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CATALYTICALLY CONVERTING A HYDROCARBONACEOUS FEED

The present invention relates to a process for the catalytic conversion of a hydrocarbonaceous feed comprising contacting the hydrocarbonaceous feed in a moving-bed reactor with particulate catalyst, to obtain reactor effluent and spent catalyst, separating spent catalyst from reactor effluent, regenerating spent catalyst in a regenerator by contacting spent catalyst with air under conditions to combust coke deposited on the catalyst to obtain regenerated catalyst which is supplied to the moving-bed reactor.

Such a process is called a fluid catalytic cracking process (FCC). In such a process the hydrocarbonaceous feed is catalytically converted into lighter cracked products which find application, for example, as motor fuels, diesel fuels, oils and chemical feedstocks. In the FCC process, the feed is contacted at elevated temperatures in the range of from 450 to 800 °C and a pressure in the range of from 0.1 to 1 MPa with a suitable particulate catalyst. The mass ratio of catalyst used relative to the feed to be converted is suitably in the range of from 3:1 to 100:1, and the contact time is suitably less than 10 seconds. The particulate catalyst suitably includes acidic molecular sieve crystals, clay and a binder. Such a catalyst is well known as such; a description of the catalyst can, for example, be found in Applicant's co-pending European patent application No. 95 201 948.7 filed on 14 July 1995. In the specification the term "molecular sieve catalyst" will be used to refer to this particulate catalyst.

In recent years it has become common practice to convert increasingly high boiling range hydrocarbonaceous

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feeds, which contain small amounts of metals such as nickel and vanadium. These metals will deposit on the catalyst particles in the coke formed in the conversion. When during regeneration coke is combusted, the metals are retained on the catalyst particles. Vanadium has a detrimental effect on the stability of the molecular sieve employed in the catalyst, whereas nickel is detrimental for the coke selectivity and hydrogen make in that with an increasing nickel content more gaseous products, hydrogen and light hydrocarbons such as methane, are formed and more coke is deposited on the catalyst particles.

Applicant's co-pending European patent application No. 95 201 948.7 filed on 14 July 1995 relates to a process for the catalytic conversion of a hydrocarbonaceous feed comprising contacting the hydrocarbonaceous feed in a moving-bed reactor with particulate catalyst. The catalyst particles comprise a core surrounded by a shell, wherein the core is a molecular sieve catalyst, and wherein the shell comprises a substantially non-acidic meso- or macroporous oxidic or oxyanionic material.

These catalyst particles were prepared by contacting freshly prepared molecular sieve catalyst particles with a coating fluid containing precursors of a substantially non-acidic meso- or macroporous oxidic or oxyanionic material.

Applicant now had found that during the FCC process the detrimental effect of an accumulation of metals which takes place can be countered when spent catalyst is treated with this coating fluid.

Therefore the present invention relates to a process for the catalytic conversion of a hydrocarbonaceous feed comprising contacting the hydrocarbonaceous feed in a moving-bed reactor with particulate catalyst, to obtain

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reactor effluent and spent catalyst, separating spent catalyst from reactor effluent, regenerating spent catalyst in a regenerator by contacting spent catalyst with air under conditions to combust coke deposited on the catalyst to obtain regenerated catalyst which is supplied to the moving-bed reactor, wherein at regular intervals spent catalyst or regenerated catalyst is contacted with a coating fluid comprising precursors of a substantially non-acidic meso- or macroporous oxidic or oxyanionic material.

The coating fluid is a suspension of the precursor in a gas or in a liquid solvent, and suitably it is a colloidal dispersion of the precursor, which dispersion is also referred to as an aerosol (dispersion of solids in a gas) or a sol (dispersion of solids in a liquid solvent).

During coating the catalyst particles are hot, and when the hot particles are contacted with the coating fluid in the form of a dispersion of precursor in gas, the precursor will be deposited on the catalyst particles and a shell of a substantially non-acidic meso- or macroporous oxidic or oxyanionic material is formed. When the hot catalyst particles are coated with the coating fluid, the solvent will evaporate and a shell of a substantially non-acidic meso- or macroporous oxidic or oxyanionic material is formed.

The amount of coating fluid should be so selected that sufficient precursor is available to obtain a shell having a thickness in the range of from 0.05 to 20 micrometer.

Suitable non-acidic mesoporous oxidic or oxyanionic material include non-acidic oxidic or oxyanionic compounds of elements selected from groups 2A, 2B, 3A, 3B, 4A, 4B and the lanthanide series of the Periodic Table of Elements, for example clays such as kaolin and

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meta-kaolin, alumina, silica, magnesia, calcia, titania, zirconia, yttria, ceria, lanthana, tin oxide, aluminium phosphate, magnesium aluminate, and mixtures thereof. Examples of macroporous oxidic or oxyanionic material
5 include alpha-alumina and silica, for example in the form of amorphous silica.

In the specification and in the claims the term "microporous material" is used to refer to a material having pore sizes of smaller than 1.0 nm (nanometer) and
10 suitably in the range of from 0.3 to 0.9 nm, the term "macroporous material" is used to refer to a material having pore sizes greater than 50 nm and suitably greater than 100 nm, and the term "mesoporous material" is used to refer to a material having pore sizes which are
15 between the pore sizes of microporous material and the pore size of macroporous material.

The spent or regenerated catalyst particles can be contacted with the coating liquid in several ways, the coating liquid can be sprayed into the regenerator or it
20 can be injected into the transport conduits extending the reactor and the regenerator.

Alternatively a side-stream of regenerated catalyst can be removed from the regenerator and passed to a separate vessel provided with means to create, during
25 normal operation, a fluidized bed in the vessel. The coating liquid is then sprayed into the vessel and coated catalyst particles are withdrawn from the vessel.

In examples 1A through 1J of Applicant's co-pending European patent application No. 95 201 948.7 and in the
30 below example coating liquids are described which can be used in the present invention. With this information a skilled person will be able to prepare a coating liquid that will yield the substantially non-acidic meso- or macroporous oxidic or oxyanionic material under the
35 conditions prevailing in his FCC process.

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The invention will now be described by way of example in more detail with reference to the following examples.

In the examples particulate catalyst was contacted with a feed described in Table 1 in a micro-activity testing unit at a temperature of 540 °C and at atmospheric pressure.

Table 1. Composition of the feed used in the examples, in the Table, %m denotes per cent by mass and ppmm denotes parts per million based on mass.

Gravity, API	21.8
Hydrogen, %m	12.3
Sulphur, %m	0.85
Nitrogen, %m	0.20
Vanadium, ppmm	8.60
Nickel, ppmm	4.10
Conradson Carbon, %m	3.66
Kinematic viscosity at 100°C, mm ² /s	16.2
Aromatic Carbon, %m	15.5

In the examples use was made of spent catalyst, in the form of the Advance R927 catalyst from AKZO Nobel, which had been sampled from a commercial FCC unit. The spent catalyst contained approximately 1 %m of coke. A batch of this spent catalyst was used as such in the example not according to the invention, and in the example according to the invention a batch of this spent catalyst coated with silica was used (this catalyst is referred to as coated spent cat).

Prior to the test in the micro-activity testing unit the spent catalyst was treated at 600 °C in air to remove hydrocarbonaceous deposits.

The coating procedure to manufacture the coated spent catalyst was as follows. An amount of 400 gram the spent catalyst was loaded in a spray coating apparatus, model

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STREA-1 manufactured by Niro-Aeromatic Fielder. The solids were fluidized in an air flow having a temperature of 80 °C at the inlet. An amount of 354 gram of an aqueous silica sol, Nyacol 2040NH4 (containing 40 %m of silica), was sprayed into the fluidized bed at a rate of 600 ml/minute using an atomizing pressure of 2 bar to spray the liquid through a nozzle having an outlet opening with a diameter of 0.5 mm. The product was dried in a separate furnace at 120 °C in air for 2 hours and subsequently calcined for 2 hours at 550 °C in air, followed by a treatment at 600 °C in air to remove any hydrocarbonaceous deposits. The product so obtained is the coated spent catalyst sample according to the invention.

The effect of the coating is a reduced coke yield and a reduced yield of gaseous components, hydrogen and methane, as can be seen from Tables 2 and 3.

Table 2. Coke yield as a function of the mass ratio of catalyst to the feed (C/O in kg/kg), wherein the coke yield is in %m based on the mass of the feed.

C/O	Coke yield	
	Spent catalyst	Coated spent cat
1.87	7.14	--
1.95	--	7.76
2.62	--	7.83
2.74	8.26	--
3.54	--	9.03
3.83	9.55	--
4.59	11.1	--
4.81	--	11.0
5.60	12.8	--
6.70	--	13.4

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Table 3. Ratio of hydrogen yield to methane yield as a function of the net conversion, which is the sum of yield of gaseous components and gasoline (in %m, based on the feed).

Net conversion	hydrogen yield to methane yield	
	Spent catalyst	Coated spent cat
35.24	0.5128	--
37.55	--	0.4359
42.99	0.5714	--
44.07	--	0.5102
51.66	--	0.5728
51.78	0.6549	--
55.82	0.6667	--
57.06	--	0.6102
58.03	0.6763	--
62.22	--	0.6258

- 5 Tables 2 and 3 clearly illustrate the beneficial effect of coating spent catalyst during the FCC process.

C L A I M S

1. Process for the catalytic conversion of a hydrocarbonaceous feed comprising contacting the hydrocarbonaceous feed in a moving-bed reactor with particulate catalyst, to obtain reactor effluent and
5 spent catalyst, separating spent catalyst from reactor effluent, regenerating spent catalyst in a regenerator by contacting spent catalyst with air under conditions to combust coke deposited on the catalyst to obtain
10 regenerated catalyst which is supplied to the moving-bed reactor, wherein at regular intervals spent catalyst or regenerated catalyst is contacted with a coating fluid comprising precursors of a substantially non-acidic meso- or macroporous oxidic or oxyanionic material.