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(71) Applicants (for all designated States except US): **BP OIL INTERNATIONAL LIMITED** [GB/GB]; Chertsey Road, Sunbury-on-thames, Middlesex TW16 7BP (GB). **BP CORPORATION NORTH AMERICA INC.** [US/US]; 4101 Winfield Road, Warrenville, IL 60555 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **CORMA CANOS, Avelino** [ES/ES]; 4101 Winfield Road, Mc 5 East, Warrenville, IL 60555 (US). **RUNDELL, Douglas** [US/US]; 4101 Winfield Road, Mc 5 East, Warrenville, IL 60555 (US). **SAUVANAUD, Laurent, Louis Andre** [FR/ES]; 4101 Winfield Road, Mc 5 East, Warrenville, IL 60555 (US). **YALURIS, George** [US/US]; 4101 Winfield Road, Mc 5 East, Warrenville, IL 60555 (US).

(74) Agent: **SCHOETTLE, Ekkehard**; Bp America Inc., 4101 Winfield Road, Warrenville, IL 60555 (US).

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(54) Title: PROCESS FOR REGENERATING COKED PARTICLES

(57) Abstract: A process for regenerating coked particles, which process comprises contacting a hydrocarbon feedstock with solid particles in a reaction zone to produce coked particles, which coked particles are transferred to a regeneration zone in which they are contacted with steam to produce hydrogen and at least one or more oxides of carbon, wherein the solid particles comprise one or more of the following components: (i) an aluminosilicate zeolite comprising one or more of Mn, Ti and Zn; (ii) a Ce-containing aluminosilicate zeolite with a Ce loading of at least 0.05wt% and/or a molar ratio of total other rare earth elements : Ce in the range of from 0:1 to 5:1; (iii) a magnesium and aluminium-containing anionic clay; (iv) a material with the Perovskite structure.

PROCESS FOR REGENERATING COKED PARTICLES

This invention relates to a method of regenerating coked particles, and more specifically to a method of regenerating coked particles in processes such as hydrocarbon coking and catalytic cracking.

The upgrading of low value, high boiling point fractions of crude oil into lower boiling point hydrocarbons, which can be used in the production of higher value fuels such as gasoline, diesel and kerosene is an important aspect of crude oil refining, and a number of hydrocarbon coking and cracking processes have been developed in order to achieve this aim. Such processes are becoming increasingly important in the exploitation of heavy crude oil sources, such as tar sands and shale oils, and also in processing heavy crudes that are extracted from mature and declining oil wells.

Examples of coking and cracking processes commonly used in crude oil refineries include fluidised catalytic cracking (FCC), hydrocracking, delayed coking, visbreaking, flexicoking and fluid coking. A number of these processes are described in the Kirk-Othmer Encyclopaedia of Chemical Technology, Third Edition, volume 17, pages 205-217.

Coking processes are generally used to upgrade very heavy, low value fractions such as vacuum residues having high Conradson carbon content, typically above 5wt%, to produce lighter hydrocarbon components and coke. In fluid coking, for example, the hydrocarbon feedstock is sprayed into a reactor comprising a fluidised bed of hot particles. On contact with the particles, the hydrocarbon undergoes a cracking reaction to produce light hydrocarbons such as C₁ to C₄ hydrocarbons, naphtha, distillates, and the additional formation of coke, which is subsequently removed. Often the added particles are coke particles, a portion of which can be ground to an appropriate size and returned to the coking reactor. Alternatively, or additionally, particles such as silica or sand particles can be used which are regenerated to remove coke before being returned to the coking reactor, as described for example in GB 792,763. In flexicoking, the coke and/or coked particles are gasified by contact with steam and/or oxygen in a regeneration zone, as described in the Kirk-Othmer Encyclopaedia of Chemical Technology, Vol 17, Third Edition, page 214.

Catalytic cracking processes, such as FCC, typically involve contacting the hydrocarbon feedstock with a solid acid catalyst at high temperature, which results in their

catalytic decomposition into smaller hydrocarbons. The hydrocarbon feedstocks are typically lighter than those used for coking processes, having a lower Conradson carbon content, for example heavy gas oils or vacuum gas oils, or even some of the heavier gas oils produced in the aforementioned coking reactions.

5 In a typical FCC process, the catalyst is lifted up through the cracking reactor (also known as a "riser") by the action of vapourised hydrocarbons in the feedstock, and also by the co-feeding of a fluidising or lifting gas. The smaller, lower boiling hydrocarbons leave the reactor together with the fluidising gas, where they are separated and typically further processed to produce fuel stocks. Another product of the reaction is solid carbonaceous
10 residue, or coke, some of which deposits on the catalyst and contributes to its deactivation. To regenerate the catalyst, FCC processes typically remove catalyst from the reactor and feed it to a regenerator, where the coke is removed. Optionally, the catalyst undergoes a stripping step before being fed to the regeneration zone to remove any adsorbed product or unreacted hydrocarbons, which would otherwise reduce yields if left on the catalyst and fed
15 to the regenerator.

Typically, in FCC and coking processes, coke is removed from catalyst particles by combustion in the presence of oxygen to produce predominantly carbon dioxide (CO₂). Heat generated by the combustion can be used to balance heat lost from the process during the endothermic cracking reactions. However, where large quantities of coke are formed,
20 for example when processing oils having a high Conradson carbon content (which can be measured using analytical method ASTM D-189), the heat produced on combustion can rise to levels which can damage or destroy the catalyst and associated reactor equipment. Additionally, the regeneration unit may not be able to supply the quantity of oxygen required to oxidise the large quantity of coke on the catalyst. Therefore, processing of such
25 oils cannot easily be achieved without either limiting the quantity of catalyst regenerated, or diluting the feedstock with oils having lower coking potential, for example feedstocks with lower Conradson carbon values.

One reported method of reducing heat generation is described in US 4,888,156, which relates to the use of so-called catalyst coolers, in which the regenerator comprises
30 heat exchange tubes that remove heat from the process, for example using a water coolant.

Yet another way to reduce the quantity of heat generated in the regeneration zone is to use a lean oxygen supply, such that only partial combustion of the coke occurs to

produce carbon monoxide (CO). The CO produced can be further combusted in a separate reactor to produce CO₂ and additional heat, without causing catalyst damage. The additional heat from this second oxidation or combustion can be captured, for example through heating a steam supply. US 6,660,683 provides a summary of the different types of oxidation mode that can be used in regenerating FCC catalysts.

A further process involving the use of combustion for regenerating coked catalyst is described by Hedrick et al, the Annual Meeting of the National Petrochemical and Refiners Association March 19-21 2006, who describe a process for upgrading heavy crude oils for distribution through a pipeline by catalytically cracking a portion of the heavy crude to produce lower boiling point hydrocarbons, which are blended (or "cut") with the crude oil to improve its flow properties. The coked catalyst is regenerated by combustion or partial oxidation and recycled. Additionally, in US 2007/0034550, a process for improving flow properties of crude oil is described, in which a first crude stream is processed, including cracking in the presence of catalyst, in which the cracked stream is mixed with a second, unprocessed crude stream to increase the API value. The spent catalyst is regenerated by oxidation before recycle.

In the aforementioned cases, the main product of coke removal is CO₂, a so-called greenhouse gas, which is typically released into the atmosphere. It would be advantageous if the release of carbon dioxide into the atmosphere could be reduced. It would also be advantageous if the coke regeneration produced useful products that could be used in other processes, for example as feedstocks to chemicals or refinery processes.

An alternative method of removing coke from a catalyst or other solid is to react the coke with steam. For example, US 2,518,775 describes a process in which coked FCC catalyst is reacted with steam and oxygen in a regenerator to produce predominantly carbon monoxide and hydrogen, which can be fed to a Fischer-Tropsch synthesis unit for producing hydrocarbons. US 5,362,380 describes a process in which steam in the absence of oxygen is used to regenerate a coked FCC catalyst.

Carbon dioxide can be used to regenerate coked catalyst. For example, US 4,425,259 and US 4,450,241 describe FCC processes in which high Conradson carbon value feedstocks are contacted with an FCC catalyst modified with various metals, selected from Li, Na, K, Sr, V, Ta, Mo, Re, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Cu, Ag, Au, Sn and Bi. These aim to improve the reforming rate with CO₂ in the regenerator, which CO₂ is

produced during combustion in the presence of oxygen. Additionally, they describe the addition of a CO₂-rich feed to the regenerator to produce CO from the combination of CO₂ and coke-derived carbon to mitigate the exotherm produced during regeneration.

US 5,362,380 describes the reaction of coked FCC catalyst with steam in the absence
5 of oxygen to produce a gas composition comprising hydrogen, methane and carbon dioxide, from which a hydrogen-rich gas can be separated.

US 4,207,167 describes the regeneration of a coked FCC catalyst in a mixture of steam and air to produce carbon monoxide, which is further reacted with water in a different reactor to produce carbon dioxide and hydrogen. The hydrogen is separated, and
10 is fed to a refinery hydrocracking process, or alternatively to other processes.

US 4,244,811 describes regeneration of a coked FCC catalyst in a mixture of steam and air to produce a gaseous stream rich in CO or H₂, in which the FCC catalyst comprises oxides of tungsten and/or niobium, optionally additionally comprising one or more of tantalum oxide, hafnium oxide, chromium oxide, titanium oxide and zirconium oxide,
15 optionally supported on an inorganic refractory oxide selected from alumina, silica, zirconia, boria, thoria, magnesia, zirconium-titanate, titania, chromia, kieselguhr and mixtures thereof, which are stated to be extremely efficient cracking catalysts, and do not deactivate after prolonged exposure to steam at high temperature, or at least deactivate at a lower rate than traditional zeolite Y-based FCC catalysts.

US 6,585,883 describes a process for the catalytic removal of coke deposits in a refinery reactor unit, in which coke deposits are treated with a catalyst that is effective in converting coke to hydrogen and carbon monoxide in the presence of steam. Suitable catalysts are stated to include, inter alia, alkoxyated and non-alkoxyated cerium, titanium and zirconium oxides, lead, cobalt, vanadium and silver oxides; alkali and alkaline earth
25 metal carbonates and hydroxides, and group VIII transition metal oxides.

US 3,915,844 also describes a coking process in which asphalt feedstock is contacted with an alkali metal compound (such as a hydroxide, oxide or carbonate) to produce cracked hydrocarbons and coke, in which the coke is gasified and the alkali-metal compound regenerated by contact with steam. The alkali-metal compound is stated to be
30 active for reducing sulphur in the cracked hydrocarbons.

A further FCC process is described in WO 2007/082629, which relates to the use of Al and Mg-mixed oxides to improve middle distillate yield in catalytic cracking. US

7,347,929 describes a catalytic cracking process in which a magnesium and aluminium hydrotalcite oxide material is used as part of the catalyst composition to reduce sulphur levels in the resulting gasoline. However, these disclosures do not address the issue of catalyst coking or of any advantages associated in processing feedstocks with high

5 Conradson carbon content.

US 4,452,693 describes a coking process in which hydrocarbons are contacted with a perovskite material that comprises at least one alkaline-earth metal constituent. It is stated that the coked perovskite material can be regenerated by burning in oxygen.

10 US 4,522,706 describes a fluid coking process for hydrocarbons with high Conradson carbon content in the presence of perovskite materials, and regeneration of coked perovskite particles using oxygen.

US 4,055,513 describes a catalyst comprising a perovskite containing at least one transition metal composited with a support comprising a metal oxide and a spinel on the surface of said metal oxide, and its use in hydrocarbon conversion reactions.

15 US 4,412,911 describes the regeneration of perovskite catalysts that have been partially deactivated through contact with steam, regeneration being achieved by use of reducing gases such as hydrogen and/or carbon monoxide.

US 5,364,517 and US 5,565,181 describe the use of perovskite-containing additives for an FCC catalyst to reduce NO_x emissions during regeneration by combustion.

20 There remains a need for an improved catalytic cracking process, in particular a fluidised catalytic cracking (FCC) process, capable of processing hydrocarbon feedstocks which have a high Conradson carbon content.

There also remains a need for an improved process for regenerating coked particles.

25 According to the present invention, there is provided a process for regenerating coked particles, which process comprises contacting a hydrocarbon feedstock with solid particles in a reaction zone to produce coked particles and product hydrocarbons, which coked particles are transferred to a regeneration zone in which they are contacted with steam, such that at least a portion of the coke reacts to produce hydrogen and at least one or more oxides of carbon, characterised by the solid particles comprising one or more of the
30 following components:

(i) an aluminosilicate zeolite comprising one or more of Mn, Ti and Zn;

- (ii) a Ce-containing aluminosilicate zeolite with a Ce loading of at least 0.05wt% and/or a molar ratio of total other rare earth elements : Ce in the range of from 0 to 5;
- (iii) a magnesium and aluminium-containing anionic clay;
- (iv) a material with the Perovskite structure.

5 In the process of the present invention, coked particles can be at least partially regenerated by contact with steam in a regeneration zone. The steam reacts with coke to produce hydrogen and one or more oxides of carbon, typically CO and/or CO₂. It has been found that coke removal from particles that comprise or are made from any one or more of compositions (i) to (iv) can be achieved with high efficiency. This is advantageous, as it
10 can improve the lifetime of the particles in the process when used for carrying out hydrocarbon conversion reactions in which coke is formed as a product or by-product. An additional benefit with using any one or more of compositions (i) to (iv) in the process of the present invention is a reduction in the severity of operating conditions required in the regeneration zone for regenerating the coked particles to an extent sufficient for them to be
15 recycled to the reaction zone, which reduces the overall energy requirements of the process. A further benefit is that the contact time necessary for regenerating the coked particles in the regeneration zone can be reduced, which allows a reduction of the size of the reactor and associated equipment and services required to operate the regeneration zone. Yet another benefit is that the quantity of steam required for regeneration is reduced,
20 which further reduces the energy costs associated with operating the regeneration zone, and also contributes to improved catalyst lifetime.

In the process of the present invention, a hydrocarbon feedstock is contacted with solid particles in a reaction zone. The hydrocarbon reacts, and produces a carbonaceous residue, or coke, at least some of which deposits on the catalyst to produce a coked
25 catalyst. Typically, lighter hydrocarbons are additionally produced, for example light hydrocarbons such as one or more C₁ to C₄ hydrocarbons, naphtha and distillates.

In one embodiment of the invention, the reaction in the reaction zone is the catalytic cracking of hydrocarbons, for example fluidised catalytic cracking (FCC) of hydrocarbons. In another embodiment, the reaction in the reaction zone is hydrocarbon coking, for
30 example a fluid coking reaction. Lighter hydrocarbons produced in such reactions can be used in the production of hydrocarbon fuels such as diesel, kerosene, aviation gasoline,

gasoline, jet fuel, heating oil, fuel oil and liquefied petroleum gases (LPG) such as propane and/or butane.

In the reaction zone, a hydrocarbon feedstock comprising one or more hydrocarbons is contacted with the solid particles, resulting in the catalyst, or at least a portion of the catalyst, becoming at least partially coked through the formation of a carbonaceous residue, or coke.

In one embodiment of the present invention, the process uses hydrocarbon feedstocks which have high Conradson carbon content, for example Conradson carbon content of 0.5wt% or more, for example 2wt% or more, such as 5wt% or more, or 7wt% or more (as determined by method ASTM D189). Typically, the Conradson carbon content is 30wt% or less.

In one embodiment, the reaction zone can be operated such that 1 wt% or more of the feedstock hydrocarbon is deposited on the catalyst as coke, for example 5wt% or more, 8wt% or more, or 12wt% or more. Typically, 50wt% or less of the feedstock hydrocarbons deposit on the catalyst as coke, for example 40wt% or less, such as 35wt% or less.

Hydrocarbon feedstocks having high Conradson carbon content, and which can cause the formation of large quantities of coke, include heavy crude oil fractions such as atmospheric residue, vacuum residue or vacuum gas oil. Heavy crude oil fractions are generally more prevalent in low quality crude oils, which are typically less expensive to purchase. Therefore, being able to process heavy fractions with increased efficiency enables crude oils of lower quality and cost to be processed in a crude oil refinery, which can be beneficial to the production costs of the fuels. This is of particular benefit as lower quality crude oils are becoming increasingly more predominant. Crude oil sources that tend to produce greater quantities of the heavier crude oil fractions include acidic oil sand crudes, crudes from tar sands, crudes from oil shale and bitumen, and Orinoco belt heavy crudes.

Hydrocarbon cracking reactions, such as FCC, are typically used in the production of high value fuel hydrocarbons, for example gasoline, kerosene or diesel, from heavy and generally lower value crude oil fractions comprising relatively larger hydrocarbon molecules, for example heavy crude oil distillate fractions such as atmospheric residue, heavy gas oil, vacuum gas oil and vacuum residue, optionally after having undergone hydrotreatment or hydrocracking.

Coking reactions are typically carried out on high Conradson carbon feedstocks, for example heavy crude oil distillate fractions such as atmospheric residue, vacuum residue, tar sand crudes and bitumens. This lowers the Conradson carbon content of the resulting product hydrocarbon stream, which can be fed to other refinery processes, for example catalytic cracking reactions such as FCC or hydrocracking, or hydrodesulphurisation.

The particles of the present invention can be made from a single component. Alternatively, the particles can comprise a plurality of components, at least one of which is selected from one of components (i) to (iv) as defined below.

As an example, composition (i) and composition (ii) are catalytically active towards the catalytic cracking of hydrocarbons. Thus, in one embodiment of the invention, the reaction in the reaction zone is the catalytic cracking of hydrocarbons in the presence of a hydrocarbon cracking catalyst, in which the hydrocarbon cracking catalyst comprises particles that are made of or comprise one or more of components (i) and (ii). In a further embodiment the hydrocarbon cracking catalyst comprises a mixture of particles, some of which are particles that are made from or comprise one or more of components (i) and/or (ii), and some of which are particles made from or comprising one or more other catalytic cracking catalyst composition. In this embodiment, the use of component (i) and/or component (ii) help to partially improve coke regeneration throughout the catalyst as a whole, thus providing a means to tailor the catalyst to establish optimum efficiency in regeneration, and optionally optimum efficiency of both catalyst activity and regeneration. Additionally, the overall catalyst can be tailored so as to enable control over the quantity of heat generated in the regeneration zone, as described in more detail below.

In another embodiment, the particles are used in hydrocarbon coking reactions. As an example, particles comprising component (iii) and/or component (iv) that become coked in reactions such as fluid coking and/or flexicoking are able to be regenerated efficiently in the regeneration zone in the presence of steam.

In a further embodiment of the invention, the reaction is a catalytic cracking reaction, and the catalyst comprises particles made from components (iii) and (iv). Components (iii) and (iv) may have some catalytical activity themselves towards cracking reactions, although their activity can be improved by combining them with particles made from or comprising other components with higher catalytic activity. In yet a further embodiment, the higher catalytic activity components comprise one or more of components (i) and (ii).

By using one or more of catalyst components (i) to (iv) in accordance with the present invention, high regeneration efficiency can be achieved. Additionally, by adding particles made from or comprising one or more of components (i) to (iv) to an existing catalyst, catalytic activity and catalyst regeneration efficiency can be tailored, as can the quantity of heat generated in the regeneration zone, which helps tailor and control heat integration with other zones, such as the reaction zone and optional catalyst stripping zone. Thus, in one embodiment, conditions in the regeneration zone can be controlled by controlling the composition of the catalyst, through controlling the quantities of one or more of components (i) to (iv) therein. This can be achieved by varying the rate of addition of fresh supplies of the one or more of components (i) to (iv) to the catalyst, for example the rate of their addition to the reaction zone.

Where more than one of components (i) to (iv) are present, then each component can be present in separate solid particles, such that there is a mixture of solid particles where each solid particle comprises only one of the components. Alternatively or additionally, each solid particle can comprise more than one component, for example where one component is used as a binder for the other component or components. Having separate particles for each of the components has the benefit of ease of retrofit and ease of tailorability. For example, in a hydrocarbon cracking process, catalytic activity can be optimised by varying the relative concentrations of particles having different catalytic activity towards the catalytic cracking. For example, increasing the concentration of catalytically inert particles or particles of low catalytic activity, for example particles comprising one or more of components (iii) and (iv), preferably in the absence of any other catalytically active components. This can help regulate catalytic activity by reducing the concentration of relatively high activity catalyst components in the catalyst bed, and hence reduces reaction rate and the extent of coke deposition. In another embodiment, the concentration of solid particles comprising components of relatively high activity can be increased in order to increase the extent and rate of catalytic cracking, which in one embodiment would entail the addition of particles comprising one or more of components (i) and (ii). This avoids the need for a complete catalyst change-out. Additionally, the quantity of the added component can be changed with time to adapt to changes in catalytic activity or coking behaviour, allowing the catalyst performance to be varied dynamically.

The coked particles are transferred to the regeneration zone for removal or partial removal of the coke by contact with steam. Using one or more of components (i) to (iv), the extent of coke removal in the presence of steam has been found to be surprisingly high.

Typically, steam reforming reactions are uncatalysed, and take place at temperatures of 900°C or more, for example in the range of from 900 to 1100°C. Typical regeneration temperatures used for processes such as coking or cracking reactions are lower than this, for example below 900°C such as 870°C or less or 800°C or less, while typically also being 600°C or above to enable sufficient reaction to occur. These lower temperature conditions are required as the components of the solid particles can otherwise be damaged, for example components that have catalytic activity towards cracking reactions. However, at such low temperatures, little or no steam reforming of coke takes place. It has been found that coke deposited on any one or more of catalyst components (i) to (iv) can be removed by steam reforming reactions at the lower temperatures typically used in regeneration zones. This allows coke to be removed from the coked particles through endothermic steam reforming reactions, which enables high quantities of coke to be removed from coked particles under typical regeneration conditions. It also enables hydrocarbon feedstocks with a high potential for coke formation (for example feedstocks with high Conradson carbon content) to be fed to the reaction zone and processed without excessive heat production during regeneration.

In the regeneration zone, the coked particles are contacted with steam under conditions sufficient to convert at least a portion of the coke into hydrogen and one or more oxides of carbon. Typically, the reaction is a steam reforming reaction. As the quantity of steam generated in situ from the cracking reaction in the reaction zone or from reactions that take place within the regeneration zone for example, is generally insufficient to enable the steam reforming reaction to occur to a sufficient extent, then it is preferred that additional steam is added to the regeneration zone.

In another preferred embodiment of the invention, oxygen is additionally fed to the regeneration zone so that exothermic combustion and/or partial combustion of the coke occurs. The heat so-generated can compensate for the endothermic reforming reactions that also take place in the regeneration zone in the presence of steam. It can also compensate for other sources of heat loss in the process, such as any endothermic reaction occurring in the reaction zone, such as cracking of hydrocarbons, and also the

vapourisation of hydrocarbon feedstock on contact with the solid particles in the reaction zone.

Oxygen can be supplied in pure or substantially pure form, for example at a purity of greater than 95% by volume, such as greater than 99% by volume. Alternatively, the oxygen can be provided in a more dilute form as a mixture with other gases such as nitrogen and/or argon, for example at a concentration of 50% by volume or less, such as 30% by volume or less. In one embodiment, the source of oxygen is air. In a further embodiment, the steam and oxygen can be pre-mixed before being fed to the regeneration zone.

By varying the oxygen : steam ratio fed to the regeneration zone, the heat generated therein can be controlled, and enables further control over the heat balance of a process in which the regeneration zone is incorporated. Thus, where the regeneration zone requires additional heat to maintain temperature therein, then the oxygen to steam ratio in the regeneration zone can be increased. If the temperature in the regeneration zone is too high, then the oxygen to steam ratio in the regeneration zone can be reduced to mitigate any excessive temperature. This can be controlled by monitoring the temperature in the regeneration zone, and adapting the oxygen and/or steam flows accordingly if the temperature drifts outside a pre-determined value or range of values.

The temperature of the regeneration zone has an impact on the temperature of the reaction zone where regenerated catalyst particles are recycled to the reaction zone. Thus, where the temperature in the reaction zone needs to be increased, the oxygen to steam ratio on the regeneration zone can be increased to increase the temperature of recycled catalyst. Conversely, if the temperature in the reaction zone needs to be reduced, then the oxygen to steam ratio in the regeneration zone can be reduced to reduce the temperature of the recycled catalyst.

Preferably, the mole ratio of oxygen to steam fed to the regeneration zone is greater than 0, for example 0.001 or more such as in the range of from 0.001 to 90, for example 0.001 to 20, 0.001 to 10, 0.05 to 20 or 0.05 to 10. Controlling the oxygen to steam mole ratio helps to prevent excessive temperature in the regeneration zone causing damage to the solid particles therein. The oxygen to steam ratio in the regeneration zone can alternatively be expressed in the form of a steam reforming to combustion ratio (i.e. the percentage of coke removed by steam reforming compared to that removed by combustion). Thus,

increasing the oxygen to steam ratio causes the steam reforming to combustion ratio to reduce, and vice versa.

Increasing the oxygen : steam mole ratio increases the extent of conversion of coke and/or CO to CO₂, and decreases the CO:CO₂ molar ratio in the product gases generated in the regeneration zone. Additionally, less H₂ and CO are produced, while more heat is released. Conversely, decreasing the oxygen : steam mole ratio results in greater production of H₂ and CO, decreases the production of CO₂, increases the CO:CO₂ molar ratio in the product gases, and releases less heat. Thus, altering the oxygen to steam molar ratio can be used to control the composition of the product gases from the regeneration zone, and also the heat generated therein, which provides a means of controlling or maintaining heat balance in the process. It also provides a means of protecting the solid particles (e.g. catalyst particles) in the regeneration zone from damage should the temperature rise above a certain level.

Heat generated in the regeneration zone can be transferred to other parts of the process, for example by heating one or more of the feeds to the reaction zone, such as the hydrocarbon feedstock or any fluidising or lifting gas, or to the regeneration zone, such as the feed of oxygen-containing gas or the supply of steam. Transfer of heat in this way minimises energy consumption and costs associated with maintaining the temperature of the reaction and/or regeneration zones. In another embodiment, the heat from the regeneration zone can be used to heat a supply of pressurised steam which can be transported elsewhere, for example to heat process streams in the present process or in other processes, for example other processes co-located on an integrated refinery or petrochemical site.

The recycling of regenerated and hot catalyst from the regeneration zone to the reaction zone is another way in which heat can be transferred back to the reaction zone from the regeneration zone, thus reducing the heating requirements of the hydrocarbon feedstock or any other streams that are fed to the reaction zone.

In a preferred embodiment of the invention, sufficient oxygen is fed to the regeneration zone such that the regenerated particles, when recycled to the reaction zone, have sufficient heat to vapourise, or partially vapourise, the hydrocarbon feedstock, which improves the efficiency of catalyst fluidisation in the reaction zone.

The regeneration zone is typically operated at temperatures at or above 600°C. Additionally, the temperature is typically maintained at a value of 870°C or less, for example 800°C or less. Generally, higher temperatures can lead to degradation of the solid particles and plant equipment, whereas at lower temperatures the rate of coke removal can be insufficient. Pressures can be in the range of from 1 to 200 bara (0.1 to 20 MPa), for example from 1 to 100 bara (0.1 to 10 MPa), such as from 1 to 20 bara (0.1 to 2 MPa) or 1 to 10 bara (0.1 to 1 MPa).

In one embodiment of the invention, the process comprises more than one regeneration zone, for example two regeneration zones or more than two regeneration zones. The regeneration zones can be arranged in series or in parallel. The regeneration zones are typically in the form of separate regeneration vessels.

In one embodiment, the process comprises two or more regeneration zones arranged in series, the first regeneration zone receiving coked particles from the reaction zone and/or optional stripping zone, the second regeneration zone receiving solid particles that have been regenerated at least in part in the first regeneration zone, and so on.

The oxygen : steam molar ratios fed to each regeneration zone can be the same or different. The most suitable oxygen : steam ratio used in each regeneration zones is dependent on the temperature of the solid particles removed from the reaction zone or optional stripping zone, or from the preceding regeneration zone. The oxygen to steam molar ratio fed to the first regeneration zone can be higher than that fed to the second regeneration zone, or alternatively can be lower. Steam can be fed to all regeneration zones, or alternatively only to selected regenerations, for example to a single regeneration zone. Each regeneration zone can receive a mixture comprising oxygen and steam, or alternatively oxygen in the absence of steam or steam in the absence of oxygen.

In one embodiment, where the coked particles removed from the reaction zone and/or optional stripping zone are at a relatively high temperature, for example a temperature of greater than 750°C, then the amount of oxygen relative to steam fed to the first regeneration zone is desirably restricted so as to reduce the probability of damaging temperatures from exothermic combustion reactions arising within the first regeneration zone. Alternatively, where the temperature of the coked particles removed from the reaction zone and/or optional stripping zone is relatively low, for example at a temperature of less than 650°C or less than 600°C, then oxygen is preferably fed to the first

regeneration zone at a concentration sufficient to generate temperatures high enough for steam reforming reactions of the coke to occur at an adequate rate.

In one embodiment, oxygen is fed to the first regeneration zone, optionally together with steam. The presence of oxygen enables sufficient heat to be generated in the first
5 regeneration zone to enable steam reforming of coke to take place, which is often required because of the temperature of the coked particles removed from the reaction zone and/or optional stripping zone being insufficient to enable steam reforming reactions of the coke to take place. The quantity of oxygen provided to the first regeneration zone is preferably sufficient to generate enough heat to enable steam reforming to take place, but not too great
10 so as to generate too high a temperature in the first regeneration zone that could lead to damage to process equipment or the solid particles, particularly catalytically active particles. In one embodiment, the temperature maintained in the first regeneration zone is in the range of from 650 to 750°C. The oxygen to steam molar ratio fed to the first regeneration zone in one embodiment is less than 10, for example less than 1. In a further
15 embodiment, in the gases produced in the first regeneration zone, the combined concentration of carbon monoxide and hydrogen (on a molar basis) is greater than the concentration of carbon dioxide.

In the second regeneration zone, the oxygen to steam molar ratio fed thereto can be higher than that fed to the first regeneration zone, and optionally no steam is fed to the
20 second regeneration zone. This enables the coked particles that have been at least partially regenerated in the first regeneration zone to undergo more complete regeneration in the second regeneration zone. As the amount of coke on the particles fed to the second regeneration zone is reduced compared to the first regeneration zone, then a higher concentration of oxygen can be fed thereto without causing excessively high temperatures
25 to be reached. Additionally, a higher oxygen : steam molar ratio in the second regeneration zone increases the level of coke removal, and the reduced concentration of added steam mitigates any damage of the catalyst if an excessive temperature increase occurs. Excessively high temperatures in the presence of steam can further damage the solid particles over and above the effects of high temperature alone, for example by causing
30 hydrothermal degradation of zeolite, hydrotalcite or perovskite components that may be present. The temperature maintained in the second regeneration zone in one embodiment

is in the range of from 650 to 800°C. The molar ratio of oxygen to steam fed to the second regeneration zone in one embodiment is greater than 0.1, for example 1 or more.

In a further embodiment of the invention, solid particles from the second regeneration zone can be returned to the first regeneration zone in order to provide an additional means of temperature control therein. Thus, where the particles in the second regeneration zone are hotter than those in the first regeneration zone, then a portion of the solid particles from the second regeneration zone can be fed to the first regeneration zone to provide additional heat therein. Conversely, where the solid particles from the second regeneration zone are cooler than those in the first regeneration zone, then the cooler solid particles from the second regeneration zone can be fed to the first regeneration zone to help mitigate the formation of excessively high temperatures therein.

In another embodiment, only some of the coked particles that have undergone regeneration in one regeneration zone are fed to another regeneration zone, the others being fed back to the reaction zone. In yet another embodiment of the invention, gases produced in one regeneration zone can be fed to another regeneration zone.

The temperature in each regeneration zone can be controlled independently by supplying sufficient steam or oxygen to ensure reaction sufficient to maintain the temperature within the desired limits. For example if greater heat generation is required then the extent of regeneration through oxidation can be increased, as oxidation is an exothermic process, whereas steam reforming is endothermic. Alternatively, if less heat generation is required, then the process can be modified to ensure regeneration through steam reforming is the predominant reaction. This can be achieved by increasing or decreasing the quantity or concentration of steam or oxygen to the relevant regeneration zone. In a further embodiment, the process comprises more than two regeneration zones, in which oxygen is fed to one or more of the regeneration zones, and steam to the remaining regeneration zones.

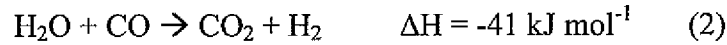
Although the process can comprise more than one regeneration zone, an advantage associated with operation using a single regeneration zone is that less process equipment required, for example only one regeneration vessel.

Coke typically comprises carbon-containing residue, and hence the steam reforming reaction can be summarised by equation (1) below:



Steam can further react with carbon monoxide, through the water-gas shift reaction as expressed in equation (2):

5



If oxygen is also co-fed to the regeneration zone, for example in the form of air or as a pure supply of oxygen, then some partial oxidation of the carbon occurs, as summarised in equation (3) below, although some over-oxidation to CO_2 can also occur.

10



Carbon dioxide can react further with carbon to produce more carbon monoxide, through carbon dioxide coke reforming according to equation (4);

15



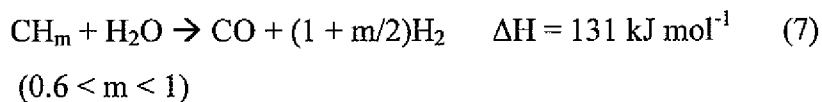
Hydrogen produced according to equations (1) and (2) can also react with carbon to produce methane through coke methanation according to equation (6).

20



Coke steam reforming in general can be represented by the following equation:

25



Producing carbon monoxide can be advantageous, particularly in combination with hydrogen, as a hydrogen/carbon monoxide mixture (or syngas) can be used to make fuels, through Fischer-Tropsch synthesis for example, or can be used in petrochemicals

30

manufacture, for example in the production of alcohols or ethers such as methanol, ethanol and dimethyl ether. Additionally, hydrogen produced through reactions such as (1) and (2), for example, can be utilised in a crude oil refinery, such as in hydrotreating and hydrocracking processes.

5 In a further embodiment of the invention, where there is more than one regeneration zone arranged in series such that partially regenerated solid particles from a previous regeneration zone are fed to a subsequent regeneration zone, regeneration gases from the previous regeneration zone comprising the gaseous products of coke removal therein are fed to the subsequent regeneration zone as a regenerating gas in addition to any separate
10 supply steam and/or oxygen that may be fed thereto. This reduces the quantities of steam and/or oxygen that are required.

 An advantage of the process of the present invention, particularly where the reaction in the reaction zone is catalytic cracking, is that hydrocarbon feedstocks having a high potential to form coke (for example feedstocks with a high Conradson carbon content) can
15 be processed without the need for any dilution with other hydrocarbon feedstocks with lower coking potential (for example feedstocks having low Conradson carbon content). Hence, it is suitable for the processing of low value feedstocks with high coking potential, without the problems associated with catalyst degradation in the regeneration zone through excessively high temperatures, and without the catalyst therein becoming deactivated too
20 quickly through inefficient removal of coke.

 During processes where the catalyst is fluidised and/or when catalyst is transferred to and/or from the regeneration zone, for example in FCC or fluid coking reactions, the catalyst may be subject to attrition resulting in the formation of small particles of catalyst dust, or "fines". The fines are preferably removed from the process, for example by being
25 removed from the reactor with any reactant, inert, fluidising, lifting or regeneration gases in either or both of the reaction zone or regeneration zone, where they can be separated for example through a cyclone separator. Catalyst lost from the process through fines production can be replenished by feeding fresh catalyst to the regeneration and/or reaction zone.

30 The reaction zone can be provided with a feed of fresh solid particles, and also regenerated coked particles from the regeneration zone. The transfer of coked particles from the reaction zone to the regeneration zone, optionally via a stripping zone, and also

the transfer of regenerated particles from the regeneration to the reaction zone is preferably continuous. Transfer can be achieved by use of nitrogen, steam, air or hydrocarbon feedstock, for example.

5 The process of the present invention can comprise a stripping zone, in which the coked particles, before regeneration in the regeneration zone, are treated to remove any unreacted feedstock hydrocarbons or any products such as product hydrocarbons that may be absorbed or adsorbed on the catalyst before regeneration occurs. This reduces loss of feedstock and product hydrocarbons, and makes the coked particle regeneration more efficient. Stripping can be achieved by contacting the coked particles with a stripping gas,
10 for example nitrogen and/or steam. Reactants and other product hydrocarbons collected from the catalyst by the stripping gas can be added to the product hydrocarbons removed from the reaction zone.

The solid particles are made from or comprise one or more of components (i), (ii), (iii) and (iv), as defined below.

15 In one embodiment, the solid particles can be made from or comprise an aluminosilicate zeolite comprising one or more metals selected from Ti, Mn and Zn. The metal loading of the zeolite is typically 0.05wt% or more, and is typically 10wt% or less, for example 4wt% or less. These materials are referred to herein as type (i). They are catalytically active for catalytic cracking reactions, and enable increased rates of coke
20 removal through reforming to be achieved in the regeneration zone compared to catalysts free of these metals. In addition, less coke is formed on the catalyst during the cracking reaction. Loadings of Ti and Zn below 1.5wt% tend to cause the generation of lower quantities of hydrogen during hydrocarbon cracking reactions than are typically produced at higher loadings. The production of hydrogen, in particular during catalytic cracking
25 processes such as FCC, can cause an overloading of apparatus (for example pumps and compressors) associated with the separation of liquefied petroleum gases, such as propane, propenes, butanes and butenes, from lighter so-called "dry" gas products such as hydrogen or methane. This reduces the quantity of hydrocarbon feedstock that can be processed, and can be detrimental to process efficiency.

30 The metal-modified aluminosilicate zeolites can be prepared by known procedures, for example by ion-exchange techniques, or through impregnating the zeolite using a

solution of the relevant metal or metals, typically aqueous solutions of the metal salts such as nitrate, sulphate, carbonate, acetate, or halide salts.

In another embodiment, the solid particles comprise or are made from a Ce-containing zeolite, which is catalytically active for catalytic cracking reactions. The presence of cerium causes increased quantities of coke to form on the catalyst particles compared to cerium-free particles. At the same time, the presence of cerium enables the coke to be more easily removed from the particles through steam reforming reactions. The Ce loading of the zeolite is typically 0.05wt% or more, preferably 0.15wt% or more. The zeolite typically comprises 2wt% or less of Ce, preferably 1.5wt%, or less, such as 1.0wt% or 0.5wt% or less. An optimum Ce loading in which a good balance between coke formation not being excessive, and coke regeneration through steam reforming being sufficiently high, is in the range of from 0.1 to 0.5wt%. These Ce-containing zeolite materials are referred to herein as type (ii).

As other rare earth elements are also typically present in catalyst formulations in addition to Ce, especially catalysts active for hydrocarbon cracking reactions such as FCC, then molar ratio of the total other rare earth elements : Ce is typically in the range of from 0:1 to 5:1, for example in the range of from 0:1 to 2:1, and preferably in the range of from 0:1 to 1:1.

The solid particles can comprise or be made from a magnesium- and aluminium-containing anionic clay. Improved regeneration efficiency can be achieved when the anionic clay additionally comprises one or more of Ce, Ca, Mn, Fe, Co, Cu and Zn. Where the additional elements, when incorporated into the anionic clay, are trivalent (henceforth M(III)), such as Ce, then the $[M(III) + Al] / [Al + Mg + M(III)]$ molar ratio for each trivalent M(III) is preferably in the range of from 0.01 to 1, and more preferably in the range of from 0.01 to 0.5. Where the additional elements, when incorporated into the anionic clay, are divalent (henceforth M(II)), such as Zn, the $Al / [Mg + Al + M(II)]$ molar ratio for each divalent M(II) is preferably in the range of from 0.01 to 1, and more preferably in the range of from 0.01 to 0.5. Anionic clays typically comprise a positively charged layered oxide framework, with anionic counter-ions between the layers, and can have a wide variety of anions X in the inter-laminar region, for example one or more of halide (such as Cl^- and/or Br^-), NO_3^- and CO_3^{2-} . In one embodiment, the anionic clay is a magnesium and aluminium-containing layered double hydroxide (LDH), preferably a

hydrotalcite. The anionic clay can optionally additionally comprise Si. These anionic clay materials are referred to herein as type (iii). The additional metals can be added to the anionic clay using techniques such as impregnation. Such methods are exemplified by those described in WO 2008/003091. Although generally less active than typical zeolite Y or USY-based FCC catalysts towards catalytic cracking reactions, the rate of coke removal through steam reforming is relatively high.

Use of anionic clays can have further advantages, in that they can assist in the elimination of NO_x and SO_x (oxides of nitrogen and sulphur) that can be produced in the regeneration zone. Additionally, anionic clays can also entrap and remove metal impurities from the hydrocarbon feedstock, such as vanadium which is a common component in crude oil.

The solid particles can be made from or comprise a material with the perovskite structure, which is the structure adopted by calcium titanate (CaTiO₃). The perovskite structure is often represented generally by the formula ABO₃, where A and B are cations of different sizes, with A conventionally being the larger cation. The mole ratio of A:B is dependent on the charges of the corresponding cations. A or B can each comprise more than one cation. Preferably, at least one of the cations in the perovskite is selected from one or more of La, Sr, Mn, Fe, Ce, Ni, Co, Ag, Nb, Cs, K, Rb, Ba and Pb, preferably one or more of La, Sr, Mn, Fe, Ce, Ni and Co. In one embodiment, one or more of Ti, V, Cu, Cr, Ca, Zr, Mo, Zn, W, Hf, Sn, alkaline earth elements, and other lanthanide elements are additionally present in the perovskite. In another embodiment, the perovskite comprises La and Mn. In a further embodiment, the perovskite comprises La, Sr, Fe and Co. The perovskite materials are referred to herein as type (iv). Although these materials are generally less active than typical zeolite Y-based FCC catalysts towards cracking reactions, the rate of coke deposition thereon is large, which can reduce the quantity of coke formation on active catalyst components with which it can be mixed or otherwise incorporated. In addition, the rate of coke regeneration by steam reforming in the regeneration zone has been found to be very high, which increases the quantity of coke removed in the regeneration zone, and balances the effects of increased coke deposition. The perovskite can be supported, formed, grown, deposited and/or mixed with oxide supports, for example silica, alumina, alumina-silica, aluminophosphate, ceria, lanthana, praseodymia, yttria, neodymia, samaria, europia, gadolinia, titania, zirconia, vanadia and

mixtures thereof. A further effect of perovskite materials is that they can also contribute to the removal or entrapment of metal impurities in the hydrocarbon feedstock. Preferably, the support is selected such that the surface area of the supported Perovskite is greater than $100 \text{ m}^2 \text{ g}^{-1}$, which enables more efficient regeneration in the regeneration zone. In another embodiment, the type (iv) material can be supported on or mixed with a type (iii) material, such as a magnesium- and aluminium-containing hydrotalcite.

Use of solid particles made from or comprising component (i) and/or (ii) in catalysed reactions, such as catalytic cracking or FCC, is advantageous in that they combine the benefits of good catalytic activity towards the cracking reaction while at the same time being able to be efficiently regenerated in the presence of steam. This enables hydrocarbon feedstocks with high Conradson carbon content to be processed efficiently, and even without the need to be diluted with low Conradson carbon content hydrocarbon feedstocks.

Use of solid particles made from or comprising component (iii) and/or (iv) is advantageous for coking reactions due to the high rate of coke formation thereon, which improves the extent of coke removal from a hydrocarbon feedstock. The rate of coke removal from materials (iii) and/or (iv) in the regeneration zone in the presence of steam is also high, which balances the effects of the high extent of coke deposition thereon.

In one embodiment of the invention, the reaction in the reaction zone is a catalysed cracking process such as FCC, and the catalyst comprises component (i) and/or (ii) together with component (iii) and/or (iv). In another embodiment, in addition to one or more of components (i) to (iv), the catalyst can comprise additional components, such as one or more additional catalysts. For example, for a hydrocarbon cracking process such as FCC, the catalyst can comprise one or more additional components which are active catalysts for hydrocarbon cracking reactions, for example those comprising aluminosilicate zeolites having the FAU structure type (according to the International Zeolite Association classification), which includes zeolite Y and dealuminated analogues thereof, such as ultra-stable zeolite Y (USY). Examples include La^{3+} and Ce^{3+} modified versions of zeolite Y and/or USY, as reported, for example, by Cheng et al in Handbook of Heterogeneous Catalysis (2nd Edition) 2008, Vol 6, pp2741-2778. Other zeolites include ZSM-5, beta, ferrierite, L and mordenite. In a further embodiment, the catalyst comprises one or more of these zeolites together with one or more of components (iii) and/or (iv).

In addition to any one or more of components (i) to (iv), the solid particles can comprise additional components as matrix, fillers and binders, for example one or more of alumina, silica, silica-alumina, aluminophosphate, other zeolites, various clays (e.g. kaolin, sepiolite, olivine and montmorillonite), lanthana, yttria, praseodymia, neodymia, samaria, europia, gadolinia, titania and zirconia. The choice of matrix, filler or binder depends, inter alia, on the reaction that is catalysed, and the crush strength and attrition resistance requirements.

The solid particles can be in any shape or form suitable for the application, such as microspheres, extrudates or pellets. For use in fluidised catalyst beds, for example fluidised catalytic cracking or fluid coking reactions, microspheres such as spray-dried microspheres are preferred in order to facilitate transfer between reaction, regeneration and optional stripping zones, and to improve the efficiency of fluidisation. Microspheres typically have particle sizes in the range of from 40 to 200 μm , for example 50 to 150 μm or 55 to 125 μm . Typically, the Davison attrition index value for fluidised particles, such as those used in fluidised catalytic cracking or fluidised de-coking reactions, is less than 50, preferably less than 30, and more preferably less than 20. The Davison attrition index is described in WO 2000/051731.

The process comprises a reaction zone, a regeneration zone and optionally a stripping zone. In the reaction zone, the hydrocarbon feedstock is preferably heated under non-oxidising conditions, typically at a temperature in the range of from 400 to 700°C, for example from 400 to 600°C, and a pressure in the range of from 1 to 10 bara (0.1 to 1 MPa), for example 2 to 4 bara (0.2 to 0.4 MPa). The solid particles can be maintained in a fluidised state by feeding a fluidising or lifting gas upwards through the catalyst bed. Examples of fluidising or lifting gases include steam, nitrogen, light hydrocarbons such as one or more C₁ to C₄ hydrocarbons, naphtha, and light cycle oil.

The hydrocarbon feedstock is typically fed into the reaction zone directly into the portion of the reaction zone comprising the solid particles, where it reacts to produce shorter chain hydrocarbons which are removed from the reaction zone together with the fluidising gas, and subsequently separated. In one embodiment, liquid-phase hydrocarbon feedstock can be fed directly upwards through a catalyst bed, where it contacts hot solid particles. The hot particles cause evaporation of all or at least a portion of the hydrocarbon feedstock, which aids catalyst fluidisation. Additionally, light hydrocarbons or other

products produced during cracking will also contribute to fluidisation. Preferably, liquid hydrocarbon feedstock is introduced to the reaction zone as small droplets, or forms small droplets once introduced. The small droplets have diameters typically in the range of 10 to 100 micrometers. Droplet formation can be facilitated by the co-addition of steam, which also acts to assist fluidisation of the solid particles. In a further embodiment, catalyst and liquid hydrocarbon feedstock can be fed downwards through the reaction zone, as described for example in US 5,296,131 and US 5,449,496.

Typical contact times of the feedstock hydrocarbons with the solid particles in the fluidised bed or riser (which will also comprise coked particles and optionally recycled regenerated particles) are in the range of from 0.001 to 300 seconds, for example 0.01 to 100 seconds or 0.1 to 50 seconds, preferably 0.1 to 10 seconds, and more preferably 0.5 to 10 seconds. Typically, the solid particles to feedstock hydrocarbon weight ratio (often termed the catalyst to oil ratio) is in the range of from 1 to 100, preferably from 2 to 20.

There now follows non-limiting examples illustrating the invention.

Experimental

Prior to steam reforming experiments a microactivity test (MAT) apparatus was used to coke various materials by contacting the material with a vacuum gas oil (VGO) at a temperature of 500°C for 30 seconds at atmospheric pressure, where the catalyst to oil mass ratio (CTO) was 3. In an alternative procedure, an atmospheric residue was used, and a temperature of 530°C, to generate the coked sample.

Experiment 1 - Temperature Programmed Steam Reforming

Coked sample was contacted with wet helium gas using a procedure and apparatus similar to that used for temperature programmed desorption (TPD) analysis. A flow of helium (100mL/min at room temperature) at atmospheric pressure was bubbled through water to produce a wet helium supply with a water partial pressure of 2.64 kPa at 22°C, before being contacted with the coked sample. The temperature was then raised from room temperature to 750°C at a rate of 10°C/min, and held at 750°C for 600 minutes. The carbon content of the sample before and after the TPD experiment was determined by elemental analysis. Gases generated during the experiment were continually analysed by mass

spectrometry. From the data obtained, comparative rates of coke removal between different coked samples could be calculated.

Experiment 2 - Coke Reforming at Constant Temperature

5 The rate of coke reforming was evaluated using MAT apparatus, in which 1 g coked material was loaded into a tube reactor together with 2g of a pre-heater charge of carborundum™ (silicon carbide). The temperature was raised as quickly as possible to a chosen temperature between 600 and 770°C under a nitrogen flow of 40mL/min (at room temperature). Emissions of hydrogen and methane were typically observed during the
10 heating procedure, which accounted for 3 to 20wt% of the total coke mass initially present in the material, depending primarily on the maximum temperature and the type of sample. Pressure used was atmospheric pressure, or marginally above atmospheric pressure, i.e. in the range of from 1 atm to about 1.1 atm.

 Once the temperature was stabilised, water was added at a rate of 0.035 to 0.1 g per
15 minute, and the nitrogen flow was set to 15 to 100 mL/minute (at room temperature) to regulate the water pressure to between 30 and 90% of the total pressure. This was continued for 5 to 20 minutes depending on the sample.

 The water flow was then stopped, and nitrogen at a flow rate of 80mL/minute (at
20 room temperature) was used to strip the catalyst of any remaining water or reforming products over a 5 minute period. The remaining coke on the catalyst was burned in the presence of air. Coke content of the sample was calculated from the quantity of CO₂ evolved during combustion, which was measured using an IR (infrared) detector.

Material 1

25 This was a commercially available alumina-bound FCC catalyst obtained from Engelhard.

Material 2

 This was prepared using an incipient wetness technique, by impregnating some of
30 Material 1 with an aqueous solution of manganese nitrate. The pore volume of a given mass of Material 1 was calculated. Based on the pore volume, a solution of manganese (II) nitrate tetrahydrate solution was prepared at a concentration sufficient to ensure that the

pores were filled with sufficient manganese to give a loading of 2 wt%. The manganese content of the resulting dried Mn-impregnated solid, as measured by ICP (Inductively Coupled Plasma) analysis, was 2.13wt%.

5 Material 3

This was prepared by impregnating some of Material 1 with an aqueous solution of titanium (IV) n-butoxide, in an analogous way to the impregnation method of Material 2. The target titanium loading of the catalyst was 2wt%. After drying the Ti-loading, as measured by ICP analysis, was 2.48 wt%.

10

Material 4

This was prepared by impregnating some of Material 1 with an aqueous solution of cerium (III) nitrate hexahydrate, in an analogous way to the impregnation method of Material 2. The target cerium loading of the catalyst was 0.25wt%. After drying the Ce-loading, as measured by ICP analysis, was 0.19 wt%.

15

Material 5

This was prepared by impregnating some of Material 1 with an aqueous solution of cerium (III) nitrate hexahydrate, in an analogous way to the impregnation method of Material 2. The target cerium loading of the catalyst was 2wt%. After drying, the Ce-loading as measured by ICP analysis was 1.5 wt%.

20

Material 6

This was a hydrotalcite sample prepared by coprecipitation of an acid solution containing nitrate salts of aluminium and magnesium by the addition under constant stirring of a basic solution containing sodium carbonate and sodium hydroxide in quantities sufficient to form the hydrotalcite gel. The relative molar quantities of components in the composition was calculated according to the formula $(1-R) M^{2+} : (R) M^{3+} : \frac{2}{3} Na_2CO_3 : (2+R) NaOH$, where M^{2+} and M^{3+} are the divalent and trivalent cations respectively (in this case Mg and Al respectively), and R is the target molar ratio of trivalent cation compared to the sum of trivalent and divalent cation (i.e. $R = M^{3+} / (M^{2+} + M^{3+})$). After mixing and precipitation, the suspension was aged for 12 hours at 60°C. The solid was filtered off,

25

30

washed with water and calcined in air at 550°C for 3 hours. The target Al/(Al + Mg) molar ratio was 0.25, i.e. in the formula provided above $R = 0.25$. The molar ratio determined by ICP analysis was 0.28.

5 Material 7

This was a hydrotalcite sample prepared in an analogous way to Material 6, but in which the aluminium nitrate and magnesium nitrate solution additionally contained copper (II) nitrate solution. The target Al/(Mg + Al + Cu) molar ratio was 0.25. The target copper content was 2wt% of the final hydrotalcite. The molar ratio and copper content determined from ICP analysis were 0.27 and 1.85wt% respectively.

Material 8

This was a hydrotalcite sample prepared in an analogous way to Material 6, but in which the aluminium nitrate and magnesium nitrate solution additionally contained cerium (III) nitrate solution. The target (Al+Ce)/(Mg + Al + Ce) molar ratio was 0.25. The target cerium content was 2wt% of the final hydrotalcite. The (Al+Ce)/(Mg + Al + Ce) molar ratio and cerium content determined from ICP analysis were 0.27 and 1.8wt% respectively.

Material 9

This was a perovskite with a metal stoichiometry of $\text{La}_{0.4}\text{Sr}_{0.6}\text{Fe}_{0.8}\text{Co}_{0.2}$. It was prepared using the procedure of Serra et al, Topics in Catalysts, 40 (2006), 123-131.

Material 10

This was a hydrotalcite sample prepared in an analogous way to Material 6, but in which the aluminium nitrate and magnesium nitrate solution additionally contained cerium (III) nitrate solution. The target (Al+Ce)/(Mg + Al + Ce) molar ratio was 0.25. The target cerium content was 0.21wt% of the final hydrotalcite. The (Al+Ce)/(Mg + Al + Ce) molar ratio and cerium content determined from ICP analysis were 0.27 and 0.25wt% respectively.

Results of steam reforming using Experiment 1 are shown in Table 1. Samples were initially coked using VGO.

Table 1: Coke formation and removal.

Material	Coke content before Expt.1 (wt%)	Coke content after Expt.1 (wt%)	Coke Removed (%)	Relative reforming rate ^a
1	1.04	0.41	61	1
2	1.27	0.27	79	2
3	1.19	0.33	72	1.3
4	1.40	0.25	82	2
5	1.65	0.27	84	2
6	1.17	0.20	83	5
7	3.93	0.45	89	8
8	1.59	0.30	82	6
9	0.69	0.01	99	30

^a Compared to Material 1, which had a reforming rate constant, K, of 1×10^{-5} .

5 Compared to Material 1, the zeolite-catalysts, metal-impregnated catalysts, perovskite and hydrotalcite materials all showed a superior percentage of coke removal, and a superior coke reforming rate.

The relative cracking performance of materials 1 to 5 are compared in Table 2 below, which highlight the relative yields of hydrogen and coke in the presence of the different cracking catalyst materials.

10

Table 2. Relative coke and hydrogen yield

Material	Relative hydrogen yield	Relative coke yield	MAT Conversion (wt%) ^a
1	1	1	59
2	0.9	0.9	62
3	2	1.2	56
4	1	1	61
5	2.5	1.3	58

^a Sum of gasoline + total gas + coke yields.

These results demonstrate that Materials 1 to 5 (of types (i) and (ii)) are all active towards cracking reactions, hence the additional rate of removal of coke through steam reforming in the cases of materials 2 to 5 enables more coke to be removed with lower generation of heat.

5 Some of the materials were also contacted with steam using Experiment 2. Table 3 shows the results of coke steam reforming using Experiment 2, together with the gas composition obtained. The samples were coked using VGO. Steam reforming was conducted at 750°C for 20 minutes in which the atmosphere was 90% steam.

10 Table 3. Composition of reformed gases and carbon balance, samples coked with VGO

Material	Coke Conversion (wt%)	CO Yield (%) ^a	CO ₂ Yield (%) ^a	CH ₄ Yield (%) ^a	H ₂ /CO molar ratio.
1	12	9	2	1	2.1
2	18	6	17	2	2.3
6	64	13	43	8	4.8

^a Based on percentage of coke converted.

These results confirm the increased extent of coke removal by steam reforming for solid particles having compositions of type (i).

15

Table 4. Composition of reformed gases and carbon balance of samples coked with ATR

Material	Coke Conversion (wt%)	CO yield (%) ^b	CO ₂ yield (%) ^b	CH ₄ yield (%) ^b	H ₂ /CO molar ratio.
Ref. 1	10	8	2	<1	1.7
9	34	10	23	1	5.9
10 ^a	69	4	65	<1	40

^a reforming temperature was 700°C instead of 750°C and reforming time was 5 minutes instead of 20 minutes.

^b Based on percentage of coke converted.

20

Table 4 shows the results of coke steam reforming using Experiment 2, in which the samples were initially coked using an atmospheric residue (ATR) having a Conradson

Coke content of 8%. Steam reforming was conducted at 750°C for 20 minutes with an atmosphere of 90% steam.

5 These results highlight the improved coke removal through steam reforming of anionic clay materials (type (iii)) modified with a metal such as cerium, and also a perovskite material (type (iv)).

Further tests were performed using Experiment 2 where steam and air were fed simultaneously. Table 5 details the operating conditions and obtained yields.

These results demonstrate the feasibility of regenerating coked particles using a combination of steam and oxygen.

10

Table 5. Coke Conversion and gas composition by simultaneous reforming and combustion.

Material	11	9
Operation temperature (°C)	770	730
Run length (min)	20	3
Water pressure (kPa)	90	30
Oxygen pressure (kPa)	0.6	2
Coke conversion (wt%)	84	80
CO yield (%) ^a	21	10
CO ₂ yield (%) ^a	62	70
CH ₄ yield (%) ^a	1	<0.5
H ₂ /CO molar ratio	2.7	10

^a Based on percentage of coke converted.

15

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Claims

1. A process for regenerating coked particles, which process comprises contacting a hydrocarbon feedstock with solid particles in a reaction zone to produce coked particles, which coked particles are transferred to a regeneration zone in which they are contacted with steam to produce hydrogen and at least one or more oxides of carbon, wherein the solid particles comprise one or more of the following components:
 - (i) an aluminosilicate zeolite comprising one or more of Mn, Ti and Zn;
 - (ii) a Ce-containing aluminosilicate zeolite with a Ce loading of at least 0.05wt% and/or a molar ratio of total other rare earth elements : Ce in the range of from 0:1 to 5:1;
 - (iii) a magnesium and aluminium-containing anionic clay;
 - (iv) a material with the Perovskite structure.
2. A process as claimed in claim 1, in which the reaction is a coking reaction.
3. A process as claimed in claim 2, in which the reaction is a fluid coking reaction.
4. A process as claimed in claim 2 or claim 3, in which at least a portion of the solid particles are made from or comprise one or more of components (iii) and (iv).
5. A process as claimed in claim 1, in which the reaction in the reaction zone is a catalysed hydrocarbon cracking reaction.
6. A process as claimed in claim 5, in which the reaction is fluidised catalytic cracking.
7. A process as claimed in claim 6, in which the solid particles comprise a mixture of particles having different catalytic cracking activity, and the catalytic activity is controlled by varying the relative ratios of the particles of different catalytic activity.
8. A process as claimed in claim 7, in which catalyst activity is controlled by varying the relative quantities of the particles having different catalyst activity.
9. A process as claimed in any one of claims 1 to 8, in which the hydrocarbon feedstock is derived from crude oil.
10. A process as claimed in any one of claims 1 to 9, in which the hydrocarbon feedstock has a Conradson carbon content of 0.5wt% or more.
11. A process as claimed in claim 10, in which the Conradson carbon content is 2wt% or more.

12. A process as claimed in any one of claims 1 to 11, in which 1wt% or more of the feedstock hydrocarbons are deposited on the solid particles as coke.
13. A process as claimed in any one of claims 1 to 12, in which an oxygen-containing gas is additionally fed to the regeneration zone.
- 5 14. A process as claimed in claim 13, in which the oxygen : steam molar ratio fed to the regeneration zone is in the range of from 0.001 to 20.
15. A process as claimed in any one of claims 1 to 14, in which the reaction zone is operated at a temperature in the range of from 400 to 700°C, and a pressure in the range of from 0.1 to 1 MPa.
- 10 16. A process as claimed in any one of claims 1 to 15, in which the regeneration zone is operated at a temperature in the range of from 600 to 800°C, and a pressure in the range of from 0.1 to 20 MPa.
17. A process as claimed in any one of claims 1 to 16, additionally comprising a stripping zone, to which the coked particles are fed before being transferred to the
15 regeneration zone, in which stripping zone the coked particles are contacted with a stripping gas to remove unreacted feedstock hydrocarbons and product hydrocarbons.
18. A process as claimed in any one of claims 1 to 17, in which coked particles are transferred to the regeneration zone, optionally via a stripping zone, and regenerated
20 particles from the regeneration zone are transferred back to the reaction zone continuously.
19. A process as claimed in any one of claims 1 to 18, in which the product hydrocarbons are used to make one or more hydrocarbon fuels, selected from one or more of diesel, kerosene, aviation gasoline, gasoline jet fuel, and liquefied petroleum
25 gases (LPG).
20. A process as claimed in any one of claims 1 to 19, in which the solid particles comprises a type (i) component, and the Ti, Mn or Zn content of the component is in the range of from 0.05 to 10 wt%.
21. A process as claimed in claim 20, in which the Ti, Mn or Zn content is 4wt% or less.
- 30 22. A process as claimed in claim 20 or 21, in which the type (i) component comprises Ti and/or Zn, and the Ti and/or Zn content is 1.5wt% or less.

23. A process as claimed in any one of claims 1 to 22, in which the solid particles comprise a type (ii) component, and the Ce content is in the range of from 0.05 to 2 wt%.
24. A process as claimed in claim 23, in which the molar ratio of total other rare earth elements : cerium is in the range of from 0 : 1 to 2 : 1.
25. A process as claimed in any one of claims 1 to 24, in which the solid particles comprise a type (iii) component and comprise one or more additional elements that are trivalent when incorporated into the anionic clay, M(III), wherein the molar ratio $[Al + M(III)] / [Al + Mg + M(III)]$ for each M(III) is in the range of from 0.01 to 1.
26. A process as claimed in any one of claims 1 to 25, in which the solid particles comprise a type (iii) component, and comprise one or more additional elements that are divalent when incorporated into the anionic clay, M(II), wherein the molar ratio $Al / [Al + Mg + M(II)]$ for each M(II) is in the range of from 0.01 to 1.
27. A process as claimed in any one of claims 1 to 26, in which the solid particles comprise a type (iii) component, and the anionic clay comprises one or more additional elements selected from Ce, Ca, Mn, Fe, Co, Cu and Zn.
28. A process as claimed in any one of claims 1 to 27, in which the solid particles comprise a type (iv) component, and at least one of the cations in the perovskite is selected from one or more of La, Sr, Mn, Fe, Ce, Ni, Co, Ag, Nb, Cs, K, Rb, Ba and Pb.
29. A process as claimed in claim 28, in which the perovskite additionally comprises one or more element selected from Ti, V, Cu, Cr, Ca, Zr, Mo, Zn, W, Hf, Sn, alkaline earth elements, and other lanthanide elements.
30. A process as claimed in any one of claims 1 to 29, in which the perovskite comprises La and Mn.
31. A process as claimed in any one of claims 1 to 30, in which the perovskite comprises La, Sr, Fe and Co.
32. A process as claimed in any one of claims 1 to 31, comprising a second regeneration zone arranged in series or in parallel to the regeneration zone (the first regeneration zone).

33. A process as claimed in claim 32, in which the first and second regeneration zones are arranged in series, such that solid particles are removed from the first regeneration zone and fed to the second regeneration zone.

5 34. A process as claimed in claim 32 or claim 33, in which the oxygen to steam molar ratio fed to the first regeneration zone and the second regeneration zone are different.

35. A process as claimed in claim 34, in which the oxygen : steam molar ratio fed to the first regeneration zone is lower than the oxygen : steam molar ratio fed to the second regeneration zone.

10 36. A process as claimed in any one of claims 32 to 35, in which solid particles from the second regeneration zone are recycled to the first regeneration zone.

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INTERNATIONAL SEARCH REPORT

International application No

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Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 5-24, 32-36(completely); 1(partially)

a process for regenerating coked particles wherein the solid particles comprise an aluminosilicate zeolite comprising one or more of Mn, Ti and Zn

2. claims: 5-24, 32-36(completely); 1(partially)

a process for regenerating coked particles wherein the solid particles comprise a Ce-containing aluminosilicate zeolite

3. claims: 2-4, 9-19, 25-36(completely); 1(partially)

a process for regenerating coked particles wherein the solid particles comprise a magnesium and aluminium-containing anionic clay

4. claims: 2-4, 9-19, 25-36(completely); 1(partially)

a process for regenerating coked particles wherein the solid particles comprise a material with the Perovskite structure

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