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(54) Title: REFORMING NAPHTHA WITH BORON-CONTAINING LARGE-PORE ZEOLITES

(57) Abstract

Catalytic reforming processes using boron-containing large-pore zeolites.

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REFORMING NAPHTHA WITH BORON-CONTAINING LARGE-PORE ZEOLITES

BACKGROUND OF THE INVENTION

Catalytic reforming is a process for treating naphtha fractions of petroleum distillates to improve their octane rating by producing aromatic components and isomerizing paraffins from components present in naphtha feedstocks. Included among the hydrocarbon reactions occurring in reforming processes are: dehydrogenation of naphthenes to aromatics, dehydrocyclization of paraffins to aromatics, and hydrocracking of paraffins to lighter gases with a lower boiling point than gasoline. Hydrocracking reactions which produce light paraffin gases are not desirable as they reduce the yield of products in the gasoline range.

Natural and synthetic zeolitic crystalline aluminosilicates and borosilicates are useful as catalysts. The use of ZSM-type catalysts and processes are described in U.S. Patent Nos. 3,546,102, 3,679,575, 4,018,711 and 3,574,092. Zeolite L is also used in reforming processes as described in U.S. Patent Nos. 4,104,320, 4,447,316, 4,347,394 and 4,434,311.

Borosilicate zeolites are especially useful in catalytic reforming. Methods for preparing high silica content zeolites that contain framework boron are described in U.S. Patent No. 4,269,813.

The use of intermediate pore borosilicate zeolites for catalytic reforming is described in European Patent Application No. 188,913. In this application, ZSM-5,

ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48 and zeolite beta have been identified as intermediate pore borosilicate zeolites.

A method for controlling catalytic activity of large-pore boron-containing zeolites is described in European Patent Application No. 234,759.

SUMMARY OF INVENTION

According to the present invention, a process is provided for catalytic reforming. The process comprises contacting a hydrocarbon feedstream under catalytic reforming conditions with a composition comprising large-pore borosilicate zeolites having a pore size between 6 and 8 angstroms. Preferably, the large-pore borosilicate zeolites are boron beta zeolite, (B)SSZ-24, SSZ-31 and SSZ-33.

Boron beta zeolite is described in commonly assigned co-pending application U.S. Serial No. 377,359 (Docket No. B-3924), filed concurrently herewith, and entitled "Low-Aluminum Boron Beta Zeolite", the disclosure of which is incorporated herein by reference.

(B)SSZ-24 is described in commonly assigned co-pending application U.S. Serial No. 377,357 (Docket No. B-3952), filed concurrently herewith, and entitled "Zeolite (B)SSZ-24", the disclosure of which is incorporated herein by reference.

SSZ-33 is described in commonly assigned co-pending application U.S. Serial No. 377,358 (Docket No. B-3889), filed concurrently herewith, and entitled "Zeolite SSZ-33", the disclosure of which is incorporated herein by reference.

SSZ-31 is described in commonly assigned co-pending application U.S. Serial No. _______ (Docket No. B-3986), filed concurrently herewith, and entitled "New Zeolite SSZ-31", the disclosure of which is incorporated herein by reference.

According to a preferred embodiment, the large-pore borosilicate zeolites may be used in a multi-stage catalytic reforming process. These zeolites may be located in one or more of the reactors, with conventional platinum and rhenium catalysts located in the remaining reactors.

The reforming process may be accomplished by using fixed beds, fluid beds or moving beds for contacting the hydrocarbon feedstream with the catalysts.

Among other factors, the present invention is based on our finding that large-pore borosilicates including boron beta zeolite [(B)Beta], SSZ-33, (B)SSZ-24 and SSZ-31 have unexpectedly outstanding reforming properties. These include high sulfur tolerance, high catalyst stability, and high catalyst activity.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to reforming processes employing large-pore borosilicate zeolites. A large-pore zeolite is defined herein as a zeolite having a pore size between 6 and 8 angstroms. A method of determining this pore size is described in Journal of Catalysis (1986); Vol. 99, p. 335 (D. S. Santilli). A large-pore zeolite may be identified by using the pore probe technique described in Journal of Catalysis (1986); Vol. 99, p. 335 (D. S. Santilli). This method allows measurement of the steady-state concentrations of compounds within the pores of materials. 2,2-dimethylbutane (22DMB) enters the large pores and the concentration in the pores is measured using this technique.

According to preferred embodiments of our invention, SSZ-33, (B)SSZ-24, SSZ-31 and low-aluminum boron beta zeolite [(B)beta] are large-pore borosilicate zeolites with high catalyst activity in the reforming process.

SSZ-33 is defined as a zeolite having a mole ratio of an oxide selected from silicon, germanium oxide and mixtures thereof to an oxide selected from boron oxide or mixtures of boron oxide with aluminum oxide, gallium oxide or iron oxide, greater than about 20:1 and having the X-ray diffraction lines of Table 1. The X-ray diffraction lines of Table 1 correspond to the calcined SSZ-33.

Table 1

2θ	d/n	$100 \times I/I_0$
7.86	11.25	90
20.48	4.336	100
21.47	4.139	40
22.03	4.035	90
23.18	3.837	64
26.83	3.323	40

(B)SSZ-24 is defined as a zeolite having a mole ratio of an oxide selected from silicon oxide, germanium oxide, and mixtures thereof to an oxide selected from boron oxide or mixtures of boron oxide with aluminum oxide, gallium oxide, and iron oxide, between 20:1 and 100:1 and having the X-ray diffraction lines of Table 2. The X-ray diffraction lines of Table 2 correspond to the calcined (B)SSZ-24.

Table 2

2θ	d/n	$100 \times I/I_0$
7.50	11.79	100
13.00	6.81	16
15.03	5.894	8
19.93	4.455	35
21.42	4.148	48
22.67	3.922	60
25.15	3.541	3
26.20	3.401	22
29.38	3.040	12
30.43	2.947	12

Boron beta zeolite is a zeolite having a mole ratio of an oxide selected from silicon oxide, germanium oxide, and mixtures thereof to an oxide selected from boron oxide, or mixtures of boron oxide with aluminum oxide, gallium oxide or iron oxide, greater than 10:1 and wherein the amount of aluminum is less than 0.10% by weight and having the X-ray diffraction lines of Table 3. The X-ray diffraction lines of Table 3 correspond to the calcined boron beta zeolite.

Table 3

2 θ	d/n	100 x I/I_o	Shape
7.7	11.5	85	Broad
13.58	6.52	9	
14.87	5.96	12	Broad
18.50	4.80	3	Very Broad
21.83	4.07	15	
22.87	3.89	100	Broad
27.38	3.26	10	
29.30	3.05	6	Broad
30.08	2.97	8	

SSZ-31 is defined as a zeolite having a mole ratio of an oxide selected from silicon oxide, germanium oxide, and mixtures thereof to an oxide selected from aluminum oxide, gallium oxide, iron oxide, and mixtures thereof greater than about 50:1, and having the X-ray diffraction lines of Table 4. The X-ray diffraction lines of Table 4 correspond to the calcined SSZ-31.

Table 4

2 θ	d/n	100 x I/I_o	Shape
6.08	14.54	9	
7.35	12.03	9	
8.00	11.05	7	Broad
18.48	4.80	11	
20.35	4.36	9	Broad
21.11	4.21	100	
22.24	4.00	56	
24.71	3.60	21	
30.88	2.90	7	

The large-pore borosilicates can be used as reforming catalysts to convert light straight run naphthas and similar mixtures to highly aromatic mixtures. Thus, normal and slightly branched chained hydrocarbons, preferably having a boiling range above about 40°C and less than about 250°C, can be converted to products having a substantial aromatics content by contacting the hydrocarbon feed with the zeolite at a temperature in the range of from about 400°C to 600°C, at pressures ranging from atmospheric to 20 atmospheres, LHSV ranging from 0.1 to 15, and a recycle hydrogen to hydrocarbon ratio of about 1 to 10.

The reforming catalyst preferably contains a Group VIII metal compound to have sufficient activity for commercial use. By Group VIII metal compound as used herein is meant the metal itself or a compound thereof. The Group VIII noble metals and their compounds, platinum, palladium, and iridium, or combinations thereof can be used. The most preferred metal is platinum. The amount of Group VIII metal present in the conversion catalyst should be within the normal range of use in reforming catalysts, from about 0.05 to 2.0 wt. percent, preferably 0.2 to 0.8 wt. percent. In addition, the catalyst can also contain a second Group VII metal. Especially preferred is rhenium.

The zeolite/Group VIII metal catalyst can be used with or without a binder or matrix. The preferred inorganic matrix, where one is used, is a silica-based binder such as Cab-O-Sil or Ludox. Other matrices such as alumina, magnesia and titania can be used. The preferred inorganic matrix is nonacidic.

It is critical to the selective production of aromatics in useful quantities that the conversion catalyst be substantially free of acidity, for example, by exchanging the sites in the zeolite with metal ions, e.g., Group I and Group II ions. The zeolite is usually prepared from mixtures containing alkali metal hydroxides and thus, have alkali metal contents of about 1-2 wt. %. These high levels of alkali metal, usually sodium or potassium, are unacceptable for most other catalytic applications because they greatly deactivate the catalyst for cracking reactions by reducing catalyst acidity. Therefore, the alkali metal is removed to low levels by ion exchange with hydrogen or ammonium ions. By alkali metals as used herein is meant ionic alkali metals or their basic compounds. Surprisingly, unless the zeolite itself is substantially free of acidity, the alkali metal is required in the present process to reduce acidity and improve aromatics production. Alkali metals are incorporated by impregnation or ion exchange using nitrate, chloride or carbonate salts.

The amount of alkali metal necessary to render the zeolites substantially free of acidity can be calculated using standard techniques based on the aluminum, gallium or iron content of the zeolites. If a zeolite free of alkali metal is the starting material, alkali metal ions can be ion exchanged into the zeolite to substantially eliminate the acidity of the zeolite. An alkali metal content of about 100%, or greater, of the acid sites calculated on a molar basis is sufficient.

Where the metal ion content is less than 100% of the acid sites on a molar basis, the test described in U.S. Patent No. 4,347,394, which patent is incorporated totally herein by reference, can be used to determine if the zeolite is substantially free of acidity.

The preferred alkali metals are sodium, potassium, and cesium, as well as other Groups IA and IIA metals. The zeolites can be substantially free of acidity only at very high silica:alumina mole ratios; by "zeolite consisting essentially of silica" is meant a zeolite which is substantially free of acidity without base poisoning.

A low sulfur feed is preferred in the reforming process; but due to the sulfur tolerance of these catalysts, feed desulfurization does not have to be as complete as with conventional reforming catalysts. The feed should contain less than 10 parts per million sulfur. In the case of a feed which is not low enough in sulfur, acceptable levels can be reached by hydrogenating the feed with a hydrogenating catalyst which is resistant to sulfur poisoning. An example of a suitable catalyst for this hydrodesulfurization process is an alumina-containing support and a minor catalytic proportion of molybdenum oxide, cobalt oxide and/or nickel oxide. A platinum on alumina hydrogenating catalyst can also work. In which case, a sulfur sorber is preferably placed downstream of the hydrogenating catalyst, but upstream of the present reforming catalyst. Examples of sulfur sorbers are alkali or alkaline earth metals on porous refractory inorganic oxides, zinc, etc. Hydrodesulfurization is typically conducted at 315-455°C, at 200-2000 psig, and at a LHSV of 1-5.

It is preferable to limit the nitrogen level and the water content of the feed. Catalysts and processes which are suitable for these purposes are known to those skilled in the art.

After a period of operation, the catalyst can become deactivated by coke. Coke can be removed by contacting the catalyst with an oxygen-containing gas at an elevated temperature. If the Group VIII metal(s) have agglomerated, then it can be redispersed by contacting the catalyst with a chlorine gas under conditions effective to redisperse the metal(s). The method of regenerating the catalyst may depend on whether there is a fixed bed, moving bed, or fluidized bed operation. Regeneration methods and conditions are well known in the art.

The reforming catalysts preferably contain a Group VIII metal compound to have sufficient activity for commercial use. By Group VIII metal compound as used herein is meant the metal itself or a compound thereof. The Group VIII noble metals and their compounds, platinum, palladium, and iridium, or combinations thereof can be used. Rhenium and tin may also be used in conjunction with the noble metal. The most preferred metal is platinum. The amount of Group VIII metal present in the conversion catalyst should be within the normal range of use in reforming catalysts, from about 0.05-2.0 wt. %.

Example 1

Preparation of Platinum-(B)SSZ-24

The borosilicate version of (B)SSZ-24 was prepared for use as a reforming catalyst. The zeolite powder was impregnated with $Pt(NH_3)_4 \cdot 2NO_3$ to give 0.8 wt. % Pt. The material was calcined up to 550°F in air and maintained at this temperature for three hours. The powder was pelletized on a Carver press at 1000 psi and broken and meshed to 24-40.

Example 2

Reforming Test Results

(B)SSZ-24 from Example 1 was tested as a reforming catalyst. The conditions for the reforming test were as follows. The catalyst was prereduced for 1 hour in flowing hydrogen at 950°F and atmospheric pressure. Test conditions were:

Total Pressure = 200 psig
H_2/HC Molar Ratio = 6.4
WHSV = 6 hr^{-1}

The catalyst was initially tested at 800°F and then at 900°F. The feed was an iC_7 mixture supplied by Philips Petroleum Company. The catalyst from Example 1 was tested with these results.

	Feed	Products	
Temperature, °F		800°F	900°F
Conversion %	0	79.6	100
Toluene, wt. %	0.5	22.1	21.9
C_5-C_8 Octane, RON	63.7	86.8	105.2
C_5+ Yield, wt. %	100	54.9	35.4
Aromatization Selectivity, %		32.1	30.2
Toluene in the C_5+ Aromatics %		86.6	72.7

As shown by the complete conversion, this catalyst is capable of converting all types of feedstock molecules.

Example 3

Preparation and Testing of a Neutralized Platinum-Aluminum-Boron SSZ-24

Aluminum was substituted into the borosilicate version of (B)SSZ-24 by refluxing the zeolite with an equal mass of $Al(NO_3)_3 \cdot 9H_2O$ overnight. Prior to use, the aluminum nitrate was dissolved in H_2O at a ratio of 50:1. The product contained acidity due to the aluminum incorporation, and this would lead to unacceptable cracking losses. Two back ion exchanges with KNO_3 were performed and the catalyst was calcined to 1000°F. Next, a reforming catalyst was prepared as in Example 1. It was tested as in Example 2.

	Feed	Products	
Temperature, °F		800	900
Conversion %	0	53.0	95.1
Toluene, wt. %	0.5	22.6	26.6
C_5-C_8 Octane, RON	63.7	78.1	99.6
C_5+ Yield, wt. %	100	81.5	46.2
Aromatization Selectivity, %		47.1	35.7
Toluene in the C_5+ Aromatics %		90.6	78.1

By comparison with Example 2, the incorporation of aluminum, accompanied by its neutralization, gives a less active, but more selective catalyst.

Example 4

Preparation and Testing of a Platinum-Boron-Beta Catalyst

The borosilicate version of boron beta was impregnated with $Pt(NH_3)_4 \cdot 2NO_3$ to give 0.8 wt. % Pt. The material was calcined up to 550°F in air and maintained at this temperature for three hours. The powder was pelletized on a Carver press at 1000 psi and broken and meshed to 24-40. The catalyst was tested as shown in Example 2 with the exception that operation at both 200 and 50 psig were explored.

Pressure, psig	200	50	200
Temperature, °F	800	800	900
Conversion %	88.8	77.0	100
Toluene, wt. %	19.1	39.3	16.9
C_5-C_8 Octane, RON	89.5	90.6	104.3
C_5+ Yield, wt. %	46.9	77.4	30.2
Aromatization Selectivity, %	25.4	54.5	25.3
Toluene in the C_5+ Aromatics %	84.9	93.7	67.8

The catalyst is quite stable and the values are averaged over at least 20 hours of run time.

Example 5

Preparation and Testing of a Platinum-Cobalt-Boron-Beta Catalyst

Cobalt was incorporated into the boron beta as described in Example 3 with $Co(NO_3)_2 \cdot 6H_2O$ as the cobalt source replacing

$Al(NO_3)_3 \cdot 9H_2O$ as the aluminum source in Example 3. The catalyst was calcined to 1000°F, and a Platinum reforming catalyst was prepared as described in Example 1. It was tested as described in Example 2 except the WHSV was 12 and operation at both 200 and 100 psig was evaluated.

Pressure, psig	200	100
Temperature, °F	800	800
Conversion %	83.3	86.0
Toluene, wt. %	18.8	27.3
C_5-C_8 Octane, RON	85.3	90.3
C_5+ Yield, wt. %	59.8	63.7
Aromatization Selectivity, %	27	37
Toluene in the C_5+ Aromatics %	83.3	85.9

By comparison with Example 4, the incorporating of cobalt gives a more active catalyst. The catalyst has good stability at 800°F.

Example 6

Preparation of Pt-SSZ-33

SSZ-33 was prepared for use as a reforming catalyst. The zeolite powder was impregnated with $Pt(NH_3)_4 \cdot 2NO_3$ to give 0.8 wt. % Pt. The material was calcined up to 550°F in air and maintained at this temperature for three hours. The powder was pelletized on a Carver press at 1000 psi and broken and screened to 24-40 mesh.

Example 7

Preparation of Pt-Zinc-SSZ-33

Zinc was incorporated into the novel large-pore borosilicate SSZ-33 by refluxing $Zn(Ac)_2 \cdot H_2O$ as described in Example 3. The product was washed, dried, and calcined to 1000°F, and then impregnated with $Pt(NH_3)_4 \cdot 2NO_3$ to give 0.8 wt.% Pt. The material was calcined up to 550°F in air and maintained at this temperature for three hours. The powder was pelletized on a Carver press at 1000 psig, broken, and meshed to 24-40. It was tested as described in Example 2. Results are as follows:

Pressure, psig	200
Temperature, °F	900
Conversion %	71.1
Toluene, wt. %	28
C_5-C_8 Octane, RON	85
C_5+ Yield, wt. %	74.2
Aromatization Selectivity, %	44.5
Toluene in the C_5+ Aromatics %	88.5

Example 8

Testing of Pt-SSZ-33 and Pt-Zinc-SSZ-33

The catalysts of Examples 6 and 7 were tested with a partially reformed naphtha at:

Total Pressure = 50 psig
H_2/HC Molar Ratio = 3
LHSV = 2 hr^{-1}

These conditions simulate use of the catalyst in the last reactor of a multi-stage reforming process. An analysis of the feed and products is shown below.

	Feed	Products	
Molecular Sieve		Pt-SSZ-33	Pt-Zn-SSZ-33
Temperature, °F		780	860
Composition, wt. %			
C_4-	0	13.4	9.4
C_5's Total	0	8.3	7.0
C_6 Paraffins	8.7	8.3	7.7
C_6 Naphthenes	1.0	0.9	0.9
Benzene	1.6	3.5	2.6

	Feed	Products	
C_7 Paraffins	8.6	2.9	4.5
C_7 Naphthenes	0.2	0.1	0
Toluene	8.8	13.3	11.6
C_8 Paraffins	5.8	0.5	0
C_8 Naphthenes	0.1	0	0
C_8 Aromatics	21.1	22.7	23.8
C_9 Paraffins	2.1	0	0
C_9+ Aromatics	32.3	26.4	31.4
Octane, RON	94.6	101.0	101.0
C_5+ Yield, LV% of the Feed	100.0	86.0	89.0

These examples illustrate the ability of both catalysts to upgrade partially reformed naphtha. Incorporation of zinc improves the liquid product selectivity, apparently by reducing dealkylation of existing aromatics.

Example 9

Comparison of Unsulfided and Sulfided Platinum Boron Beta

The borosilicate version of Beta was impregnated with $Pt(NH_3)_4{\cdot}2NO_3$ as in Example 4. The catalyst was sulfided at 950°F for 1 hour in the presence of hydrogen.

Test conditions were:

Temperature = 800°F
H_2/HC Molar Ratio = 6.4
WHSV = 6

	Unsulfided Pt/(B)beta		Sulfided Pt/(B)beta	
Pressure, psig	200	200	200	200
Time, hrs.	3	18	3	18
Feed Conversion, %	96.9	95.8	79.1	81.6
C_5+ Yield, wt. %	37.6	40.2	59.4	57.0
Calculated RON	93.0	92.8	87.5	88.4
Aromatization Selectivity, %	19.4	21.3	35.2	34.0

Example 10

Comparison of Sulfided Pt/(B)beta and Sulfided Pt/(B)beta with 52% SiO_2 Binder

800°F, 200 psig, 6 WHSV, 6.4 H_2:HC

	Pt/(B)beta		Bound Pt/(B)beta	
Time, hrs.	3	18	3	18
Feed Conversion, %	79.1	81.6	52.7	57.7
C_5+ Yield, wt. %	59.4	57.0	86.5	82.1
Calculated RON	87.5	88.4	79.5	80.2
Aromatization Selectivity	35.2	34.0	52.9	47.0

800°F, 50 psig, 6 WHSV, 6.4 H_2:HC

	Pt/(B)beta		Bound Pt/(B)beta	
Time, hrs.	3	18	3	18
Feed Conversion, %	87.9	86.5	62.6	61.5
C_5+ Yield, wt. %	64.3	66.0	84.4	85.0
Calculated RON	97.8	96.5	84.4	83.7
Aromatization Selectivity	50.8	51.5	56.3	55.5

Example 11

Comparison of Sulfided Pt/(B)beta and Sulfided Pt/Cs-(Al)-(B)beta

800°F, 200 psig, 6 WHSV, 6.4 H_2:HC*

	Pt/(B)beta	Pt/Cs-(Al)-(B)beta
Feed Conversion, %	79.6	48.0
C_5+ Yield, wt. %	59.7	93.7
Calculated RON	87.9	77.0
Propane + Butanes, wt. %	18.8	2.3
Toluene, wt. %	25.6	25.9
Arom. Selectivity	35.7	56.0

*Data averaged for first five hours.

800°F, 50 psig, 6 WHSV, 6.4 H_2:HC**

	Pt/(B)Beta		Pt/Cs-(Al)-(B)beta	
Time, hrs.	3	18	3	18
Feed Conversion, %	87.9	86.5	46.0	40.0
C_5+ Yield, wt. %	64.3	66.0	95.0	96.0
Calculated RON	97.8	96.5	77.0	74.5
Arom. Selectivity	50.8	51.5	59.5	58.0
Propane + Butanes, wt. %	31.4	28.1	3.3	2.5
Toluene, wt. %	42.0	41.8	26.0	22.0

**Interpolated data.

Example 12

Preparation and Testing of Pt-Boron-SSZ-31

The borosilicate version of SSZ-31 was prepared for use as a reforming catalyst. The zeolite powder was impregnated with $Pt(NH_3)_4 \cdot 2NO_3$ to give 0.7 wt. % Pt. The material was calcined up to 600°F in air and maintained at this temperature for three hours. The powder was pelletized on a Carver press at 1000 psi, broken, and screened to 24-40 mesh.

Pt-Boron-SSZ-31 was tested for reforming using an iC_7 feed mixture (Philips Petroleum Company) as follows:

Reaction Conditions	Run 1	Run 2
Temperature, °F	800	800
Total pressure, psig	200	50
H_2/Hydrocarbon Mole Ratio	6.4	6.4
Feed rate, WHSV, hr^{-1}	6	6

Results	Feed	Run 1	Run 2
Conversion, %	0	68.1	69.7
Aromatization Select.	0	39.4	54.7
Toluene, wt. %	0.7	24.6	36.0
C_5-C_8 Octane, RON	63.9	82.8	87.6

WHAT IS CLAIMED IS:

1. A catalytic reforming process which comprises contacting a hydrocarbonaceous feedstream under catalytic reforming conditions with a composition comprising large-pore borosilicate zeolites having a pore size greater than 6 and less than 8 angstroms.

2. A process in accordance with Claim 1 wherein said large-pore borosilicate zeolites contain less than 1000 parts per million aluminum.

3. A process in accordance with Claim 2 wherein said large-pore borosilicate zeolites are boron beta zeolite, boron SSZ-24, boron SSZ-31, and SSZ-33.

4. A process in accordance with Claims 1, 2 and 3 wherein the boron in the large-pore borosilicate zeolites is partially replaced by a Group IIIA metal, or a first row transition metal.

5. A process in accordance with Claim 4 wherein the replacing metal is cobalt, zinc, aluminum, gallium, iron, nickel, tin and titanium.

6. A process in accordance with Claims 1, 2, 3 and 4 wherein the hydrogenation/dehydrogenation component of said large-pore borosilicate zeolites is a Group VIII metal.

7. A process in accordance with Claim 6 wherein the hydrogenation/dehydrogenation component of said large-pore borosilicate zeolite comprises platinum.

8. A process in accordance with Claim 6 wherein said large-pore borosilicate zeolite contains an alkali metal component.

9. A process in accordance with Claims 1, 2, 3 and 4 wherein the hydrogenation/dehydrogenation component of said large-pore borosilicate zeolite comprises rhenium and platinum.

10. A process in accordance with Claims 1, 2, 3 and 4 wherein the hydrogenation/dehydrogenation component of said large-pore borosilicate zeolites comprises platinum and tin.

11. A process in accordance with Claims 1, 2 and 3 comprising using a fixed, moving or fluid bed reformer.

12. A process in accordance with Claims 1, 2 and 3 which is a multi-stage catalytic reforming process.

13. A process in accordance with Claim 12 where the large-pore borosilicate zeolite is used in the last reactor to convert the remaining light paraffins not converted by the Pt Re/Al_2O_3 or Pt Sn/Al_2O_3 catalysts used in the upstream reactors.

14. A process in accordance with Claim 12 where the large-pore borosilicate zeolite is used in the last stage of a multi-stage catalytic reforming process where the operating pressure of the last stage is much lower than the upstream stage.

15. A process in accordance with Claim 1 wherein the feedstream contains less than 1 part per million sulfur.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US90/03765

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): C10G 35/09
U.S. CL: 208/138

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	208/134,138

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	US, A, 4,268,420 KLOTZ 19 May 1981	1-15
A	US, A, 4,327,236 KLOTZ 27 April 1982	1-15
A	US, A, 4,584,089 UNMUTH ET AL. 22 April 1986	1-15
X	US, A, 4,839,027 ABSIL ET AL. 13 June 1989	1-15

* Special categories of cited documents: [15]

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
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- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 01 AUGUST 1990	Date of Mailing of this International Search Report [2] 11 MAR 1991
International Searching Authority [1] ISA/US	Signature of Authorized Officer [20] Ngoc Ho Nguyen NGUYEN NGOC-HO For CURTIS R. DAVIS INTERNATIONAL DIVISION

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