B-259 526 discloses the use of dealumination in producing zeolite ECR-17. The preferred dealumination method involves a combination of steam
20 treatment and acid leaching, or chemical treatments with silicon halides. The acid used is preferably a mineral acid, such as HCl, HNO_3 or H_2SO_4 , but may also be weaker acids such as formic, acetic, oxalic, tartaric acids and the like. U.S. Patent No.
25 4,388,177 discloses the preparation of a natural ferrierite hydrocracking catalyst by treatment with oxalic acid to impart catalytic activity for converting slightly branched as well as straight chain hydrocarbons in hydrodewaxing and naphtha
30 upgrading. Increased activity is believed to arise from removal of iron, sodium and other impurities by such treatment.

It is known to use certain basic materials to deactivate the Brönsted acid sites on the surface of

aluminosilicate catalysts. U.S. Patent 4,520,221 and U.S. Patent 4,568,786, Chen, et al., which are expressly incorporated herein disclose bulky amines, such as di-tert-butyl pyridine, as such basic materials.

U.S. Patent No. 5,080,878 describes production of high viscosity index lubes by converting olefins over medium pore zeolites, e.g., ZSM-23, which are surface inactivated by contacting with aqueous fluorosilicate salt to replace external zeolite aluminum with silicon.

U.S. Patent No. 4,870,038 discloses the use of surface-inactivated zeolites such as ZSM-23 in olefin oligomerization processes which produce substantially linear hydrocarbons suitable for lubes or alkylating for preparing alkylbenzenes or alkylphenylsulfonates. The zeolites are surface-inactivated by contacting with bulky pyridine compound, e.g., 2,4,6-collidine.

The present invention seeks to provide a process for producing substantially linear hydrocarbons by oligomerizing a lower olefin over a surface-inactivated zeolite catalyst.

Accordingly, the invention resides in a process for oligomerizing an olefin which comprises contacting the olefin with a catalyst comprising a zeolite which has Brönsted acid activity, which is capable of sorbing 10 to 40 mg 3-methylpentane at 90°C and 90 torr (12 kPa), per g dry zeolite when in the hydrogen form, and which has been treated with a dicarboxylic acid under conditions to effect a reduction of at least 20% in the surface acidity of the zeolite, as determined by tri-tertiarybutylbenzene conversion, without substantial reduction in the overall activity of the zeolite as indicated by alpha value.

The preferred catalysts for use in the process of the invention, exemplified by ZSM-22, ZSM-23, and ZSM-35, are members of a unique class of zeolites. They have channels described by 10-membered rings of
5 T (=Si or Al) or oxygen atoms, i.e., they are intermediate pore zeolites, distinct from small pore 8-ring or large pore 12-ring zeolites. They differ, however, from other intermediate pore 10-ring zeolites, such as ZSM-5, ZSM-11, ZSM-57 or stilbite,
10 in having a smaller 10-ring channel. If the crystal structure (and hence pore system) is known, a convenient measure of the channel cross-section is given by the product of the dimensions (in angstrom units) of the two major axes of the pores. These
15 dimensions are listed in the "Atlas of Zeolite Structure Types" by W. M. Meier and D. H. Olson, Butterworths, publisher, Second Edition, 1987. The values of this product, termed the Pore Size Index, are listed in Table A.

TABLE A				
Pore Size Index				
Type	Largest Ring Size	Zeolite	Axes of Largest Channel, A	Pore Size Index
5	8	Chabazite Erionite Linde A	3.8 x 3.8 3.6 x 5.1 4.1 x 4.1	14.4 18.4 16.8
10	10	ZSM-22 ZSM-23 ZSM-35 ALPO-11	4.4 x 5.5 4.5 x 5.2 4.2 x 5.4 3.9 x 6.3	24.2 23.4 22.7 24.6
15	10	ZSM-5 ZSM-11 Stilbite ZSM-57 (10)	5.3 x 5.6 5.3 x 5.4 4.9 x 6.1 5.1 x 5.8	29.1 28.6 29.9 29.6
20	12	ZSM-12 Mordenite Beta (C-56) Linde-L Mazzeite (ZSM-4) ALPO ₄ -5	5.5 x 5.9 6.5 x 7.0 6.2 x 7.7 7.1 x 7.1 7.4 x 7.4 7.3 x 7.3	32.4 45.5 47.7 50.4 54.8 53.3

It can be seen that small pore, eight-ring zeolites have a Pore Size Index below about 20, the intermediate pore, 10-ring zeolites of 20-31, and large pore, 12-ring zeolites above about 31. It is also apparent, that the 10-ring zeolites are grouped in two distinct classes; Type 2 with a Pore Size Index between 22.7 and 24.6, or more broadly between 20 and 26, and Type 3 with a Pore Size Index between 28.6 and 29.9, or more broadly, between 28 and 31.

The zeolites useful for this invention are those of Type 2 with a Pore Size Index of 20-26.

The Type 2 zeolites are distinguished from the other types by their sorption characteristics towards 3-methylpentane. Representative equilibrium sorption data and experimental conditions are listed in Table B.

Type 2 zeolites sorb in their intracrystalline voids 10 to 40 mg of 3-methylpentane at 90°C, 90 torr (12 kPa) 3-methylpentane, per gram dry zeolite in the hydrogen form. In contrast, Type 3 zeolites sorb greater than 40 mg 3-methylpentane under the same conditions.

The equilibrium sorption data are obtained most conveniently in a thermogravimetric balance by passing a stream of inert gas such as helium containing the hydrocarbon with the indicated partial pressure over the dried zeolite sample held at 90°C for a time sufficient to obtain a constant weight.

Samples containing cations such as sodium or aluminum ions can be converted to the hydrogen form by well-known methods such as exchange at temperatures between 25° and 100°C with dilute mineral acids, or with hot ammonium chloride solutions followed by calcination. For mixtures of zeolites with amorphous material or for poorly

crystallized samples, the sorption values apply only to the crystalline portion.

This method of characterizing the Type 2 zeolites has the advantage that it can be applied to new zeolites whose crystal structure has not yet been determined.

TABLE B
Equilibrium Sorption Data of Medium Pore Zeolites
Amount sorbed, mg/g zeolite

10	Type	Zeolite	3-Methylpentane ^{a)}
	2	ZSM-22	20
		ZSM-23	25
		ZSM-35	25
15	3	ZSM-5	61
		ZSM-12	58
		ZSM-57	70
		MCM-22	79

a) at 90°C, 90 torr (12 kPa) 3-methylpentane

ZSM-22 is more particularly described in U.S. Patent No. 4,556,477. ZSM-22 and its preparation in microcrystalline form using ethylpyridinium as directing agent is described in U.S. Patent No. 4,481,177. For purposes of the present invention, ZSM-22 is considered to include its isotypes, e.g., Theta-1, Gallo-Theta-1, NU-10, ISI-1, and KZ-2.

ZSM-23 is more particularly described in U.S. Patent No. 4,076,842. For purposes of the present invention, ZSM-23 is considered to include its isotypes, e.g., EU-13, ISI-4, and KZ-1.

ZSM-35 is more particularly described in U.S. Patent No. 4,016,245. For purposes of the present invention, ZSM-35 is considered to include its isotypes, e.g., ferrierite, FU-9, ISI-6, NU-23, and Sr-D. An example of a piperidine-derived ferrierite is more particularly described in U.S. Patent No.

4,343,692. Other synthetic ferrierite preparations are described in U.S. Patent Nos. 3,933,974; 3,966,883; 4,000,248; 4,017,590; and 4,251,499. Further descriptions of ferrierite are found in Bibby
5 et al, "Composition and Catalytic Properties of Synthetic Ferrierite," Journal of Catalysis, 35, pages 256-272 (1974).

The zeolite catalyst used is preferably at least partly in the hydrogen form, e.g., HZSM-22, HZSM-23,
10 or HZSM-35. Other metals or cations thereof, e.g. rare earth cations, may also be present. When the zeolites are prepared in the presence of organic cations, they may be quite inactive possibly because the intracrystalline free space is occupied by the
15 organic cations from the forming solution. The zeolite may be activated by heating in an inert or oxidative atmosphere to remove the organic cations, e.g. by heating at over 500°C for 1 hour or more. The hydrogen form can then be obtained by base
20 exchange with ammonium salts followed by calcination, e.g., at 500°C in air. Acid treatment may result in dealumination and is therefore not typically practiced. Other cations, e.g. metal cations, can be introduced by conventional base exchange or
25 impregnation techniques.

In order to obtain desired olefin oligomerization activity/selectivity, the zeolite, preferably in the hydrogen form, should have an alpha value between 5 and 400, preferably between 10 and
30 100 when used in the catalyst of the present invention. Alpha value, or alpha number, of a zeolite is a measure of zeolite acidic functionality and is more fully described together with details of its measurement in U.S. Patent No. 4,016,218, J. Catalysis,
35 6, pp. 278-287 (1966) and J. Catalysis,

61, pp. 390-396 (1980). The experimental conditions cited in the latter reference are used for characterizing the catalysts described herein.

The surface acidity of the catalyst can be
5 determined by conversion of tri-tertiarybutylbenzene (TTBB), a bulky molecule that can only react with the acid sites on the zeolite crystal surface. Dealkylation of TTBB is a facile, reproducible method for measuring surface acidity of catalysts. External
10 surface acidity can be measured exclusive of internal activity for zeolites with pore diameters up to and including faujasite. As a test reaction, dealkylation of TTBB occurs at a constant temperature in the range of from 25 to 300°C and preferably in
15 the range 200 to 260°C.

The experimental conditions for the test used herein include a temperature of 200°C and atmospheric pressure. The dealkylation of TTBB is carried out in a glass reactor (18 cm x 1 cm OD) containing an 8 g
20 14/30 VycorTM chip preheater followed by 0.1 g catalyst powder mixed with VycorTM chips. The reactor is heated to 200°C in 30 cc/g nitrogen for 30 minutes to remove impurities from the catalyst sample. Ten g/ hr of TTBB dissolved in toluene (7%
25 TTBB) is injected into the reactor. The feed vaporizes as it passes through the preheater and passes over the catalyst sample as vapor. After equilibrium is reached the nitrogen is switched to 20 cc/min hydrogen. The test is then run for 30 minutes
30 with the reaction products in a cold trap.

The reaction products are analyzed by gas chromatography. The major dealkylation product is di-t-butylbenzene (DTBB). Further dealkylation to t-butylbenzene (TBB) and benzene (B) occurs but to a
35 lesser extent.

Conversion of TTBB is calculated on a molar carbon basis. Dealkylation product weight %s are each multiplied by the appropriate carbon number ratio to convert to the equivalent amount of TTBB, i.e. DTBB x 18/14, TBB x 18/10 and B x 18/6. These values are then used in the following conversion equation where asterisks indicate adjustment to the equivalents.

$$\% \text{ Conversion} = \frac{\text{DTBB}^* + \text{TBB}^* + \text{B}^*}{\text{TTBB} + \text{DTBB}^* + \text{TBB}^* + \text{B}^*} \times 100$$

In addition, thermal background experiments using reactors filled with VycorTM chips only show no TTBB conversion due to VycorTM or other reactor components.

Limiting surface acidity of the above catalysts is effective to prevent undesired reactions on the zeolite surface which are not subject to the shape-selective constraints imposed upon those reactions occurring within the zeolite interior. According to the present invention, the zeolite is contacted with dicarboxylic acid under conditions resulting in a reduction in surface acidity (as measured by tri-tertiarybutylbenzene conversion) of at least 20%, preferably at least 50%, more preferably at least 75%, without a significant reduction in overall activity as measured by alpha test. By significant reduction in overall activity is meant a reduction in alpha value of not greater than 20%.

Prior to or following contact with dicarboxylic acid, the zeolite may be composited with a porous matrix material, such as alumina, silica, titania, zirconia, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions, such as

silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia, and silica-magnesia-zirconia. The matrix may be in the form of a cogel. The relative proportions of zeolite component and inorganic oxide gel matrix may vary widely with the zeolite content ranging from between 1 to 99, more usually 5 to 80, percent by weight of the composite.

Suitable dicarboxylic acids for use in the process of this invention include oxalic, malonic, succinic, glutaric, adipic, citric, tartaric, maleic, phthalic, isophthalic, terephthalic, fumaric or mixtures thereof. Oxalic acid is preferred. The dicarboxylic acid may be used in solution, such as an aqueous dicarboxylic acid solution.

Generally, the acid solution has a concentration in the range from 0.01 to 4 M. Preferably, the acid solution concentration is in the range 1 to 3 M.

The dicarboxylic acid is generally in a volume solution to volume catalyst ratio of at least 1:1, preferably at least 4:1.

Treatment time with the dicarboxylic acid solution is as long as required to provide the desired reduction in surface acidity. Generally the treatment time is at least 10 minutes and preferably, is at least 1 hour.

More than one dicarboxylic acid treatment step may be employed in the process of the present invention for enhanced deactivation of surface acidity.

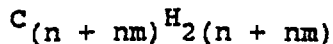
The treatment temperature is generally in the range 0° to about reflux. Preferably, the treatment temperature is from 15°C to 93°C (60°F to 200°F), and more preferably from 49°C to 82°C (120°F to 180°F).

The dicarboxylic acid treatment may also be combined with other dealumination techniques, such as steaming and chemical treatment.

While not wishing to be bound by theory, it is
5 believed that the dicarboxylic acid combines with aluminum in the treated zeolite to form an aluminum-containing species which is larger than the zeolite surface pore openings of constrained medium pore zeolites. This results in dealumination only at the
10 surface of these zeolites.

The oligomerization process of the present invention involves contacting an olefinic feedstock with the treated zeolite catalyst at a temperature less than 260°C, a weight hourly space velocity less
15 than 1; and a pressure of at least 2000 kPa, more preferably at a temperature of 170 to 240°C, a weight hourly space velocity of 0.05 to 0.40; and a pressure of 5200 to 11000 kPa, and most preferably at a temperature of 190 to 220°C, a weight hourly space
20 velocity of 0.1 to 0.3; and a pressure of 6200 to 7600 kPa.

The process of the present invention is particularly useful for the oligomerization of lower olefins, preferably C₃ to C₆ olefins and most
25 preferably propylene and/or butene. When propylene or butene are oligomerized according to processes described herein, a mixture of liquid hydrocarbon products are formed. More particularly, this mixture of hydrocarbons may comprise at least 95% by weight
30 of mono-olefin oligomers of the empirical formula



where n is 3 or 4 and m is an integer from 1 to 6, said mono-olefin oligomers comprising at least 20 percent by weight of olefins having at least 12
35 carbon atoms, said olefins having at least 12 carbon

atoms having an average of from 0.80 to 2.00 methyl side groups per carbon chain, said olefins not having any side groups other than methyl.

5 It will be understood that methyl side groups are methyl groups which occupy positions other than the terminal positions of the first and last (i.e., alpha and omega) carbon atoms of the longest carbon chain. This longest carbon chain is also referred to herein as the straight backbone chain of the olefin.
10 The average number of methyl side groups for the C_{12} + olefins is preferably within the range 0.80 to 2.00, and more preferably within the range 1.3 to 1.7 methyls/ C_{12} .

15 These oligomers may be separated into fractions by conventional distillation separation. When propylene is oligomerized, olefin fractions containing the following numbers of carbon atoms can be obtained: 6, 9, 12, 15, 18 and 21. When butene is oligomerized, olefin fractions containing the
20 following numbers of carbon atoms may be obtained: 8, 12, 16, 20, 24 and 28. It is also possible to oligomerize a mixture of propylene and butene and to obtain a mixture of oligomers having at least 6 carbon atoms.

25 By fractionating an oligomerization product prepared by processes described herein, a mixture of hydrocarbons can be obtained comprising at least 95 (e.g., at least 98) percent by weight of mono-olefins having 12 carbon atoms, a straight backbone chain of
30 at least 10 carbon atoms, and an average of from 0.40 to 2.00 methyl side groups per carbon chain. These C_{12} olefins may comprise at least 5 (e.g., from 5 to 40) mole percent dodecene (i.e., a C_{12} olefin having no methyl side groups), at least 30 (e.g., from 30 to
35 90) mole percent methylundecene (i.e., a C_{12} olefin

having one methyl side group) and at least 5 (e.g., from 5 to 40) mole percent dimethyldecene (i.e., a C_{12} olefin having two methyl side groups).

Another hydrocarbon fractionation product may be
5 a mixture of hydrocarbons comprising at least 95
(e.g., at least 98) percent by weight of mono-olefins
having 15 carbon atoms, a straight backbone chain of
at least 13 carbon atoms, and an average of from 0.40
to 2.00 methyl side groups per carbon chain. These
10 C_{15} olefins may comprise at least 5 (e.g., from 5 to
40) mole percent pentadecene (i.e., a C_{15} olefin
having no methyl side groups) at least 30 (e.g., from
30 to 90) mole percent methyltetradecene (i.e., a C_{15}
olefin having one methyl side group) and at least 5
15 (e.g., from 5 to 40) mole percent dimethyltridecene
(i.e., a C_{15} olefin having two methyl side groups).

Another hydrocarbon fractionation product may be
a mixture of hydrocarbons comprising at least 95
(e.g., at least 98) percent by weight of mono-olefins
20 having 16 carbon atoms, a straight backbone chain of
at least 14 carbon atoms, and an average of from 0.40
to 2.00 methyl side groups per carbon chain. These
 C_{16} olefins may comprise at least 5 (e.g., from 5 to
40) mole percent hexadecene (i.e., a C_{16} olefin
25 having no methyl side groups) at least 30 (e.g., from
30 to 90) mole percent methylpentadecene (i.e., a C_{16}
olefin having one methyl side group) and at least 5
(e.g., from 5 to 40) mole percent dimethyltetradecene
(i.e., a C_{16} olefin having two methyl side groups).

Another hydrocarbon fractionation product may be
30 a mixture of hydrocarbons comprising at least 95
(e.g., at least 98) percent by weight of mono-olefins
having 18 carbon atoms, a straight backbone chain of
at least 16 carbon atoms and an average of from 0.40
35 to 2.00 methyl side groups per carbon chain. These

C₁₈ olefins may comprise at least 5 (e.g., from 5 to 40) mole percent octadecene (i.e., a C₁₈ olefin having no methyl side groups) at least 30 (e.g., from 30 to 90) mole percent methylheptadecene (i.e., a C₁₈ olefin having one methyl side group) and at least 5 (e.g., from 5 to 40) mole percent dimethylhexadecene (i.e., a C₁₈ olefin having two methyl side groups).

These olefin mixtures, particularly the above-mentioned fractionation products, may be used as is or may be blended with other olefins such as various straight chain olefins (i.e. olefins having no methyl side groups) to provide further olefin mixtures.

One use for olefin oligomers described herein, particularly C₁₂ fractions of the oligomers, is as alkylating agents in a process for the selective alkylation of an aromatic compound (e.g., benzene) with a relatively long chain length alkylating agent to produce substantially linear phenylalkanes. Catalysts and reaction conditions for this alkylation process are disclosed in the aforementioned U.S. Patent No. 4,301,317. The resultant phenylalkanes are useful as intermediates in the production alkylphenylsulfonate detergents and surfactants.

The following examples illustrate the oligomerization process of the present invention.

EXAMPLE 1

Preparation of ZSM-23

ZSM-23 was prepared by charging 85.5 parts water to an autoclave followed by 2.64 parts KOH solution (45% by weight), 1.0 part aluminum sulfate (17.2% Al₂O₃) and 0.5 parts ZSM-23 seeds (100% basis). After mixing thoroughly, 14.5 parts of Ultrasil VN3 precipitated silica (Nasilco), then 5.1 parts of pyrrolidine were added and mixed thoroughly. The autoclave was heated to 160°C with stirring and

maintained at these conditions until crystallization was complete. The product was identified as ZSM-23 by X-ray diffraction. After flashing the pyrrolidine, the slurry was cooled, washed, filtered and dried. 65 parts of the dried ZSM-23 were combined with 35 parts of SiO_2 (Hi-Sil, a product of PPG Industries Chemical Division, dry milled and extruded to form 1/16 inch pellets which were dried at 120°C. The pellets were then calcined in flowing nitrogen for 2 hours at 538°C and 3 hours in air at the same temperature. The cooled catalyst was exchanged with 1 N NH_4NO_3 (5 cc/g catalyst) at room temperature for one hour then washed with water. The exchange procedure was repeated and the catalyst dried at 120°C. The exchanged extrudate was then calcined at 538°C in flowing air for 3 hours. The resulting catalyst exhibited an alpha activity of 27 and a surface acidity of 4.6.

EXAMPLE 2

20 Surface Acidity Reduction

A sample of ZSM-23 from Example 1 was treated with 2 M oxalic acid at 71°C for one hour. The treated sample was washed with water, dried at 150°C for 8 hours, and calcined at 375°C for 3 hours. The resulting catalyst had an alpha value of 33 and a surface acidity of 2.1. While the reduction in alpha value is within the accuracy of the alpha test, the reduction in surface acidity represents a significant decrease.

EXAMPLE 3

30 Surface Acidity Reduction

A second sample of ZSM-23 from Example 1 was treated with 2 M oxalic acid at 71°C for two hours. The treated sample was washed with water, dried at

150°C for 8 hours, and calcined at 375°C for 3 hours. The resulting catalyst had an alpha value of 29 and a surface acidity less than 0.1.

EXAMPLE 4

5 **Surface Acidity Reduction with Collidine**

 A third sample of 7.7 g of the ZSM-23 catalyst from Example 1 having a silica/alumina ratio of 110:1 was treated with 0.059g collidine/g of catalyst by contacting the catalyst with a dilute collidine-pentane solution containing 0.0454 g collidine which is an amount sufficient to poison 25% of acid sites present in the zeolite component of the catalyst. The collidine adsorbed very rapidly and completely to the catalyst. The catalyst was dried slowly and then
15 purged with nitrogen.

EXAMPLE 5

Oligomerization Propylene with ZSM-23 at 225°C

 The catalysts of Examples 1, 2, 3 and 4 were evaluated in a semi-batch autoclave for activity, product selectivity, and product structure with
20 propylene feed on demand for five hours at 5620 kPa (800 psig) and 225°C. Under the above conditions, unmodified ZSM-23 catalyst of Example 1 typically yielded 38 g/hr of liquid product with an average
25 methyl branching of 1.9 methyl branches per C₁₂. Collidine-modified ZSM-23 catalyst of Example 4 typically yielded 16 g/hr of liquid product with an average methyl branching of 1.3 methyl branches per C₁₂. The semi-batch evaluation is reproducible to ±
30 2 g/hr of liquid product.

 A sample of ZSM-23 catalyst of Example 3 was evaluated in a semi-batch autoclave under typical oligomerization conditions of 225°C, 5602 kPa (800 psig) for 5 hours. The catalyst yielded 109 g/hr of
35 liquid product that had an average methyl branching

of 1.5 branches per C_{12} . The activity of the oxalic acid treated catalyst was over three times the unmodified ZSM-23 and over six times that of the collidine modified ZSM-23 catalyst of Example 4.

5 Product methyl branching of the oxalic acid treated catalyst was within the branching target of 1.3 to 1.7 methyls/ C_{12} necessary for preparing desirable chemical intermediates. The oxalic acid treated catalyst did not require treatment with collidine to
10 achieve the desired product quality.

The determination of Branching Index is a useful and sensitive method for assessing the degree of linearity of a molecule or molecular mixture. The index is determined as follows: the C_6 and C_9
15 oligomers are first removed from the sample and the C_{12+} fraction is hydrogenated using Pd/charcoal catalyst in acetic acid. The hydrogenated sample is extracted from the acetic acid into deuteriochloroform and the 1H NMR spectrum determined. The branching
20 index is defined as the ratio of the intensity (area) of the resonance due to CH_3 (0.7-1.0 ppm) divided by the sum of the intensities (areas) of the resonances due to CH_3 (0.7-1.0 ppm) and CH_2 (1.1-1.8 ppm). The number of methyl groups per molecule is defined by
25 the equation:

$$Me/molecule = B.I. * (n+1) / 150$$

where B. I. = branching index as defined above and
n = carbon number of the fraction of interest.

30 This calculated number of methyls per molecule includes the two terminal methyl groups. Therefore, to determine the actual number of methyl side groups, e.g., mid-chain methyl groups, these two terminal methyl groups must be subtracted from the total
35 methyl/molecule value calculated.

CLAIMS:

1. A process for oligomerizing an olefin which comprises contacting the olefin with a catalyst comprising a zeolite which has Brönsted acid activity, which is capable of sorbing 10 to 40 mg 3-methylpentane at 90°C and 90 torr (12 kPa), per g dry zeolite when in the hydrogen form, and which has been treated with a dicarboxylic acid under conditions to effect a reduction of at least 20% in the surface acidity of the zeolite, as determined by tri-tertiarybutylbenzene conversion, without substantial reduction in the overall activity of the zeolite as indicated by alpha value.
2. The process of claim 1 wherein said contacting is carried out at a temperature less than 260°C, a weight hourly space velocity less than 1; and a pressure of at least 2000 kPa.
3. The process of claim 1 wherein said contacting is carried out at a temperature of 170 to 240°C, a weight hourly space velocity of 0.05 to 0.40; and a pressure of 5200 to 11000 kPa.
4. The process of claim 1 wherein said contacting is carried out at a temperature of 190 to 220°C, a weight hourly space velocity of 0.1 to 0.3; and a pressure of 6200 to 7600 kPa.
5. The process of claim 1 wherein said zeolite is selected from ZSM-22, ZSM-23, and ZSM-35.



6. The process of claim 1 wherein said zeolite is ZSM-23.
7. The process of claim 1 wherein said surface acidity is reduced by at least 50%.
- 5 8. The process of claim 1 wherein said dicarboxylic acid is contained in an aqueous dicarboxylic acid solution at a concentration in the range 0.01 to 4 M.
- 10 9. The process of claim 1 wherein said dicarboxylic acid is selected from oxalic, malonic, succinic, glutaric, adipic, maleic, phthalic, isophthalic, terephthalic, fumaric, tartaric acid and mixtures thereof.
- 15 10. The process of claim 1 wherein said dicarboxylic acid is oxalic acid.
11. The process of claim 1 wherein said dicarboxylic acid treatment is effected for a time of at least 10 minutes, at a temperature in the range of 15°C to 93°C (60°F to 200°F).
- 20 12. The process of claim 1 wherein said lower olefin comprises C₃ to C₆ olefin.



* C L M S *

OLIGOMERIZATION OF OLEFINS

ABSTRACT

A process for producing substantially linear hydrocarbons by oligomerizing a lower olefin at elevated temperature and pressure comprises contacting the lower olefin under oligomerization conditions with constrained intermediate pore siliceous acidic zeolite, e.g., ZSM-22, -23 or -35, having Brönsted acid activity. The zeolite is pre-treated with a dicarboxylic acid, e.g. oxalic acid, under conditions to effect a reduction of at least 20% in the surface acidity of the zeolite, as determined by tri-tertiarybutylbenzene conversion, without substantial reduction in the overall activity of the zeolite as indicated by alpha value.