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(54) **Process for increasing the aromaticity of a hydrocarbonaceous feedstock.**

(57) Process for increasing the aromaticity of a hydrocarbonaceous feedstock comprising hydrocarbons of the C_1-C_{12} range which process comprises contacting the feedstock at a temperature of 450 to 700 °C and a pressure of 1 to 40 bar with a ferrierite catalyst having a SiO_2/Al_2O_3 molar ratio greater than 25.

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The present invention relates to a process for increasing the aromaticity of a hydrocarbonaceous feedstock wherein use is made of a ferrierite catalyst.

A typical example of a catalytic application of a ferrierite type of catalyst is the so-called hydrodewaxing process of highly paraffinic feedstocks, wherein the paraffinic content of the feedstock is considerably reduced. Another application is for instance the upgrading of naphthas. The ferrierite catalyst to be applied in such an upgrading process has typically a low SiO_2/Al_2O_3 molar ratio.

It has now been found that a ferrierite catalyst having a high SiO_2/Al_2O_3 molar ratio can very attractively be applied for increasing the aromaticity of a relatively light hydrocarbonaceous feedstock.

Accordingly, the present invention relates to a process for increasing the aromaticity of a hydrocarbonaceous feedstock comprising hydrocarbons of the C_1-C_{12} range which process comprises contacting the feedstock at a temperature of 450 to 700 °C and a pressure of 1 to 40 bar with a ferrierite catalyst having a SiO_2/Al_2O_3 molar ratio greater than 25.

In this way a very attractive yield of aromatics can be obtained. Moreover, the ferrierite catalyst applied has a high stability, i.e. the process according to the present invention can be carried out for a long time before the catalytic activity of the catalyst substantially decreases.

Suitably, the ferrierite catalyst to be applied has a SiO_2/Al_2O_3 molar ratio up to 120.

Preferably, the ferrierite catalyst to be applied in the process according to the present invention has a SiO_2/Al_2O_3 molar ratio of 50 to 90.

If desired, the ferrierite catalyst may contain one or more hydrogenation metal components.

Preferably, the ferrierite catalyst to be applied in the process according to the present invention is substantially in its hydrogen form.

It should be noted that in the context of the present invention the term ferrierite catalyst includes apart from ferrierite as such other tectometallosilicates having a ferrierite structure. Such tectometallosilicates include FU-9, ISI-6, Nu-23, ZSM-21, ZSM-35 and ZSM-38. However, ferrierite as such is preferred.

The hydrocarbonaceous feedstock to be subjected to the process according to the present invention is preferably a hydrocarbonaceous feedstock comprising hydrocarbons of the C_5-C_{12} range.

Preferably, the hydrocarbonaceous feedstock comprises a hydrocarbon mixture boiling in the gasoline range. Suitably, the hydrocarbonaceous feedstock comprises essentially a hydrocarbonaceous feedstock boiling in the gasoline range.

The hydrocarbon mixture boiling in the gasoline range is preferably obtained by catalytic cracking although it may be obtained by other cracking processes such as thermal cracking, delayed coking, visbreaking and flexicoking. Such a gasoline feedstock may contain substantial amounts of sulphur, for instance more than 250 ppmw.

While the full gasoline range fraction from a a catalytic cracking reactor may be included in the feedstock, it is preferred to employ as hydrocarbon mixture a cut thereof substantially boiling in the range of 70 to 220 °C, preferably in the range of 70 to 180 °C

Other suitable feedstocks to be processed in accordance with the present invention comprise substantially naphthenes-containing hydrocarbon mixtures, for instance straight-run naphthas, or mixtures of hydrocarbonaceous material which may be derived from a cracking process and substantially naphthenes-containing hydrocarbonaceous material.

Suitably, a further gas fraction comprising hydrocarbons of the C_1-C_4 range is co-processed with the hydrocarbonaceous feedstock. Preferably, such a gas fraction is recovered from the process according to the present invention. In other words the gas fraction recovered from the process according to the present invention can suitably be recycled to the reaction zone comprising the ferrierite catalyst. In this way an even more attractive yield of aromatics is obtained.

Preferably, the process according to the present invention is carried out at a temperature of from 450-650 °C and a pressure of from 1-40 bar.

More preferably, the process according to the present invention is carried out at a temperature up to 550 °C and a pressure of from 3 to 20 bar.

Although the process according to the present invention is essentially carried out in the absence of hydrogen it should be noted that a small amount of hydrogen may be present in order to reduce the coke make on the ferrierite catalyst.

Suitably, at least part of the effluent recovered therefrom is subsequently subjected to a hydrotreating step. In this way sulphur-containing feedstocks can very attractively be upgraded in respect of both aromatics and sulphur content.

Suitably, in the hydrotreating step use can be made of an alumina-containing catalyst, for instance a silica-alumina-containing catalyst having both desulphurization and denitrogenation activity. Preferably, use is made in the hydrotreating step of a metal-containing alumina catalyst, whereby the metal is at least one

of the Group VIB and/or Group VIII metals, preferably at least one of the metals Ni, Co or Mo. The catalysts which can suitably be used in the hydrotreating step comprise commercially available catalysts and can be prepared by methods known in the art. The hydrotreating step can suitably be carried out at a temperature of 230 to 370 °C and a hydrogen partial pressure of 2 to 30 bar.

Both process steps can be carried out using a series of reactors or in a stacked-bed configuration. Use of a series of reactors is preferred.

The ferrierite catalyst to be used in the process according to the present invention can be subjected to a regeneration treatment, for instance a semi-continuous regeneration.

The present invention will now be illustrated by means of the following Examples.

Example 1 - Catalyst A

Commercially available ferrierite ex Toya Soda, which ferrierite was in the ammonium form and had a SiO_2/Al_2O_3 molar ratio of 18, was pressed, crushed and sieved to obtain a 30-80 mesh size fraction. The particles thus obtained were calcined for 2 hours at 540 °C.

Example 2 - Catalyst B

544 g silica gel was combined with a solution of 54 g sodium hydroxide in 1000 g water and the resulting mixture was homogenized. A second solution comprising 61.4 g aluminium sulphate ($Al_2(SO_4)_3.18 H_2O$), 256 g sodium sulphate and 1000 g water was added under stirring. Finally, 218 g pyridine dissolved in 1152 g water were admixed giving a reaction gel of the composition (on molar basis) 93.5 SiO_2 . 1 Al_2O_3 . 7.4 Na_2O . 19.6 Na_2SO_4 . 30 pyridine . 1938 H_2O. This reaction gel was kept at 150 °C for a period of 75 hours until a crystalline compound was obtained. After synthesis the crystalline compound produced was separated from the reaction mixture by filtration, water washed and dried at 120 °C.

The dried compound was calcined at 500 °C, cooled down and ion exchanged such that the compound is brought in the ammonium form. The solid product was separated from the liquid by filtration, water washed, dried at 120 °C and subsequently calcined at 500 °C.

The product of the synthesis was determined by X-ray diffraction to be essentially ferrierite. The SiO_2/Al_2O_3 molar ratio was found to be 72. Before employment in the process according to the present invention the ferrierite powder was pressed, crushed and sieved in order to obtain a 30-80 mesh fraction.

Example 3 - Aromatization

Catalysts A and B were employed in the aromatization of catalytically cracked gasoline having the following properties:

Boiling range	85 - 175 °C
Total olefins (%wt)	19.2
Total saturates (%wt)	44.5
Total aromatics (%wt)	36.3
Sulphur (ppmw)	1260
Nitrogen (ppmw)	30

The experiments were conducted in a microflow fixed bed reactor in a once-through operation. The experiments were carried out at a temperature of 500 °C, a pressure of 20 bar and a space velocity of 0.5 kg/kg/hr. The catalyst particles were diluted with an equal volume of 0.1 mm SiC particles. The amounts of coke make (%wof) and the stabilities of the catalysts, in terms of aromatics content (%wt) in the product obtained, have been depicted in Table 1 as function of run time.

Table 1

	Catalyst A	Catalyst B
run time		
10 hr		
aromatics (%wt)	75	66
20 hr		
aromatics (%wt)	59	64
50 hr		
aromatics (%wt)	52	62
100 hr		
coke make (%wof)	1	1
aromatics (%wt)	51	62

From the above it will be clear that catalyst B deactivates at a far lower rate than catalyst A, whereas the coke make is substantially the same.

Claims

1. Process for increasing the aromaticity of a hydrocarbonaceous feedstock comprising hydrocarbons of the C_1-C_{12} range which process comprises contacting the feedstock at a temperature of 450 to 700 °C and a pressure of 1 to 40 bar with a ferrierite catalyst having a SiO_2/Al_2O_3 molar ratio greater than 25.

2. Process according to claim 1, wherein the ferrierite catalyst has a SiO_2/Al_2O_3 molar ratio up to 120.

3. Process according to claim 2, wherein the ferrierite catalyst has a SiO_2/Al_2O_3 molar ratio of 50 to 90.

4. Process according to any one of claims 1-3, wherein the ferrierite catalyst is substantially in its hydrogen form.

5. Process according to any one of claims 1-4, wherein the feedstock comprises hydrocarbons of the C_5-C_{12} range.

6. Process according to claim 5, wherein the feedstock comprises a hydrocarbon mixture substantially boiling in the gasoline range.

7. Process according to any one of claims 1-6, wherein a gas fraction comprising hydrocarbons of the C_1-C_4 range is co-processed with the feedstock which gas fraction has been recovered from any of the processes as defined hereinabove.

8. Process according to any one of claims 1-7, wherein the contacting is carried out at a temperature of from 450-650 °C and a pressure of from 1 to 40 bar.

9. Process according to claim 8, wherein the contacting is carried out at a temperature up to 550 °C and a pressure of from 3 to 20 bar.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 20 3335

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 327 764 (BP) * column 1, line 33 - line 43; claims 1-9 * ---	1-9	C10G35/095
X	US-A-4 323 481 (STANDARD OIL) * column 8, line 31 - line 39; claims 1,2,12-20 * ---	1-9	
X	US-A-4 292 167 (MOBIL OIL) * claims 1,6,8 * ---	1-9	
A	WO-A-8 904 860 (MOBIL OIL) * page 6, line 25 - line 31; claims 1,7,9 * ---	1-9	
A	US-A-3 890 218 (MOBIL OIL) ---		
P,X	EP-A-0 466 318 (BP) * the whole document * -----	1-9	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C10G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	03 FEBRUARY 1993	MICHIELS P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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