

Description

Background of the Invention

5 In one aspect, this invention relates to a process for cracking hydrocarbon-containing feed streams employing catalysts which contain faujasite-type zeolite. In another aspect, this invention relates to a process for cracking gas oils, recycle oils, residua, hydrotreated residua, and the like. In still another aspect, this invention relates to the use of cracking catalysts containing faujasite-type zeolites that have been partially dealuminated. U.S. Patent 4, 259, 212 discloses a cracking catalyst composition comprising
 10 discrete particles of ultra-stable Y zeolite and discrete particles of alumina, which particles are dispersed in a porous oxide matrix to produce a catalyst containing 5-40 wt-% ultra-stable Y zeolite, 5-40 wt-% alumina and 40-90% oxide matrix.

In accordance with this invention, a process for cracking a hydrocarbon-containing feed stream is provided as defined in the claims. A hydrocarbon-containing feed stream having an initial boiling point
 15 (determined according to ASTM D 1160) of at least about 204°C (400°F) is contacted with a catalyst composition comprising a dealuminated faujasite-type zeolite having a unit cell size (unit cell dimension; determined in accordance with ASTM D 3942-80) in the range of from 2.431 to 2.442 millimicrons (24.31 to 24.42 angstroms) and an alkali metal content of less than 0.2 weight percent and being substantially free of iron ions (i.e., containing less than about 0.05 weight-% Fe), under such cracking conditions as to obtain at
 20 least one normally liquid (i.e., liquid at 25°C 101.325 Pa (1 atm)) hydrocarbon-containing product stream having a lower initial boiling point and higher API₆₀ gravity than said hydrocarbon-containing feed stream.

The atomic silicon:aluminum ratio in the crystalline framework of said faujasite-type zeolite is in the range of from 8:1 to 21:1 (determined by ²⁹Si solid state nuclear magnetic resonance spectrometry). The content of alkali metal (in particular Na) in the faujasite-type zeolite is less than about 0.2 weight percent,
 25 and the catalyst is substantially free of iron ions, e.g. the content of Fe is less than about 0.01 weight percent. Preferred faujasite-type zeolites are Y-zeolites which have been partially dealuminated. Preferred hydrocarbon-containing feed streams comprise gas oils, cracker recycle oils, residua and hydrotreated residua and have preferably a boiling range (ASTM D 1160) of from 204 to 649°C (400 to 1200°F).

30 Brief Description of the Drawing

Figure 1 shows the correlation between MAT conversion of gas oil and hydrotreated resid and the unit cell size of faujasite-type zeolites.

35 Detailed Description of the Invention

The hydrocarbon-containing feed stream for the process of this invention can be any feedstock having an initial boiling point (ASTM D 1160) in excess of about 204°C (400°F), preferably boiling in the range of from 204 to 649°C (400 to 1200°F), more preferably in the range of from 260 to 593°C (500 to 1100°F).
 40 The API₆₀ gravity (measured at 16°C (60°F)) generally is in the range of from 5 to 40, preferably from 10 to 35. Frequently these feedstocks contain Ramsbottom carbon residue (ASTM D 524; generally 0.1-20 weight-%), sulfur (generally 0.1-5 weight-%), nitrogen (generally 0.05-2 weight-%), nickel (generally about 0.05-30 parts by weight per millions parts, abbreviated ppm) and vanadium (generally 0.1-50 ppm). Non-limiting examples of suitable feedstocks are light gas oils, heavy gas oils, vacuum gas oils, cracker recycle
 45 oils (cycle oils), topped crudes, residua (distillation bottoms fractions), hydrotreated topped crudes and hydrotreated residua (e.g., hydrotreated in the presence of Ni, Co, Mo- promoted alumina catalysts), coal pyrolyzates, products from extraction of coal, products from liquifaction of coal, products from tar sand, shale oils, heavy fractions of shale oils, and the like. Presently most preferred feedstocks are heavy gas oils and hydrotreated residua.

50 The faujasite-type zeolite contained in the cracking catalyst employed in the process of this invention include natural mordenite and natural faujasite from which a portion of the aluminum has been removed from the crystalline framework, as well as synthetic mordenites such as Zeolon and synthetic faujasites such as X- and Y-zeolites (also referred to as zeolite X and zeolite Y), from which a portion of Al has been removed from the crystalline framework. The constraint index as defined in U.S. Patent 4,269,695, of the
 55 faujasite-type zeolite is 0.35-0.45, preferably about 0.4.

Controlled partial removal of Al from the framework of a natural or synthetic faujasite-type zeolite, hereinafter referred to as partial dealuminating, results in a decrease of the unit cell dimension of the faujasite-type zeolite (generally from 2.54-2.46 millimicron (24.5-24.6 Å) in the starting material to the

required unit cell size of 2.431-2.442 millimicron (24.31-24.42 Å), and also in a higher Si:Al atomic ratio in the crystalline zeolite framework (generally from 2.7:1 in the starting zeolite material to the range of 8:1-21:1)

Generally, the alkali metal content and the iron content in the faujasite-type zeolite starting material (which is to undergo controlled dealumination) are already as low as required for the cracking process of this invention, and no further reduction in alkali metal and iron content is needed. If, however, the alkali metal content and the iron content of the faujasite-type zeolite starting material exceed the levels that can be tolerated in the cracking process of this invention, a partial dealuminating method must be employed that removes a portion of alkali metal and iron ions, e.g., a method comprising extraction with aqueous acid, such as the preferred dealuminating method described below. As has been shown in Example VI, an excessive alkali metal content in the partially dealuminated faujasite-type zeolite has a detrimental effect on the cracking activity of the zeolite. It is believed that iron in excess of about 0.05 weight percent also adversely affects the cracking performance of the partially dealuminated faujasite-type zeolite.

The partially dealuminated faujasite-type zeolites can be used "as is", or they can be physically admixed with at least one inorganic refractory material such as silica, alumina, silica-alumina, clay and the like, or they can be embedded in a binder matrix of at least one inorganic refractory material such as silica, alumina, silica-alumina, clay and the like. Generally, the weight ratio of zeolite to such inorganic refractory materials in the cracking catalyst is in the range of from 1:20 to 1:1.

Preferably a Y-zeolite, more preferably an ultrastable LZY zeolite marketed by Union Carbide Corporation, is partially dealuminated so as to attain the crystalline unit cell size and atomic Si:Al ratio of the crystalline framework, $(\text{Si}/\text{Al})_c$ required for the cracking process of this invention. The surface area (determined by the BET/ N_2 method; without binder) of the faujasite-type zeolite employed in the process of this invention, preferably partially dealuminated Y-zeolite, generally ranges from 500 to 1000 m^2/g , preferably from 600 to 800 m^2/g .

Any suitable method of partial dealuminating (i.e., removing a portion of aluminum from the crystalline framework) faujasite-type zeolites can be employed, such as those listed in U.S. Patent 4,430,200. A presently preferred method of partially dealuminating faujasite-type zeolites is by exposure to steam, such as at a temperature of 649-871 °C (1200-1600 °F) for 0.2-20 hours. A more preferred dealuminating method resulting in a desired unit cell size and desirably high surface area of the zeolite includes steam-treatment at 704-816 °C (1300-1500 °F) for 0.5-5 hours, followed by acid extraction with an acid such as aqueous HCl having a normality of from 10^{-3} to 5 equivalents per liter, at a temperature of 82-99 °C (180-210 °F) for 1-4 hours. The thus treated zeolite is generally thoroughly washed with deionized water, dried and calcined (preferably at about 500-600 °C, for 1-10 hours). More details are presented in Example II.

Any suitable reactor can be used for the catalytic cracking process of this invention. Generally a fluidized-bed catalytic cracking (FCC) reactor (preferably containing one or more risers) or a moving-bed catalytic cracking reactor (e.g., a Thermoform catalytic cracker) is employed, preferably a FCC riser cracking unit. Examples of such FCC cracking units are described in earlier cited U.S. Patents 4,377,470 and 4,424,116. Generally a catalyst regeneration unit (for removal of coke deposits) is combined with the FCC cracking unit as is shown in the above-cited patents.

Specific operating conditions of the cracking operation depend greatly on the type of feed, the type and dimensions of the cracking reactor and the oil feed rate. Examples of operating conditions are described in the above-cited patents and in many other publications. In an FCC operation, generally the weight ratio of catalyst to oil feed (i.e., hydrocarbon-containing feed) ratio ranges from 2:1 to 10:1, the contact time between oil feed and catalyst is in the range of 0.2 to 2.0 seconds, and the cracking temperature is in the range of from 427-649 °C (800 to 1200 °F). Generally steam is added with the oil feed to the FCC reactor so as to aid in the dispersion of the oil as droplets. Generally the weight ratio of steam to oil feed is in the range of from 0.05:1 to 0.5:1.

The separation of spent (i.e., used) cracking catalyst from gaseous and liquid cracked products and the separation into various gaseous and liquid product fractions can be carried out by any conventional separation means. The most desirable product fraction is gasoline (ASTM boiling range: 82-204 °C (180-400 °F)). Non-limiting examples of such separation schemes are shown in "Petroleum Refining" by James H. Gary and Glenn E. Handwerk, Marcel Dekker, Inc., 1975.

Generally the surface area (BET/ N_2 method) of cracking catalysts (zeolite plus amorphous silica-alumina binder matrix) is in the range of from 50 to 200 m^2/g , and the pore volume generally ranges from 0.2 to 1.0 cc/g. Since generally cracking catalysts are regenerated (preferably by steam stripping for removal of adhered oil and subsequent oxidation so as to burn off carbon deposits) and then recycled (with or without added fresh catalysts) to the cracking reactor, these recycled catalyst (called equilibrium catalysts) generally contain small amounts of metal (Ni, V) deposited from heavy oil feeds.

The following examples are presented to further illustrate the invention and are not to be considered unduly limiting the scope of this invention.

Example I

In this example the experimental methods for determining pertinent structural parameters of cracking catalyst which, contain faujasite-type zeolites, are described.

The unit cell dimension (also referred to as unit cell size; measured in millimicrons (angstroms) of the crystalline, faujasite (zeolite) framework portion of cracking catalysts (untreated or partially dealuminated) was determined by X-ray diffraction, essentially in accordance with ASTM D 3942-80.

The ratio of Si atoms to Al atoms in the crystalline zeolite framework portion of cracking catalysts was determined by ^{29}Si solid state NMR spectrometry, substantially in accordance with the procedure described by J. Klinowski et al. in Nature, April 1982, Volume 296, pages 533-536. The Si:Al atomic ratio in the crystalline framework portion is hereinafter referred to as $(\text{Si}/\text{Al})_c$.

Since zeolite-type cracking catalysts generally also contain a substantially amorphous silica-alumina portion besides the crystalline zeolite portion, the atomic ratio of Si:Al of the entire (total) catalyst composition (referred to as $(\text{Si}/\text{Al})_t$), is different from the $(\text{Si}/\text{Al})_c$ ratio. The total Si content and the total Al content of faujasite-containing cracking catalyst (i.e., crystalline framework plus non-crystalline extra-framework portion) were determined by X-ray fluorescence spectrometry employing a Siemens MRS 400 multi-channel spectrometer.

The surface area of cracking catalyst was determined in accordance with a modified BET/ N_2 method (ASTM D 3037), wherein the relative partial pressure of the gas phase, p/p_0 , was in the range of about 0.01-0.06 ($p = \text{N}_2$ partial pressure in the gas phase, at the test conditions; $p_0 =$ vapor pressure of N_2 at its boiling point under the test conditions).

The sodium content of the faujasite-containing cracking catalysts was determined by inductively-coupled plasma emission spectrometry.

Example II

This example illustrates the experimental procedure for partially dealuminating faujasite-type zeolite catalysts. The starting material was an "ultrastable" ammonium-exchanged faujasite-type Y zeolite powder, marketed by Union Carbide Corporation, Danbury, CT under the product designation of Molecular Sieve LZ-Y82. LZ-Y82 had a BET/ N_2 surface area of 770 m^2/g , a unit cell size of 2.456 millimicron (24.56 Å (angstroms)), total SiO_2 content of 72.2 weight-%, total Al_2O_3 content of 22.8 weight-%, total Na_2O content of 0.2 weight-% and total $(\text{NH}_4)_2\text{O}$ content of 4.0 weight-%. The $(\text{Si}/\text{Al})_c$ atomic ratio of the crystalline framework was 5.3, the total (bulk) $(\text{Si}/\text{Al})_t$ atomic ratio was 2.7. Three methods of dealuminating the LZ-Y82 faujasite-type zeolite were employed.

Method A (Not Preferred)

Samples of the starting material, LZ-Y82, were treated at about 90-100° C. with hydrochloric acid having a pH in the range of 1.5 to 4, for a period of 0.5-2 hour with stirring. The mixture of zeolite and HCl solution was then allowed to cool and was filtered. The filter cake was thoroughly washed with deionized water, dried overnight at about 120-200° C, and calcined at about 610° C. for about 3 hours. Evaluation of the thus treated zeolite samples indicated that at a pH of 3-4 of the HCl solution essentially no dealumination occurred (essentially no reduction in unit cell dimension and thus essentially no increase in $(\text{Si}/\text{Al})_c$ ratio was detected); whereas at a pH of 1.5-2 the unit cell dimension did noticeably decrease from about 2.456 (24.56) of the starting material to about 2.436 millimicron (24.36 angstroms), but also a substantial reduction in surface area resulted (from 770 m^2/g of the starting material to 200-500 m^2/g after acid treatment). This substantial decrease in surface area indicated that a substantial portion of the zeolite (faujasite) framework was destroyed by the heat-treatment at a pH of 1.5-2. This destruction of a substantial portion of the zeolite portion of the cracking catalyst would obviously have a detrimental effect on the cracking activity. Therefore, Method A is not a preferred dealumination method.

Method B

The starting material, LZ-Y82, was subjected to steam at atmospheric pressure. Pertinent test conditions and results are summarized in Table I.

Table I

Steam-Treatment		Properties of Faujasite		
Temp. °C (°F)	Time (Hours)	Surface Area (m ² /g)	Unit Cell Size millimicron (Å)	(Si/Al) _c
- ¹	- ¹	770	2.456 (24.56)	5.3
727 (1340)	1	745	2.442 (24.42)	7.7
" (1340)	2	677	2.442 (24.42)	-
" (1340)	4	668	2.442 (24.42)	-
" (1340)	8	643	2.440 (24.40)	-
" (1340)	16	619	2.441 (24.41)	11.5
721 (1330)	3	649	2.445 (24.45)	-
760 (1400)	3	651	2.439 (24.39)	-
816 (1500)	3	605	2.435 (24.35)	-

¹starting material.

Data in Table I show that treatment of the faujasite-type zeolite with steam resulted in a noticeable reduction in unit cell size and in a noticeable increase in (Si/Al)_c ratio (i.e., the atomic ratio of Si to Al in the crystalline framework). However, prolonged steaming at 727-816 °C (1340-1500 °F), did not reduce the unit cell size below 2.435 millimicron (24.35 angstroms) and also resulted in an undesirably high reduction in surface area (about 20% reduction). The total (Si/Al)_t atomic ratio (as defined in Example I) was about 2.9 of the steam-treated faujasite (vs. 2.7 for the untreated LZ-Y82 faujasite). Thus, even though Method B is a feasible dealumination method, it has some limitations and is presently considered a less preferred method.

Method C (Preferred)

This dealumination method is a combination of Method B and Method A, steam-treatment at 760-816 °C (1400-1500 °F), for 2-3 hours, followed by acid extraction of the steam-treated faujasite material with an aqueous HCl solution at about 90 °C (194 °F), for 2-2.5 hours, washing, drying and calcination (see Method A). Pertinent test conditions and results are summarized in Table II.

TABLE II

Steam Treatment		Normality of Acid	Properties of Faujasite		
Temp. °C (°F.)	Time (Hours)		Surface Area (m ² /g)	Unit Cell Size V(A) millimicron	(Si/Al) _c
760 (1400)	2	0.001	770	2.452 (24.56)	5.3
" (1400)	2	0.01	741	2.442 (24.42)	-
" (1400)	3	0.01	700	2.447 (24.41)	-
" (1400)	2	0.1	663	2.442 (24.42)	(22.0) ²
" (1400)	3	0.1	745	2.440 (24.40)	-
" (1400)	3	0.1	742	2.436 (24.36)	21.2
" (1400)	3	0.5	728	2.438 (24.38)	17.5
" (1400)	3	1.0	782	2.432 (24.32)	21.2
" (1400)	3	2.0	790	2.420 (24.20)	68.8
816 (1500)	3	0.01	666	2.437 (24.37)	-
" (1500)	3	0.1	739	2.438 (24.38)	-
" (1500)	3	0.5	719	2.437 (24.37)	-
" (1500)	3	1.0	777	2.435 (24.35)	-
" (1500)	3	2.0	633	2.425 (24.25)	100
					20.7

¹untreated starting material.²considered to be erroneous; should be about 8, as indicated by data in Table I.

Data in Table II clearly show:

(a) the unit cell size could be reduced from 2.456 millimicron (24.56 A) to a low value of about 2.420 millimicron (24.20 A);

(b) the atomic ratio of the crystalline portion, (Si/Al)_c, could be reduced from about 5.3 to as low as about 100;

(c) the surface area was generally not significantly affected by treatment Method C;

(d) the total atomic ratio of Si to Al (for crystalline framework plus non-crystalline portion), $(\text{Si}/\text{Al})_t$, was also increased, indicating leaching of Al from the faujasite-type zeolite.

Method C is the preferred method of dealuminating since it affords substantial reduction in unit cell size and substantial increase in $(\text{Si}/\text{Al})_c$ ratio, at an acceptably low effect on surface area. It is believed that steam treatment (the first step) stabilizes the zeolite so that the subsequent acid treatment is effective in removing Al from the crystalline framework without destroying it.

Example III

This control example illustrates tests for cracking n-hexane employing faujasite-type zeolites described in Example II. A mixture of vaporized n-hexane and nitrogen (volume ratio of C_6H_{14} to N_2 : about 1:4) was passed through a fixed bed stainless steel reactor (length: about 5cm (2 inches); diameter: about 1.3cm (0.5 inches), filled with a mixture of 0.1-0.2 grams of a faujasite zeolite (either untreated or treated in accordance with one of the methods described in Example II) and about 1.5cc of 0.07-0.15mm (100/200 mesh) quartz chips, at a time of contact between catalyst and of the hexane-nitrogen feed mixture of 0.5-9 seconds. The reactor temperature was about 500 °C. The product was analyzed by gas chromatography.

Pertinent parameters regarding the employed zeolites and the rate of conversion of n-hexane (in millimoles of hexane per gram catalyst per minute), are summarized in Table III.

Table III

Run	Steam-Treated	Acid-Treated	Surface Area (m^2/g)	Unit Cell Size millimicron (A)	$(\text{Si}/\text{Al})_c$	Rate of n-Hexane Conversion
1	No	No	770	2.456 (24.56)	5.3	323
2	No	Yes	733	2.450 (24.50)	7.2	317
3	Yes	Yes	728	2.438 (24.38)	17.5	192
4	Yes	Yes	777	2.435 (24.35)	-	129
5	Yes	Yes	782	2.432 (24.32)	21.2	69
6	Yes	Yes	633	2.425 (24.25)	100	6

¹micromoles of n-hexane converted per grams catalyst per minute.

Data in Table III clearly show that the hexane cracking activity of the zeolite cracking catalyst was highest for untreated LZ-Y82 (Run 1) and that dealumination signified by smaller unit cell size and higher Si:Al ratio in the crystalline zeolite framework, $(\text{Si}/\text{Al})_c$, had a detrimental effect on the activity of the faujasite-type zeolite material for cracking n-hexane (a representative component of naphtha streams).

Example IV

This example illustrates the cracking of a gas oil (provided by Phillips Petroleum Company, Bartlesville, OK under the designation KC Gas Oil J2543) in accordance with the microactivity test (MAT) procedure of ASTM D 3907-80 (reactor temperature; 482 °C (900 °F); catalyst to oil weight ratio 3:1). The catalyst employed in the MAT tests was a mixture of 0.35 grams of one of the faujasite-type zeolites (untreated or partially dealuminated; See Example II) and about 4.65 gm of 0.07-0.15mm (100/200 mesh) quartz chips. The gas oil feed had API gravity (at 16 °C (60 °F)) of 30.2, Ramsbottom carbon residue (ASTM D 524) of 0.23, sulfur content of 0.20 weight-%; nitrogen content of 0.08 weight-%, nickel content of 0.25 ppm (parts per million by weight), vanadium content of 9 ppm, molecular weight of 328, pour point of 38 °C (100 °F), viscosity at 99 °C (210 °F) of 39.3 SUS, an initial boiling point (ASTM D 1160) of about 288 °C (550 °F), and 90% of its volume boiling at 288-543 °C (550-1010 °F) (at ASTM D 1160 condition). Pertinent test results are summarized in Table IV).

TABLE IV

Run	Faujasite Zeolite		Measured Conversion (Wt-% of Feed)	Product (Wt-%)				
	Surface Area (m ² /g)	Unit Cell Size V(A) millimicron		Gasoline	Light Cycle Oil	Heavy Cycle Oil	H ₂	Other Gases Coke
7	770	2.456 (24.56)	34.7	21.4	27.4	37.9	0.012	8.4 4.9
8	733	2.450 (24.50)	47.0	31.5	24.8	28.2	0.012	10.1 5.3
9	702	2.448 (24.48)	51.2	36.0	24.1	24.7	0.002	11.0 4.3
10	733	2.447 (24.47)	52.6	40.4	28.0	19.4	0	8.3 4.0
11	741	2.442 (24.42)	56.1	43.6	26.9	17.0	0.002	9.2 3.3
12	700	2.441 (24.41)	60.2	46.2	26.2	13.6	0.007	9.1 4.9
13	745	2.440 (24.40)	58.4	43.7	25.8	17.7	0.004	9.7 5.0
14	728	2.438 (24.38)	60.9	46.8	25.9	13.2	0.002	10.2 3.9
15	719	2.437 (24.37)	65.7	49.3	23.5	10.8	0.003	11.4 4.9
16	742	2.436 (24.36)	61.8	47.0	26.0	12.2	0.003	10.7 4.0
17	777	2.435 (24.35)	66.9	50.4	23.2	9.9	0.008	11.4 5.1
18	782	2.432 (24.32)	59.5	44.1	24.7	15.8	0.002	10.8 4.6
19	797	2.425 (24.25)	40.8	30.6	29.2	30.0	0	6.2 4.0
20	633	2.425 (24.25)	25.6	18.2	31.2	43.2	0	3.3 4.1
21	790	2.420 (24.20)	16.7	11.7	32.5	50.8	0.005	2.1 2.9

¹Estimated from data in Table I.

Data in Table IV clearly show that, unexpectedly, gas oil conversion and gasoline yield were highest when the unit cell size of the faujasite cracking catalyst component was in the range of from 2.428 to 2.448 millimicron (24.28 to 24.48 angstroms), and better at 2.431 to 2.442 (24.31 to 24.42 angstroms) (see also Figure 1). The (Si/Al)_c ratio in the crystalline zeolite portion for the unit cell size range of 2.431-2.442 millimicron (24.31-24.42 Å) was 8:1 to 21:1.

The test data in Table IV also showed that the surface area of the faujasite-type zeolites employed was 700-800 m²/g in all runs with the exception of run 20. Thus, the cracking results are essentially functions of the degree of dealumination of the zeolite, i.e., unit cell size and (Si/Al)_o. These cracking results for gas oil are especially surprising because data in Table III (Example III) did not indicate that partially dealuminated faujasites was more effective in cracking n-hexane than untreated faujasite.

Example V

This example illustrates the cracking of a hydrotreated residuum that was obtained after hydrotreatment of an atmospheric resid in a commercial catalytic desulfurization unit of a Phillips Petroleum Company refinery. The hydrotreated resid had API⁶⁰ gravity of 22.7, Ramsbottom carbon residue of 3.1, sulfur content of 0.31 weight-%, nitrogen content of 0.12 weight-%, 1.0 ppm nickel, 96 ppm vanadium and a viscosity at 99° C (210° F) of 14.3 SUS. Catalyst mixtures and MAT test conditions were essentially the same as those described in Example IV. Pertinent catalyst parameters and test results are summarized in Table V.

TABLE V

Run	Faujasite Zeolite Surface Area (m ² /g)	Unit Cell Size (Å)	Measured Conversion (Wt-% of Feed)	Product (Wt-%)				
				Gasoline	Light Cycle Oil	Heavy Cycle Oil	H ₂	Other Gases Coke
22	770	2.456 (24.56)	40.1	23.0	15.9	44.0	0.021	9.2
23	729	2.450 (24.50)	40.8	24.2	15.7	43.6	0.018	10.0
24	680	2.446 (24.46)	54.3	36.4	16.4	29.3	0.016	11.1
25	674	2.439 (24.39)	62.9	43.6	12.6	24.6	0.022	12.8
26	651	2.438 (24.38)	60.6	43.0	18.8	20.6	0.024	12.0
27	777	2.435 (24.35)	63.0	43.8	17.8	19.2	0.016	12.4
28	633	2.435 (24.25)	34.6	24.1	18.7	46.8	0.011	5.6

Test data in Table V show the same trend as those of Table IV: conversion and gasoline yield conversion were higher for a unit cell size range of 2.446 to 2.43 millimicron (24.46 Å to 24.3 Å) (midway between runs 27 and 28), thus at a (Si/Al)_c range of 8 to 21. The graphic plot of conversion data in Tables IV and V showed that MAT conversion data for gas oil (Table IV) and hydrotreated resid (Table V) are represented by essentially the same graph (see Figure 1).

Example VI

This example illustrates the effect of the sodium content on the gas oil cracking activity of a partially dealuminated LZ-Y82 faujasite having a (Si/Al)_c ratio of about 20, prepared by steam-treatment of LZ-Y82 substantially in accordance with Method B of Example II. This partially dealuminated LZ-Y82 faujasite having a sodium content of less than 0.2 weight-% Na was then ion-exchanged by treatment with an aqueous NaCl solution (concentration, about 1 mole/l) so as to attain about 1.1 weight-% Na in the partially dealuminated zeolite material. MAT conversion and gasoline yield were measured in MAT tests using Kansas City gas oil (see Example IV) as feed. Pertinent test results are summarized in Table VI.

Table VI

Run	Faujasite Zeolite		Conversion (Wt-% of Feed)	Product (Wt-%)	
	(Si/Al) _c	Wt-% Na		Gasoline	Coke
29	~10	<0.2	61.5	45.7	3.8
30	~10	1.1	49.6	37.1	4.8

Data in Table VI clearly show that a higher sodium content in a partially dealuminated faujasite had detrimental effects on gas oil conversion, gasoline yield and coke formation. Thus, for higher gas oil cracking activity, the partially dealuminated faujasite should have an alkali metal content of less than about 0.5 weight-% alkali metal, more preferably less than about 0.2 weight-% alkali metal, in particular sodium.

Claims

1. A cracking process comprising the step of contacting a hydrocarbon-containing feed stream having an initial boiling point, determined in accordance with ASTM D 1160, of at least about 204°C (400°F), in particular wherein said hydrocarbon-containing feed stream has a boiling range of from 204°C to 649°C (400°F to 1200°F), with a catalyst composition comprising a zeolite selected from the group consisting of partially dealuminated natural faujasite, partially dealuminated mordenite, partially dealuminated synthetic faujasites and partially dealuminated synthetic mordenites, wherein said zeolite has a unit cell size, determined in accordance with ASTM D 3942-80, in the range of 2.431 to 2.442 millimicrons (24.31 to 24.42 angstroms), an atomic ratio of Si to Al in the crystalline framework (Si/Al)_c in the range of 8:1 to 21:1, a surface area, determined by the BET/N₂ method, in the range of 500 to 1000 m²/g and wherein said zeolite has an alkali metal content, in particular sodium content, of less than about 0.2 weight percent and is substantially free of iron ions, under such cracking conditions as to obtain at least one normally liquid hydrocarbon containing product stream having a lower initial boiling point and higher API₆₀ gravity than said hydrocarbon-containing feed stream.
2. A process in accordance with claim 1, wherein said hydrocarbon-containing feed stream is selected from the group consisting of light gas oils, heavy gas oils, vacuum gas oils, cycle oils, topped crudes, residua, hydrotreated topped crudes, hydrotreated residua, coal pyrolyrates, products from extraction of coal, products from liquifaction of coal, products from tar sands, shale oils and heavy fractions of shale oils.
3. A process in accordance with claim 2, wherein said hydrocarbon-containing feed stream has one or more of the following properties:
 - a) the feedstream has an API₆₀ gravity in the range of from 5 to 40;
 - b) the feedstream has a boiling range of from 260°C to 593°C (500°F to 1100°F) and an API₆₀ gravity in the range of from 10 to 35;
 - c) the feedstream contains 0.1 to 20 weight-% Ramsbottom carbon residue, 0.1 to 5 weight-% sulfur, 0.05 to 2.0 weight-% nitrogen, 0.05 to 30 ppm nickel and 0.1 to 50 ppm vanadium.
4. A process in accordance with claim 2 or 3, wherein said group consists of heavy gas oils and hydrotreated residua.
5. A process in accordance with claims 1 to 4, wherein said zeolite is partially dealuminated Y-zeolite.

This example illustrates the effect of the sodium content on the gas oil cracking activity of a partially dealuminated LZ-Y82 faujasite having a (Si/Al)_c ratio of about 20, prepared by steam-treatment of LZ-Y82 substantially in accordance with Method B of Example II. This partially dealuminated LZ-Y82 faujasite having a sodium content of less than 0.2 weight-% Na was then ion-exchanged by treatment with an aqueous NaCl solution (concentration, about 1 mole/l) so as to attain about 1.1 weight-% Na in the partially dealuminated zeolite material. MAT conversion and gasoline yield were measured in MAT tests using Kansas City gas oil (see Example IV) as feed. Pertinent test results are summarized in Table VI.

Table VI

Run	Faujasite Zeolite		Conversion (Wt-% of Feed)	Product (Wt-%)	
	(Si/Al) _c	Wt-% Na		Gasoline	Coke
29	~10	<0.2	61.5	45.7	3.8
30	~10	1.1	49.6	37.1	4.8

Data in Table VI clearly show that a higher sodium content in a partially dealuminated faujasite had detrimental effects on gas oil conversion, gasoline yield and coke formation. Thus, for higher gas oil cracking activity, the partially dealuminated faujasite should have an alkali metal content of less than about 0.5 weight-% alkali metal, more preferably less than about 0.2 weight-% alkali metal, in particular sodium.

Claims

1. A cracking process comprising the step of contacting a hydrocarbon-containing feed stream having an initial boiling point, determined in accordance with ASTM D 1160, of at least about 204 °C (400 °F), in particular wherein said hydrocarbon-containing feed stream has a boiling range of from 204 °C to 649 °C (400 °F to 1200 °F), with a catalyst composition comprising a zeolite selected from the group consisting of partially dealuminated natural faujasite, partially dealuminated mordenite, partially dealuminated synthetic faujasites and partially dealuminated synthetic mordenites, wherein said zeolite has a unit cell size, determined in accordance with ASTM D 3942-80, in the range of 2.431 to 2.442 millimicrons (24.31 to 24.42 angstroms), an atomic ratio of Si to Al in the crystalline framework (Si/Al)_c in the range of 8:1 to 21:1, a surface area, determined by the BET/N₂ method, in the range of 500 to 1000 m²/g and wherein said zeolite has an alkali metal content, in particular sodium content, of less than about 0.2 weight percent and is substantially free of iron ions, under such cracking conditions as to obtain at least one normally liquid hydrocarbon containing product stream having a lower initial boiling point and higher API₆₀ gravity than said hydrocarbon-containing feed stream.
2. A process in accordance with claim 1, wherein said hydrocarbon-containing feed stream is selected from the group consisting of light gas oils, heavy gas oils, vacuum gas oils, cycle oils, topped crudes, residua, hydrotreated topped crudes, hydrotreated residua, coal pyrolyrates, products from extraction of coal, products from liquifaction of coal, products from tar sands, shale oils and heavy fractions of shale oils.
3. A process in accordance with claim 2, wherein said hydrocarbon-containing feed stream has one or more of the following properties:
 - a) the feedstream has an API₆₀ gravity in the range of from 5 to 40;
 - b) the feedstream has a boiling range of from 260 °C to 593 °C (500 °F to 1100 °F) and an API₆₀ gravity in the range of from 10 to 35;
 - c) the feedstream contains 0.1 to 20 weight-% Ramsbottom carbon residue, 0.1 to 5 weight-% sulfur, 0.05 to 2.0 weight-% nitrogen, 0.05 to 30 ppm nickel and 0.1 to 50 ppm vanadium.
4. A process in accordance with claim 2 or 3, wherein said group consists of heavy gas oils and hydrotreated residua.
5. A process in accordance with claims 1 to 4, wherein said zeolite is partially dealuminated Y-zeolite.



6. A process in accordance with claim 1, wherein said zeolite has been partially dealuminated by a dealumination process comprising steam treatment, in particular wherein said steam treatment is carried out at 704 to 816 °C (1300 to 1500 °F) for 0.5 to 5 hours, more particularly wherein said dealumination process further comprises treatment with an aqueous acid solution after said steam treatment; in particular wherein said aqueous acid solution has a normality of from 10^{-3} to 5 equivalents per liter; more particularly wherein said treatment with an aqueous acid solution is carried out at 82 to 99 °C (180 to 210 °F) for 1 to 10 hours.
7. A process in accordance with claim 1, wherein said catalyst composition further comprises at least one inorganic refractory material, in particular wherein said at least one inorganic refractory material is selected from the group consisting of silica, alumina, silica-alumina and clay, more particularly wherein the weight ratio of said zeolite to said inorganic refractory material is in the range of from 1:20 to 1:1.
8. A process in accordance with claim 1, wherein said contacting is carried out in a fluidized bed catalyst cracking reactor, in particular wherein said contacting is carried out in the presence of steam.

Revendications

1. Procédé de craquage comprenant le stade de mise en contact d'un courant d'alimentation contenant des hydrocarbures ayant un point d'ébullition initial, déterminé conformément à l'ASTM D 1160, d'au moins environ 204 °C (400 °F), en particulier dans lequel ce courant d'alimentation contenant des hydrocarbures a un intervalle d'ébullition de 204 °C à 649 °C (400 °F à 1200 °F), avec une composition de catalyseur comprenant une zéolite choisie parmi la faujasite naturelle partiellement désaluminée, la mordenite partiellement désaluminée, les faujasites synthétiques partiellement désaluminées et les mordenites synthétiques partiellement désaluminées, dans lequel cette zéolite a une dimension de la maille cristalline, déterminée conformément à l'ASTM D 3942-80, dans l'intervalle de 2,431 à 2,442 millimicrons (24,31 à 24,42 angstroms), un rapport atomique de Si à Al dans le réseau cristallin (Si/Al)_c dans l'intervalle de 8 : 1 à 21 : 1, une surface spécifique, déterminée par la méthode BET/N₂, dans l'intervalle de 500 à 1000 m²/g, et dans lequel cette zéolite a une teneur en métal alcalin, en particulier une teneur en sodium, inférieure à environ 0,2 % en poids et est pratiquement exempte d'ions fer, dans des conditions de craquage permettant d'obtenir un courant de produit contenant au moins un hydrocarbure normalement liquide, ayant un point d'ébullition initial plus faible et une densité API₆₀ plus élevée que ce courant d'alimentation contenant des hydrocarbures.
2. Procédé selon la revendication 1, dans lequel ce courant d'alimentation contenant des hydrocarbures est choisi parmi le groupe constitué des gas-oils légers, des gas-oils lourds, des gas-oils de distillation sous vide, des huiles de recyclage, des bruts étêtés, des résidus, des bruts étêtés traités par l'hydrogène, des résidus traités par l'hydrogène, des pyrolysats de charbon, des produits d'extraction du charbon, des produits de la liquéfaction du charbon, des produits des sables asphaltiques, des huiles de schiste, et des fractions lourdes d'huile de schiste.
3. Procédé selon la revendication 2, dans lequel ce courant d'alimentation contenant des hydrocarbures présente une ou plusieurs des propriétés suivantes :
 - a) le courant d'alimentation a une densité API₆₀ dans l'intervalle de 5 à 40;
 - b) le courant d'alimentation a un intervalle d'ébullition de 260 °C à 593 °C (500 °F à 1100 °F) et une densité API₆₀ dans l'intervalle de 10 à 35;
 - c) le courant d'alimentation contient 0,1 à 20 % de résidu de carbone Ramsbottom, 0,1 à 5 % en poids de soufre, 0,05 à 2,0 % en poids d'azote, 0,05 à 30 ppm de nickel et 0,1 à 50 ppm de vanadium.
4. Procédé selon les revendications 2 ou 3, dans lequel ce groupe est constitué de gaz oils lourds et de résidus traités par l'hydrogène.
5. Procédé selon les revendications 1 à 4, dans lequel cette zéolite est une zéolite Y partiellement désaluminée.
6. Procédé selon la revendication 1, dans lequel cette zéolite a été partiellement désaluminée par un



procédé de désalumination comprenant un traitement par la vapeur, en particulier dans lequel ce traitement par la vapeur est effectué à 704 à 816 °C (1300 à 1500 °F) pendant 0,5 à 5 heures, plus particulièrement dans lequel cet procédé de désalumination comprend en outre un traitement par une solution acide aqueuse après ce traitement à la vapeur; en particulier dans lequel cette solution acide aqueuse a une normalité de 10^{-3} à 5 équivalents par litre; plus particulièrement dans lequel ce traitement par une solution acide aqueuse est effectué à 82 à 99 °C (180 à 210 °F) pendant 1 à 10 heures.

7. Procédé selon la revendication 1, dans lequel cette composition de catalyseur comprend en outre au moins une matière réfractaire minérale, en particulier, dans lequel cette matière réfractaire minérale est choisie parmi la silice, l'alumine, la silice-alumine et l'argile, plus particulièrement dans lequel le rapport pondéral de cette zéolite à cette matière réfractaire minérale est dans l'intervalle de 1 : 20 à 1 : 1
8. Procédé selon la revendication 1, dans lequel cette mise en contact est effectuée dans un réacteur de craquage à catalyseur à lit fluidisé, en particulier dans lequel cette mise en contact est effectuée en présence de vapeur.

Patentansprüche

1. Krackverfahren, umfassend die Stufe des Kontaktierens eines kohlenwasserstoffhaltigen Einsatzmaterialstroms mit einem gemäss ASTM D 1160 bestimmten Anfangssiedepunkt von mindestens etwa 204 °C (400 °F), wobei der kohlenwasserstoffhaltige Einsatzmaterialstrom insbesondere einen Siedebereich von 204 bis 649 °C (400 - 1200 °F) aufweist, mit einer Katalysatorzusammensetzung, die einen Zeolith enthält, der aus der Gruppe partiell desaluminierter, natürlicher Faujasit, partiell desaluminierter Mordenit, partiell desaluminierter, synthetische Faujasite und partiell desaluminierter, synthetische Mordenite ausgewählt ist, wobei der Zeolith eine gemäss ASTM D 3942-80 bestimmte Einheitszellgrösse im Bereich von 2,431 bis 2,442 Millimicron (24,31 bis 24,42 Å), ein Atomverhältnis von Si zu Al im Kristallgerüst (Si/Al)_c im Bereich von 8:1 bis 21:1, eine gemäss dem BET/N₂-Verfahren bestimmte Oberfläche im Bereich von 500 bis 1000 m²/g aufweist und wobei der Zeolith einen Alkalimetallgehalt, insbesondere Natriumgehalt, von weniger als 0,2 Gew.-% besitzt und im wesentlichen frei von Eisenionen ist, unter solchen Krackbedingungen, dass man mindestens einen normalerweise flüssigen, kohlenwasserstoffhaltigen Produktstrom mit einem im Vergleich zum kohlenwasserstoffhaltigen Einsatzmaterialstrom niedrigeren Anfangssiedepunkt und höheren API₆₀-Dichte erhält.
2. Verfahren nach Anspruch 1, wobei der kohlenwasserstoffhaltige Einsatzmaterialstrom ausgewählt wird aus der Gruppe leichte Gasöle, schwere Gasöle, Vakuum-Gasöle, Rückführöle, Topprückstände, Residua, dem Hydrotreating unterworfenen Topprückstände, dem Hydrotreating unterworfenen Residua, Kohlepyrolysate, Kohleextraktionsprodukte, Kohleverflüssigungsprodukte, Teersandprodukte, Schieferöle und schwere Fraktionen von Schieferölen.
3. Verfahren nach Anspruch 2, wobei der kohlenwasserstoffhaltige Einsatzmaterialstrom eine oder mehrere der folgenden Eigenschaften aufweist:
 - a) der Einsatzmaterialstrom weist eine API₆₀-Dichte im Bereich von 5 bis 40 auf;
 - b) der Einsatzmaterialstrom weist einen Siedebereich von 260 bis 593 °C (500 bis 1100 °F) und eine API₆₀-Dichte im Bereich von 10 bis 35 auf;
 - c) der Einsatzmaterialstrom enthält 0,1 bis 20 Gew.-% Ramsbottom-Kohlenstoffrückstand, 0,1 bis 5 Gew.-% Schwefel, 0,05 bis 2,0 Gew.-% Stickstoff, 0,05 bis 30 ppm Nickel und 0,1 bis 50 ppm Vanadium.
4. Verfahren nach Anspruch 2 oder 3, wobei die genannte Gruppe aus schweren Gasölen und dem Hydrotreating unterworfenen Residua besteht.
5. Verfahren nach den Ansprüchen 1 bis 4, wobei es sich beim Zeolith um partiell desaluminierter Y-Zeolith handelt.
6. Verfahren nach Anspruch 1, wobei der Zeolith durch eine Dampfbehandlung umfassendes Desaluminierungsverfahren partiell desaluminierter worden ist, wobei insbesondere die Dampfbehandlung bei



704 bis 816 °C (1300 bis 1500 °F) für 0,5 bis 5 Stunden durchgeführt wird, wobei dieses Desaluminierungsverfahren insbesondere nach der Dampfbehandlung eine Behandlung mit einer wässrigen Säurelösung umfasst; wobei insbesondere die wässrige Säurelösung eine Normalität von 10^{-3} bis 5 Äquivalente pro Liter aufweist; wobei die Behandlung insbesondere mit einer wässrigen Säurelösung 1 bis 10 Stunden bei 82 bis 99 °C (180 bis 210 °F) durchgeführt wird.

7. Verfahren nach Anspruch 1, wobei die Katalysatorzusammensetzung zusätzlich mindestens ein anorganisches, feuerfestes Material enthält, wobei dieses mindestens eine anorganische, feuerfeste Material aus der Gruppe Siliciumdioxid, Aluminiumoxid, Siliciumdioxid-Aluminiumoxid und Ton ausgewählt ist, wobei insbesondere das Gewichtsverhältnis des Zeoliths zum anorganischen, feuerfesten Material im Bereich von 1:20 bis 1:1 liegt.

8. Verfahren nach Anspruch 1, wobei das Kontaktieren in einem Wirbelschichtkatalysator-Krackreaktor durchgeführt wird, wobei das Kontaktieren insbesondere in Gegenwart von Dampf durchgeführt wird.

