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HYDROCARBON CONVERSION TO PROPYLENE WITH HIGH SILICA MEDIUM PORE ZEOLITE CATALYSTS

FIELD OF THE INVENTION

The invention relates to catalytic cracking of hydrocarbons. Particularly the
5 invention relates to a method providing improved selectivity for cracking
hydrocarbon feedstocks primarily to propylene by contacting the hydrocarbon
under cracking conditions with a catalyst selected from zeolite molecular sieves
having a high silica to alumina ratio.

BACKGROUND OF THE INVENTION

10 Thermal and catalytic conversion of hydrocarbons to olefins is an important
industrial process producing millions of pounds of olefins each year. Because of
the large volume of production, small improvements in operating efficiency
translate into significant profits. Catalysts play an important role in more selective
conversion of hydrocarbons to olefins. It is especially desirable to have catalysts
15 available that are highly selective for a particular desired product. However
catalytic cracking tends to produce complex mixtures of products with varying
degrees of specificity.

Particularly important catalysts are found among the natural and synthetic
zeolites. Zeolites are crystalline aluminosilicates with a network of AlO_4 and SiO_4
20 tetrahedra linked by oxygen atoms. The negative charge of the network is balanced
by the inclusion of protons or cations such as alkali or alkaline earth metal ions.
The interstitial spaces or channels formed by the crystalline network enable zeolites
to be used as molecular sieves in separation processes and in catalysis. There are a
large number of both natural and synthetic zeolitic structures including materials
25 with additional elements such as boron, iron, gallium and titanium. The wide
breadth of zeolite structures is illustrated in the "Atlas of Zeolite Structure Types"
by W. M. Meier, D. H. Olson and C. Baerlocher (4th ed., Elsevier/Intl. Zeolite
Assoc. (1996)).



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Catalysts containing zeolites, especially medium pore zeolites, are known to be active in cracking light naphtha to light olefins, primarily propylene and butylenes, as well as heavier hydrocarbon streams. For example U. S. Patent No. 4,922,051 describes the cracking of C_2 - C_{12} paraffinic hydrocarbons with at least 90 wt% conversion and at least 55% of the sum of C_2 - C_4 and C_6 - C_8 aromatics in the products using a composite catalyst preferably including 25% ZSM-5. U. S. Patent No. 5,389,232 discloses a process for catalytically cracking a heavy feed in a single riser reactor FCC unit, with delayed riser quench and large amounts of shape selective cracking additive is disclosed. The feed is preferably quenched after at least 1 second of riser cracking. The catalyst inventory preferably contains over 3.0 wt % ZSM-5 crystal, in the form of an additive of 12-40% ZSM-5 on an amorphous support. Quenching with recycled LCO is preferred. Delayed quenching, with this catalyst system, was reported to produce unexpectedly large amounts of C_3 / C_4 olefins, with little or no increase in coke make.

However the art has not heretofore included a class of catalysts to selectively crack higher olefin containing hydrocarbon feed streams to propylene with only small percentages of both ethylene and butylene. Previous naphtha cracking catalysts also produce a substantial percentage of either ethylene or butylene. It is especially unexpected to find a catalyst that produces a high propylene conversion while having only a modest butylene production, and at the same time low ethylene content and low aromatic content in the product mixture. The present invention identifies a group of catalysts with such selectivity.

SUMMARY OF THE INVENTION

The invention provides a method of converting a hydrocarbon feedstock to propylene comprising: contacting an olefinic hydrocarbon feedstock boiling in the naphtha range under catalytic cracking conditions with a catalyst comprising a catalyst selected from the group consisting of medium pore zeolites (<0.7 nm) having a silica to alumina ratio in excess of 200, under cracking conditions to selectively produce a product mixture of predominantly light olefins in which

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propylene is in excess of 50% of the total products. Preferably the propylene to butylene ratio is at least 2:1 or the propylene to ethylene ratio is at least 4:1. The preferred catalysts are zeolites having an 8,10 or 12 membered ring pore structure. It is especially preferred for the zeolite to be mono-dimensional. The preferred catalysts are selected from the families consisting of MFI, MEL, MTW, TON, MTT, FER, MFS, and the zeolites, ZSM-21, ZSM-38 and ZSM-48. Examples of zeolites in these families include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35 and ZSM-57. Preferably the method is carried out to produce propylene in a propylene to butylene ratio of at least 2:1 or a propylene to ethylene ratio of at least 4:1. The method also preferably produces less than 15 wt% aromatics in the product mixture. The olefinic hydrocarbon feedstock consists essentially of hydrocarbons boiling within the range of -18° to 220° C (65°F to 430°F), preferably in the range of 18° to 148°C (65°F to 300°F). The olefinic hydrocarbon feedstock comprises from about 10 wt% to about 70 wt% olefins, preferably from 20 wt% to 70 wt% olefins. Preferably the olefinic hydrocarbon feedstock comprises from about 5 wt% to about 35 wt % paraffins preferably about 10 wt% to about 30 wt % paraffins, more preferably about 10 wt% to about 25 wt % paraffins. The catalyst is contacted in the range of 400°C to 700° C, a weight hourly space velocity ("WHSV") of 1 to 1,000 hr⁻¹ and a pressure of 0.1 to 30 atm. absolute.

Alternatively the invention may be viewed as a method for producing propylene in a cracking process while minimizing production of butylene which comprises contacting an olefinic hydrocarbon feed with a high silicon zeolite containing catalyst under cracking conditions to produce at least 2 times as much propylene as the total butylenes. Another embodiment views the invention as a method for producing propylene in a cracking process while minimizing production of ethylene which comprises contacting an olefinic hydrocarbon feed with a high silicon zeolite containing catalyst under cracking conditions to produce at least 4

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times as much propylene as ethylene. The catalyst choices, feedstocks and conditions are as set out above.

DETAILED DESCRIPTION OF THE INVENTION

The invention is a method for producing high propylene in a catalytic cracking process by contacting an olefinic hydrocarbon feedstock with a medium pore zeolite (<0.7 nm) having a silica to alumina ratio above 200:1 preferably a zeolite with an eight, ten or twelve membered ring pore structure. It is especially preferred that the zeolite have a monodimensional structure. Preferred olefinic hydrocarbon feedstocks are naphthas in the boiling range of 18° to 220°C (65°F to 430°F). The naphthas may be thermally cracked naphthas or catalytically cracked naphthas. The feed should contain from at least 10 wt% to about 70 wt% olefins, preferably 20 wt% to 70 wt%, and may also include naphthenes and aromatics. For example, the naphtha may be derived from fluid catalytic cracking ("FCC") of gas oils and resids, or from delayed or fluid coking of resids. The preferred naphtha streams are derived from FCC gas oils or resids which are typically rich in olefins and diolefins and relatively lean in paraffins.

Catalytic cracking conditions mean a catalyst contacting temperature in the range of about 400°C to 750°C; more preferably in the range of 450°C to 700°C; most preferably in the range of 500°C to 650°C. The catalyst contacting process is preferably carried out at a weight hourly space velocity (WHSV) in the range of about 0.1 Hr⁻¹ to about 1,000 Hr⁻¹, more preferably in the range of about 1.0 Hr⁻¹ to about 250 Hr⁻¹, and most preferably in the range of about 10 Hr⁻¹ to about 100 Hr⁻¹. Pressure in the contact zone may be from 0.1 to 30 atm. absolute; preferably 1 to 3 atm. absolute, most preferably about 1 atm. absolute. The catalyst may be contacted in any reaction zone such as a fixed bed, a moving bed, a transfer line, a riser reactor or a fluidized bed.

Test Conditions

A series of runs in a small bench reactor was conducted on hexene as a model compound. Comparison runs were made with a ZSM-5 zeolite catalyst,

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from Intercat. Inc., of Sea Girt, New Jersey. The effluent stream was analyzed by on-line gas chromatography. A column having a length of 60 m packed with fused silica was used for the analysis. The gas chromatograph was a dual flame ionization detector equipped Hewlett-Packard Model 5880. All tabulated data are in weight per cent unless otherwise indicated.

Example 1

A 50/50 blend of n-hexane/n-hexene was contacted with (1) a ZSM-48 catalyst, or (2) a ZSM-22, each having a silica to alumina ratio in excess of 1500, and a control ZSM-5 having a silica to alumina ratio of 55. All runs were conducted at 575°C and a WHSV of 12 hr⁻¹. The results are set out in Table 1.

TABLE 1			
Catalyst	ZSM-22	ZSM-48	ZSM-5
Zeolite SiO ₂ /Al ₂ O ₃ Ratio	>1500	>1500	55
Conversion, %	38.4	43.9	46.7
Key Results, %			
Ethylene	2.1	2.5	5.6
Propylene	28.7	32.6	22.3
Butenes + Butadiene	3.3	5.4	13.1
Aromatics	0.2	0.4	1.2
Light Saturates	4.0	3.0	4.5
Selectivity for Propylene, %	74.9	74.2	47.8
Propylene/Ethylene Ratio	13.6	13.0	4.0
Propylene/Butylene Ratio	8.7	6.0	1.7

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As the data above demonstrate, exceptional propylene selectivity is achieved with the high silica medium pore zeolite catalysts.

Example 2

5 A comparison run to illustrate the effect of silica-to-alumina ratio was obtained under the same conditions as in Example 1 with samples of ZSM-22 differing only in the ratio of silica to alumina. The results are presented in Table 2.

Table 2		
Catalyst	ZSM-22	ZSM-22
Zeolite SiO₂/Al₂O₃ Ratio	>1500	120
Conversion, %	38.2	53.0
Key Results, %		
Ethylene	2.1	6.5
Propylene	28.7	24.6
Butenes + Butadiene	3.3	12.1
Aromatics	0.2	2.3
Light Satutrates	4.0	9.8
Selectivity for Propylene, %	74.9	44.4
Propylene/Ethylene Ratio	13.7	3.8
Propylene/Butylene Ratio	8.7	2.0

10 Although the overall conversion is lower with the high silica catalyst, the specificity for propylene is dramatic. In a proper system recycle of the unconverted hydrocarbon offsets the lower conversion associated with enhanced specificity where propylene demand warrants.

CLAIMS

24 OCT 2002

We claim:

1. A method of converting a hydrocarbon feedstock to propylene comprising:
5 contacting an olefinic hydrocarbon feedstock having from 10 to 70 wt.%
olefins with a catalyst selected from the group consisting of zeolites from the
families TON, MTT and MFS, and ZSM-48, where the zeolite has a silica to
alumina ratio in excess of 200, cracking conditions at reactor temperatures of
from about 400-700°C, pressures of from 0.1 atmosphere to 30 atmospheres
absolute, and weight hourly space velocities of from 0.1 hr⁻¹ to 1,000 hr⁻¹ to
10 selectively produce a product mixture of light olefins in which propylene is in
excess of 50% of the total converted product.
2. The method of claim 1 wherein the catalyst is selected from the group
consisting of ZSM-22, ZSM-23, ZSM-48 and ZSM-57.
3. The method of claim 1 wherein the method produces a product mixture having
15 a propylene to butylene ratio of at least 2:1 or a propylene to ethylene ratio of
at least 4:1.
4. The method of claim 3 wherein the process produces a propylene to butylene
ration of at least 2:1, a propylene to ethylene ratio of at least 4:1 and less than
15 wt.% aromatics.

TOTAL P.05

AMENDED SHEET