N-PARAFFIN SELECTIVE HYDROCONVERSION PROCESS USING BOROSILICATE ZSM-48 MOLECULAR SIEVES

FIELD OF THE INVENTION

The present invention is directed to borosilicate ZSM-48, methods for preparing borosilicate ZSM-48, and uses for borosilicate ZSM-48.

BACKGROUND OF THE INVENTION

C_{5+} liquids rich in normal paraffins (*n*-paraffins) are ideally suited for several applications, including use as solvents, feedstocks for ethylene production, jet fuel and jet fuel blend components, diesel fuel and diesel fuel blend components, feedstocks for isomerization to make lubricants, and the like.

Historically, C_{5+} liquids rich in normal paraffins have been prepared by selectively extracting normal paraffins from mixtures, such as petroleum. This operation is relatively expensive and is limited to the content of normal paraffins in the feedstock.

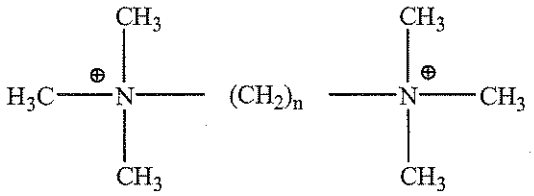
Normal paraffins can also be produced in a Fischer-Tropsch process. However, the Fischer-Tropsch process also generates heavy products that can fall outside the range of use for the above applications. If these heavy products are converted into lighter products by hydrocracking over conventional acidic catalysts, an isoparaffin-rich product will be obtained, instead of the desired normal paraffin-rich product.

Accordingly, there is a continuing need for new catalyst compositions suitable for use in hydrocarbon conversion processes, including catalysts which are *n*-paraffin selective.

SUMMARY OF THE ~~INVENTION~~DISCLOSURE

In accordance with the present ~~invention~~disclosure there is provided a borosilicate ZSM-48 molecular sieve having a mole ratio of between 40 and 400 of silicon oxide to boron oxide and having, after calcination, the powder X-ray diffraction (XRD) lines of Table 4.

The present ~~invention~~disclosure also includes a method for preparing a borosilicate ZSM-48 by contacting under crystallization conditions: (1) at least one source of silicon oxide; (2) at least one source of boron oxide; (3) at least one source of an element selected from Groups 1 and 2 of the Periodic Table; (4) hydroxide ions; and (5) a structure directing agent selected from dications represented by the following structure (1):



(1)

wherein n is an integer of from 8 to 12, inclusive.

The present ~~invention~~disclosure also includes a borosilicate ZSM-48 having a mole ratio of between 40 and 400 of silicon oxide to boron oxide and having, after calcination, the powder XRD lines of Table 4 herein below, wherein the molecular sieve is prepared by contacting under crystallization conditions: (1) at least one source of silicon oxide; (2) at least one source of boron oxide; (3) at least one source of an element selected from Groups 1 and 2 of the Periodic Table; (4) hydroxide ions; and (5) a structure directing agent selected from dications represented by structure (1), wherein n is an integer of from 8 to 12, inclusive.

The present ~~invention~~disclosure also includes a borosilicate ZSM-48 having a composition, as-synthesized and in the anhydrous state, in terms of mole ratios, as follows:

	Broad	Preferred
SiO_2/B_2O_3	40 - 400	40 - 200
Q/SiO_2	0.01 - 0.05	0.01 - 0.04

wherein Q is a structure directing agent represented by structure (1).

Where the molecular sieve formed is an intermediate material, the process of the present ~~invention~~disclosure includes a further post-synthesis processing in order to achieve the target molecular sieve.

In another aspect, the present ~~invention~~disclosure includes a process for converting hydrocarbons by contacting a hydrocarbonaceous feed under hydrocarbon converting conditions with a borosilicate ZSM-48 molecular sieve having a mole ratio of between 40 and 400 of silicon oxide to boron oxide and having, after calcination, the powder XRD lines of Table 4.

In one aspect, there is provided a process for converting a hydrocarbonaceous feed comprising contacting the feed with a borosilicate ZSM-48 molecular sieve under hydrocarbon converting conditions, the borosilicate ZSM-48 molecular sieve having a mole ratio of between 40 and 400 of silicon oxide to boron oxide and having, after calcination, an X-ray diffraction pattern substantially as shown in the following Table:

2 Theta	d-spacing (Angstroms)	Relative Absolute Intensity (%)
7.6 ± 0.30	11.56	W
8.5 ± 0.30	10.38	W
15.2 ± 0.30	5.83	W
21.5 ± 0.30	4.14	S
23.1 ± 0.30	3.84	S
24.5 ± 0.30	3.63	W
25.0 ± 0.30	3.56	W
31.7 ± 0.30	2.82	W

In another aspect, the present ~~invention~~disclosure provides a process for hydroconverting hydrocarbons, the process comprising contacting a hydrocarbonaceous feed under hydrocarbon converting conditions with a borosilicate ZSM-48 molecular sieve having a mole ratio of between 40 and 400 of silicon oxide to boron oxide and having, after

calcination, the powder XRD lines of Table 4 herein below, wherein the molecular sieve is prepared by contacting under crystallization conditions (1) at least one source of silicon oxide; (2) at least one source of boron oxide; (3) at least one source of an element selected from Groups 1 and 2 of the Periodic Table; (4) hydroxide ions; and (5) a structure directing agent selected from dications represented by structure (1), wherein n is an integer of from 8 to 12, inclusive.

In accordance with the present ~~invention~~disclosure, there is further provided a process for selectively hydroconverting C_{10+} *n*-paraffins in a hydrocarbonaceous feed to *n*-paraffin products lower in molecular weight than the C_{10+} *n*-paraffins in the feed by contacting the feed with hydrogen and an *n*-paraffin selective hydroconversion catalyst containing borosilicate ZSM-48 having a mole ratio of between 40 and 400 of silicon oxide to boron oxide and having, after calcination, the powder XRD lines of Table 4. As a non-limiting example, the feed may be contacted with the catalyst under the following conditions: a temperature from about 320°C to 420°C, a pressure between 50 and 5000 psig, and a liquid hourly space velocity (LHSV) between 0.5 and 5. The hydrocarbonaceous feed will typically contain more than about 5 wt% C_{10+} normal paraffins, usually more than about 50 wt% C_{10+} normal paraffins, and often more than about 80 wt% C_{10+} normal paraffins.

In one aspect, there is provided a process for hydroconverting a hydrocarbonaceous feed which comprises C_{14+} *n*-paraffins, the process comprising contacting the feed in the presence of hydrogen and under conditions comprising:

a) a temperature between about 320°C and 420°C,

b) a pressure between about 50 and 5000 psig, and

c) a liquid hourly space velocity between about 0.5 and 5

with a catalyst comprising borosilicate ZSM-48 and a Group 8 - 10 metal to produce a product comprising *n*-paraffin products lower in molecular weight than the C_{14+} *n*-paraffins in the feed, the borosilicate ZSM-48 molecular sieve having a mole ratio of between 40 and 400 of silicon oxide to boron oxide and having, after calcination, an X-ray diffraction pattern substantially as shown in the following Table:

2 Theta	d-spacing (Angstroms)	Relative Absolute Intensity (%)
7.6 ± 0.30	11.56	W
8.5 ± 0.30	10.38	W
15.2 ± 0.30	5.83	W
21.5 ± 0.30	4.14	S
23.1 ± 0.30	3.84	S
24.5 ± 0.30	3.63	W
25.0 ± 0.30	3.56	W
31.7 ± 0.30	2.82	W

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a powder x-ray diffraction pattern of a borosilicate ZSM-48 prepared according to Example 1 of the present invention;

Figure 2 is a scanning electron micrograph of the borosilicate ZSM-48 prepared according to Example 1 of the present invention;

Figure 3 shows a powder x-ray diffraction pattern of the borosilicate ZSM-48 prepared according to Example 2 of the present invention;

Figures 4A and 4B each show a scanning electron micrograph of the borosilicate ZSM-48 prepared according to Example 2 of the present invention;

Figure 5 shows a powder x-ray diffraction pattern of the borosilicate ZSM-48 prepared according to Example 4 of the present invention;

Figures 6A and 6B each show a scanning electron micrograph of the borosilicate ZSM-48 prepared according to Example 4 of the present invention;