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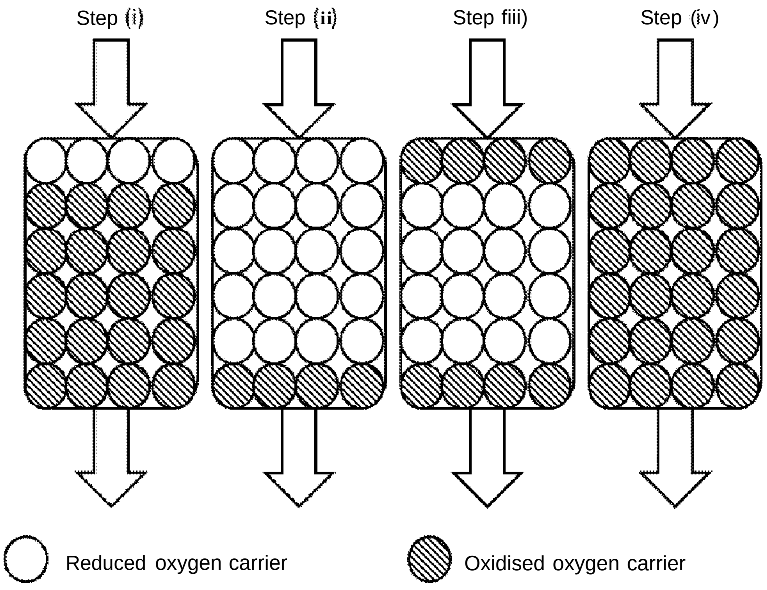
(54) **Title:** METHOD FOR SELECTIVE OXIDATION WITH A CATALYTIC COMPOSITE

Figure 1



(57) **Abstract:** The present invention provides a method for the selective oxidation of an organic molecule in a chemical looping reactor comprising a packed bed or fluidised bed, the packed bed or fluidised bed having a bed material comprising one or more catalytic composites comprising a solid-state-oxygen carrier as a primary oxygen source, the solid-state-oxygen carrier having an oxidation catalyst on a surface thereof, wherein the composite is for selective oxidation of an organic molecule in the absence of a secondary oxygen source, the method comprising repeating the following steps: (i) contacting the packed bed or fluidised bed with a fluid flow comprising the organic molecule to thereby oxidise the organic molecule; (ii) then optionally flushing the packed bed or fluidised bed with a flow of an inert gas; (iii) then regenerating the packed bed or fluidised bed with a flow of an oxygen- containing gas; (iv) then optionally flushing the packed bed or fluidised bed with a flow of an inert gas.

[Continued on next page]

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Method for selective oxidation with a catalytic composite

The present invention relates to method for the selective oxidation of an organic molecule in a chemical looping reactor. In particular, the invention allows the oxidation to take place with an oxygen-free source of the organic molecule to mitigate any explosion risk and to minimise any post-production purification steps.

EP2649059 relates to a method of optimising an alkylene oxide production, in particular ethylene oxide. The process of EP2649059 uses oxygen and ethylene to produce ethylene oxide in the presence of a silver-based catalyst and organic chloride promoters. The process involves the addition of oxygen in the feed gas at a concentration of no less than 1 mole percent. It is considered that this process has a number of potential disadvantages and draw-backs.

Firstly, there are significant safety risks associated with the introduction of oxygen in an ethylene feed gas. This is because the oxidation reaction to produce the ethylene oxide relies on the formation of a flammable mixture. At the temperatures required for the catalytic reaction, the mixtures may approach the explosion limit.

Secondly, the process efficiency is limited in a single pass conversion, requiring recycling of the gases. This is because the conversion of the ethylene is limited by the supply of gaseous oxygen in the feed. This oxygen amount is constrained to ensure that the mixture does not exceed the flammable limit. Thus the efficiency is constrained by the amount of oxygen which can safely be added to the feed gas.

Thirdly, where the oxygen is provided by using air, the product purity is low. There then needs to be a further step of processing the ethylene oxide product to remove impurities including nitrogen. Alternatively, in order to use pure oxygen as the feed gas oxygen-source, it is necessary to have an expensive pre-treatment nitrogen removal step. These treatment steps require considerable supporting processes (e.g. recompression for recycling, and N_2-separation). These steps dramatically increases the capital required for a process plant.

It will be appreciated that similar issues apply to selective oxidation reactions in general. That is, process efficiency is often limited by the need to avoid using or generating potentially explosive mixtures of oxygen and fuel gas and that steps taken to avoid such issues may complicate the overall process.

EP1052219 discloses the partial oxidation of hydrocarbons into a syngas comprising hydrogen and carbon monoxide. The reaction relies on the use of a perovskite-type ceramic mixed conductor at elevated temperatures up to 1400°C and typically at temperatures of at least 800°C.

JP S59199022 discloses a NOx reduction catalyst comprising $SrFe0_3$.

CN 105597778 discloses a strontium ferrite-loaded nano silver composite for the treatment of organic pollutants and industrial sewage.

Catalysis Letters, vol. 142, no. 8, 2012, A. Chongterdtoonskul et al., "Ethylene epoxidation activity over Ag-based catalysts on different nanocrystalline perovskite titanate supports", pages 991-1002, discloses the use of Ag-based Perovskite Titanate supports for the catalysis of ethylene epoxidation reactions.

Journal of Molecular Catalysis A: Chemical vol. 386, 15 February 2014, A. Chongterdtoonskul et al., "effect of diluent gas on ethylene epoxidation activity over various Ag-based catalysts on selective oxide supports", page 5-13, discloses the use of Ag-based Perovskite Titanate supports for the catalysis of ethylene epoxidation reactions.

Accordingly, it is desirable to provide an improved catalyst to tackle at least some of the problems associated with the prior art or, at least, to provide a commercially viable alternative thereto.

In particular, it is desirable to provide a method which lends itself for small scale, on-demand production, and which does not have the safety risks associated with known methods.

According to a first aspect there is provided a method for the selective oxidation of an organic molecule in a chemical looping reactor comprising a packed bed or fluidised bed, the packed bed or fluidised bed having a bed material comprising one or more catalytic composites comprising a solid-state-oxygen carrier as a primary oxygen source, the solid-state-oxygen carrier having an oxidation catalyst on a surface thereof, wherein the composite is for selective oxidation of an organic molecule in the absence of a secondary oxygen source,

the method comprising repeating the following steps:

(i) contacting the packed bed or fluidised bed with a fluid flow comprising the organic molecule to thereby oxidise the organic molecule;

(ii) then optionally flushing the packed bed or fluidised bed with a flow of an inert gas;

(iii) then regenerating the packed bed or fluidised bed with a flow of an oxygen-containing gas;

(iv) then optionally flushing the packed bed or fluidised bed with a flow of an inert gas.

The present invention will now be further described. In the following passages different aspects of the invention are defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

As used herein, the term "an organic molecule" is used to denote any molecule comprised of one or more carbon atoms, to which are attached other atoms of such elements as hydrogen, oxygen, and nitrogen. Other elements may also be present, such as sulphur and silicon. Generally the molecule will comprise two or more carbon atoms in rings or chains. Preferred examples of organic molecules include optionally substituted alkyl, alkenyl and alkynyl compounds, such as C_1 to C_6, alkanes, alkenes and alkynes. Suitable substitutional moieties include halogens and hydroxyl groups. The most preferred organic molecules are C_2 to C_4 alkenes and alkynes.

For efficient use in the reactor described herein, the organic molecule is preferably provided in gaseous form and the product of the process may also be in the gaseous phase. As will be appreciated, the reaction conditions can be adjusted to ensure that a molecule which would otherwise not be a gas can be provided in gaseous form. This can be achieved with a combination of reduced pressures and/or elevated temperatures.

Alternatively, the organic molecule may be provided in liquid form and the product of the process may then also be in the liquid phase. As will be appreciated, the reaction conditions can be adjusted to ensure that a molecule which would otherwise not be a liquid can be provided in liquid form. This can be achieved with a combination of increased pressures and/or reduced temperatures.

As used herein a "catalytic composite" refers to a component having at least two distinct portions. The component as a whole has catalytic properties which are provided by a portion which is formed of an oxidation catalyst. The oxidation catalyst is on a surface of a supporting portion which is formed of a solid-state-oxygen carrier. By way of example, therefore, a typical catalytic composite comprises a support portion having a surface film or membrane formed from a catalyst, or a support portion having pieces of a catalyst on the surface of the support portion. For the avoidance of doubt, the term composite requires that the carrier and the catalyst are discrete portions or phases provided together in a single component. That is, the term does not encompass a single composition component having a homogeneous composition (such as a vanadium phosphate bead).

The catalytic composite comprises a solid-state-oxygen carrier (or "carrier" or "solid oxidant" as used herein). The solid-state-oxygen carrier typically forms the support portion of the composite which supports the oxidation catalyst. A solid-state-oxygen carrier is a material which releasably contains oxygen in a microstructure thereof. By way of example, $SrFe0_3$ contains oxygen in the solid state and can release this oxygen to become $SrFeO_{(3-x)}$. This can provide a small amount of gaseous oxygen and adsorbed oxygen at the surface of the composite, depending on the temperature, and/or a small amount of sub-surface oxygen in the catalyst.

The solid-state oxygen carrier donates oxygen, but only if the metal can change its oxidation state (at the conditions at which the reaction runs). For $SrFe0_3$, for example, when oxygen is being donated, Fe reduces from *+IV\o* *+111.* Hence the most reduced form of this perovskite is $SrFe0_{2.5}$. An oxygen carrier that is suitable for chemical looping epoxidation (CLE) needs to donate oxygen in the low-temperature range. This is required by the epoxidation reaction which is possible at low temperatures only (at higher T only complete combustion is expected). Evaluating suitability of metal oxides for CLE is based on two parameters: the material's chemical potential of oxygen ($\mu 02$) and kinetics of the reaction. For CLE we want materials of high $\mu 02$, such as $SrFe0_3$. $\mu 0\,2$ can be analysed with a phase diagram of the material.

In the reactions described herein the solid-state-oxygen carrier is the primary oxygen source. Advantageously, the composite is for selective oxidation of an organic molecule in the absence of a secondary oxygen source. That is, the solid-state-oxygen carrier acts as a source of oxygen and can even generate a small amount of gaseous oxygen, and can achieve oxidation of an organic molecule with no other sources of "active" oxygen present (i.e. disregarding inert sources of solid oxygen, such as any fillers; e.g. the oxygen trapped in $Al_2 0_3$). In particular, it is possible to achieve oxidation without the presence of any gaseous oxygen being added to the process and without the reaction being performed in air.

The solid-state-oxygen carrier has an oxidation catalyst on a surface thereof (or "catalyst" as used herein). Oxidation catalysts are well known and are generally selected depending on the reaction of interest. These are discussed in more detail below. Preferably the catalytic composite consists of the solid-state-oxygen carrier and the oxidation catalyst, optionally with the presence of promoters species.

The present inventors have found that the unique structure of their catalytic composite allows them to conduct a range of conventional well known processes without the presence of added gaseous oxygen. This results in a number of safety benefits, as well as higher efficiencies and, in some cases, improved selectivity. Since the majority of oxidation reactions for small organic molecules are well known, there are very well documented and researched reaction conditions and oxidation catalysts which are used. Advantageously, the same teaching of conditions and reagents can be applied in the present invention. In particular, when adapting a well-known process, the same reaction conditions and oxidation catalyst can be employed, with the distinction that the oxidation catalyst is provided on a solid-state-oxygen carrier as a composite.

The solid-state-oxygen carrier preferably has a crystal structure. Preferred examples of suitable crystal structures, or crystal phases, include perovskite, brownmillerite, spinel, fluorite phases. Some of these structures may change crystalline phase when oxygen is removed from the material. Preferably the solid-state-oxygen carrier has a crystal structure which does not significantly change when oxygen atoms are lost therefrom. That is, preferably the phase does not change during cycling. This means that the composite remains structurally stable when the reaction is cycled with oxygen being removed from and recharged into the carrier. Preferably the crystal structure is a perovskite or brownmillerite. These structures may show considerable non-stoichiometry of oxygen which can be exploited to release oxygen without phase change. Therefore, these structures are stable for the different oxidation states resulting for oxygen loss and gain.

Preferably the solid-state-oxygen carrier used in the method described herein comprises $SrFe0_3$ and/or $SrCo0_3$ and/or $Sr_3Fe_20_7$. A particularly preferred carrier is a combination of $SrFe0_3$ and $Sr_3Fe_20_7$. Although these compounds have been described as having an absolute formula, depending on their oxygen contents, they may be present in a substoichiometric form, i.e. $SrFeO_{(3-\delta)}$ and $SrCoO_{(3-\delta)}$. These compounds have a good equilibrium partial pressure of oxygen, meaning that they can readily release oxygen to drive the desired reaction. In addition, they are structurally stable for multiple discharge and recharge steps.

Other examples of the solid-state-oxygen carrier which may be used alone, or in combination, or in combination with the Sr species discussed above, include CuO.

Preferably the solid-state-oxygen carrier has, at the reaction temperature, an equilibrium oxygen partial pressure of at least 10^{-15} bar, more preferably at least 10^{-10} bar and most preferably at least 10^{-5} bar. Methods for measuring equilibrium oxygen partial pressure are known in the art and include thermogravimetric analysis (TGA), pulse titration, X-ray diffractometry (XRD) and coulometric titration.

Preferably the solid-state-oxygen carrier comprises two or more distinct phases. Such a combination of phases allows for optimisation of the rate of oxygen release required for a given reaction.

Preferably the solid-state-oxygen carrier is doped with a catalyst promoter species. Catalyst promoter species are well known in the art and may be selected depending on the specific reaction being carried out. Examples of suitable dopants are La, Mn and Cu, and examples demonstrating the inclusion of such dopants are provided herein.

Catalysis Letters, vol. 142, no. 8, 2012, A. Chongterdtoonskul et al., "Ethylene epoxidation activity over Ag-based catalysts on different nanocrystalline perovskite titanate supports", pages 991-1002, investigates classical epoxidation (0_2 in gas feed) using $MgTi0_3$, $CaTi0_3$, $SrTi0_3$, and $BaTi0_3$. None of these species are considered to be solid-state-oxygen carriers as defined herein and this can be readily foreseen. As discussed above, evaluating suitability of metal oxides for CLE is based on two parameters: the material's chemical potential of oxygen (μ02) and kinetics of the reaction. For CLE we want materials of high μ02. μ0 2 can be analysed with a phase diagram of the material. From this review we can see that the metal oxides used in the Chongterdtoonskul would not be considered as solid state oxygen carriers: $MgTi0_3$ reduces only above 1600˚C (or melts); $CaTi0_3$ is chemically stable to at least 1970˚C (where it melts); $BaTi0_3$ is stable up to 1460˚C (also melts); $SrTi0_3$ is stable up to 1640˚C, then it separates into two phases.

Preferably the oxidation catalyst is a catalytic metal. For example, silver is a particularly preferred metal since it is oxygen permeable. This means that the silver may be provided as a membrane on the solid-state-oxygen carrier and still allow for diffusion of oxygen into and out of the composite. When using a less- or non-oxygen-permeable oxidation catalyst, it may be preferred to make sure that the catalyst does not entirely encompass the carrier. This ensures that some of the surface of the carrier is exposed for regeneration. Preferably the catalytic metal comprises copper, silver, or gold, or a combination of two or more thereof.

Preferably the oxidation catalyst forms an oxygen-permeable membrane coating on the solid-state-oxygen carrier. This ensures a high area of oxidation catalyst. Alternatively the oxidation catalyst is preferably present on the surface of the solid-state-oxygen carrier in one or more discrete regions.

Preferably the ratio of oxidation catalyst to solid-state-oxygen carrier by weight in the catalytic composite is from 1:99 to 1:4. More preferably the ratio is from 1:50 to 1:4, preferably 1:8 to 1:5, and most preferably about 1:6. These ratios give a good balance of catalyst to the carrier. This ensures that the reaction is catalysed while providing enough oxygen to drive the reaction. The specific ratio will depend on the reaction being catalysed and could be optimised by the skilled person.

Preferably the composite is in particulate form, having a mean particle size of from 10 microns to 10mm, preferably from 100 microns to 1mm. The selection of the particle size can be optimised depending on the application and, in particular, to suitable sizes for use in different reactors.

The catalytic composite may be formed by any known technique. A preferred method is incipient wetness impregnation, but any standard method in catalyst manufacture would also be suitable, including co-precipitation or wet impregnation.

The method involves a packed bed or fluidised bed having a bed material comprising one or more catalytic composites described herein. Such processing equipment is well known in the art and work on the basis of passing a reagent over or through a bed of high surface area particles. The term "bed" may be used herein to refer to either a packed bed or fluidised bed.

As will be apparent, the present method has a number of advantages over the prior art. In particular, since there is no added gaseous oxygen and the oxygen is being supplied from a solid-state carrier, the explosion risk is significantly reduced. Moreover, the single-pass efficiency can be higher, since there is no constraint on the amount of oxygen which can be added at the point of the reaction. In addition, no nitrogen removal is required, which reduces the process costs and plant investment capital. A further unexpected advantage of the process is that it may provide for higher selectivities. This is because the process may eliminate or reduce certain side reactions associated with gaseous oxygen.

According to a first step (i), the packed bed or fluidised bed is contacted with a fluid flow, preferably a gaseous flow comprising the organic molecule to thereby oxidise the organic molecule. The oxidation takes place using oxygen released from the carrier and the reaction is catalysed by the catalyst which forms part of the catalytic composite. The process step duration will depend on the kinetics of the reaction.

As will be appreciated, the fluid flow of the organic molecule may additionally comprise a carrier fluid or diluent. When the fluid flow is a gaseous flow, the carrier fluid may be an inert gas. Depending on the reaction being performed, a diluent may be necessary to prevent explosive decomposition. This is a particular issue for the treatment of concentrated ethylene oxide. The critical explosive pressure depends on temperature, the chemical identity of the inert gas, the composition of the mixture, the total pressure, and whether any liquid ethylene oxide is present. The skilled person considering a set of reaction conditions could determine the required amount of diluent for safe operation. Preferred inert diluents include the following gases: H_20 , $C0_2$, N_2, CH_4 and halogenated hydrocarbons. Selection of inert gases with higher heat capacities reduces the explosion risk.

The bed is then optionally flushed with a flow of an inert gas. This serves to substantially remove any unreacted organic molecule from the bed. This reduces a combustion risk in the subsequent steps. It will be understood that the solid-state-oxygen carrier may release gaseous (molecular) oxygen and, therefore, any purging or flushing step is not intended to completely remove oxygen from the bed. Instead, such flushing steps are intended to remove the gas used in the regeneration step to mitigate risks associated with forming an explosive mixture.

According to a second step (iii), the bed is then regenerated with a flow of an oxygen-containing gas. The oxygen-containing gas is preferably air since this is readily available and cost-effective. The regeneration step duration will depend on the extent to which the catalytic composite is oxygen-depleted and the rate if regeneration.

The bed is then optionally flushed with a flow of an inert gas. This serves to substantially remove any of the oxygen-containing gas from the bed. This reduces a combustion risk in the subsequent steps.

Preferably the fluid flow, preferably gaseous flow, of the organic molecule introduced into the bed is substantially free of molecular oxygen (0_2). That is, preferably the organic molecule is provided, optionally with a carrier gas or diluent, as a substantially molecular-oxygen-free flow. By substantially molecular-oxygen-free it is meant that the feed gas contains less than 5v%, more preferably less than 1v% oxygen and most preferably contains only unavoidable impurity levels of oxygen.

Preferably the flow of inert gas used for each flushing step comprises N_2 and/or $C0_2$. It may be desirable to flush with $C0_2$, since this may be made on site during the oxidation of the organic molecule as a by-product.

Preferably the method further comprises recovering a product fluid flow from the packed bed or fluidised bed in step (i) to obtain the oxidised organic molecule and, optionally, purifying the product fluid flow. Preferably the product fluid flow is a product gas flow. The purification step may be required to remove some small amounts of contaminants, such as inert gas from the intermediate flushing steps, unreacted feed materials and any side-products.

Preferably the method further comprises monitoring the gas flow from the packed bed or fluidised bed in step (i) to determine when the solid-state-oxygen carrier is in an oxygen-depleted state. This allows the operator to ensure the process is running at optimum yield.

Preferably the method further comprises monitoring the gas flow from the packed bed or fluidised bed in step (iii) to determine when the solid-state-oxygen carrier is in an oxygen-replenished state. This allows the operator to minimise reactor down-time.

Preferably step (i) is conducted at a packed bed or fluidised bed temperature of from 150 to 600°C. Below 150°C it is difficult to obtain a carrier which is able to reversibly release oxygen and reactions rates are slow. Above 600°C it may difficult to obtain a useful yield since the organic molecule product is prone to decomposition or combustion. For some reactions it may be possible to operate above 600°C and, in particular, it is noted that the oxidative coupling of methane (OCM) may take place at 840°C and oxidative dehydrogenation (ODH) of ethane can also occur at higher temperatures. Accordingly, an operation range of up to 900°C may be considered. A preferred operating temperature for the selective oxidation reactions is 200 to 300°C, as shown in the Examples and preferred methods discussed below.

Preferably the fluid flow of the organic molecule further comprises one or more reaction promoters. Such reaction promoters, which include Cs and Cl, are well known in the art and their selection and amounts will depend on the specific reaction being performed. Suitable promoters may be organic (in particular organic chlorides e.g. vinyl chloride) or inorganic (e.g. CsCl, $CsN0_3$). In addition, the promoter may best be added to the gas (e.g. vinyl chloride) or to the catalytic composite (e.g. CsCl, $CsN0_3$). Other examples of promoters include compounds comprising K, Na, Rh, Ba or La. Reaction promoters are well known and their application in the reactions described herein would be routine for the skilled person.

According to a preferred embodiment of the method described herein, the method is for the production of alkylene oxide from an olefin, wherein the fluid flow comprising the organic molecule comprises the olefin. Preferably such a reaction takes place where the oxidation catalyst comprises Ag and the temperature is 200 to 300°C.

According to a preferred embodiment of the method described herein, the method is for the production of ethylene oxide from ethene, wherein the fluid flow comprising the organic molecule comprises ethene. Preferably such a reaction takes place where the oxidation catalyst comprises Ag and the temperature is 200 to 300°C.

According to a preferred embodiment of the method described herein, the method is for the production of formaldehyde from methanol, wherein the fluid flow comprising the organic molecule comprises methanol. Preferably such a reaction takes place where the oxidation catalyst comprises at least one of Ag, Au and iron molybdates (such as $FeMb0_4$), and the temperature is 400 to 600°C.

According to a preferred embodiment of the method described herein, the method is for the production of propylene oxide from propene, wherein the fluid flow comprising the organic molecule comprises propene. Preferably such a reaction takes place where the oxidation catalyst comprises Ag and the temperature is 200 to 300°C.

According to a preferred embodiment of the method described herein, the method is for the production of acrolein from propene, wherein the fluid flow comprising the organic molecule comprises propene. Preferably such a reaction takes place where the oxidation catalyst comprises an ODH catalyst (oxidative dehydrogenation catalyst) and the temperature is about 400°C.

According to a preferred embodiment of the method described herein, the method is for the production of maleic anhydride from butane, wherein the fluid flow comprising the organic molecule comprises butane. Preferably such a reaction takes place where the oxidation catalyst comprises an vanadium phosphate and the temperature is about 400°C.

According to a further aspect there is provided the use of the catalytic composite described herein, especially one comprising $SrFe0_3$ and/or $SrCo0_3$ and/or $Sr_3Fe_20_7$ and/or CuO, to selectively oxidise an organic molecule in the absence of a secondary oxygen source, in particular molecular oxygen. As discussed above, the catalytic composite provides a safe approach to conducting oxidation reactions by mitigating the explosion risk which arises from the oxidation of organic molecules in the presence of gaseous oxygen. $SrFe0_3$ and/or $SrCo0_3$ and/or $Sr_3Fe_20_7$ are most preferred.

According to a further aspect there is provided the use of a catalytic composite for the selective oxidation of an organic molecule in a chemical looping reactor comprising a packed bed or fluidised bed comprising the catalytic composite,

wherein the catalytic composite comprises a solid-state-oxygen carrier as a primary oxygen source, the solid-state-oxygen carrier having an oxidation catalyst on a surface thereof, wherein the composite is for selective oxidation of an organic molecule in the absence of a secondary oxygen source,

the use comprising repeating the following steps:

(i) contacting the packed bed or fluidised bed with a fluid flow comprising the organic molecule to thereby oxidise the organic molecule;

(ii) then optionally flushing the packed bed or fluidised bed with a flow of an inert gas;

(iii) then regenerating the packed bed or fluidised bed with a flow of an oxygen-containing gas;

(iv) then optionally flushing the packed bed or fluidised bed with a flow of an inert gas.

Preferably the use is for the selective oxidation of an olefin to an alkylene oxide, wherein the fluid flow comprising the organic molecule comprises the olefin. Preferably such a reaction takes place where the oxidation catalyst comprises Ag and the temperature is 200 to 300°C.

Preferably the use is for the selective oxidation of ethene to ethylene oxide, wherein the fluid flow comprising the organic molecule comprises ethene. Preferably such a reaction takes place where the oxidation catalyst comprises Ag and the temperature is 200 to 300°C.

Preferably the use is for the selective oxidation of methanol to formaldehyde, wherein the fluid flow comprising the organic molecule comprises methanol. Preferably such a reaction takes place where the oxidation catalyst comprises at least one of Ag, Au and iron molybdates (such as $FeMb0_4$), and the temperature is 400 to 600°C.

Preferably the use is for the selective oxidation of propene to propylene oxide, wherein the fluid flow comprising the organic molecule comprises propene. Preferably such a reaction takes place where the oxidation catalyst comprises Ag and the temperature is 200 to 300°C.

Preferably the use is for the selective oxidation of propene to acrolein, wherein the fluid flow comprising the organic molecule comprises propene. Preferably such a reaction takes place where the oxidation catalyst comprises an ODH catalyst (oxidative dehydrogenation catalyst) and the temperature is about 400°C.

Preferably the use is for the selective oxidation of butane to maleic anhydride, wherein the fluid flow comprising the organic molecule comprises butane. Preferably such a reaction takes place where the oxidation catalyst comprises vanadium phosphate and the temperature is about 400°C.

Preferably the catalytic composite in the foregoing uses comprises $SrFe0_3$ and/or $SrCo0_3$ and/or $Sr_3Fe_20_7$. However, for these specific uses the catalytic composite may be selected from the broader alternatives discussed herein, namely a material which releasably contains oxygen in a microstructure thereof. Preferred examples are those having a crystal structure. Preferred examples of suitable crystal structures, or crystal phases, include perovskite, brownmillerite, spinel, fluorite phases. Preferably the solid-state-oxygen carrier has a crystal structure which does not significantly change when oxygen atoms are lost therefrom.

The invention will now be described in relation to the following non-limiting figures, in which:

Figure 1 is a schematic of the process steps when using a chemical looping reactor in the method of the present invention. The term refers to a type of reactor where the bed comprises cyclically exhausted and regenerated material, and is known for use in chemical looping combustion reactions.

Figure 2 shows concentration, selectivity and conversion profiles from a packed bed reactor operated in chemical looping mode to produce ethylene oxide, using 15 wt% $Ag/SrFe0_3$ as the catalyst. The ethylene oxide (EO) line overlaps the $C0_2$ line at 10 minutes and then forms the lower peaks at each time thereafter. The background of $C0_2$ during oxidation steps was from compressed atmospheric air. Conditions: 270°C, 1 atm, 2.0 g catalyst, gas feed of 200 mL/min (as measured at 293 K, 1 atm). Cycling times: (i) t_{red} = 1.5 min reduction with 5.16 vol% C_2H_4 in balance N_2, (ii) 2 min purge with N_2, (iii) t_{ox} = 15 min oxidation with air, (iv) 2 min purge with N_2.

Figure 3 shows effects of cycling times on the selectivity and conversion for the production of ethylene oxide. Conditions: 270°C, 1 atm, 2.0 g of 15 wt% $Ag/SrFe0_3$, feed of 200 mL/min (as measured at 293 K, 1 atm). Cycling times (unless stated otherwise): (i) t_{red} = 1.5 min reduction with 5.1 6 vol% C_2H_4 in balance N_2, (ii) 2 min purge with N_2, (iii) t_{ox} = 15 min oxidation with air, (iv) 2 min purge with $N_{2.}$

Figure 4 shows the effect of extended ex-situ reoxidation at 400°C for 2 h, performed after every 10th cycle for the production of ethylene oxide. Conditions: 270°C, 1 atm, 2.0 g of 15 wt% Ag/$SrFe0_3$, feed of 200 mL/min (as measured at 293 K, 1 atm). Cycling times: (i) t_{red} = 1.5 min reduction with 5.16 vol% C_2H_4 in balance N_2, (ii) 2 min purge with N_2, (iii) t_{ox} = 15 min oxidation with air, (iv) 2 min purge with $N_{2.}$

Figure 5 shows the effect of the support on the performance in chemical looping mode for the production of ethylene oxide. Conditions: 270°C, 1 atm, 2.0 g of catalyst, feed of 200 mL/min (as measured at 293 K, 1 atm). Cycling times: (i) t_{red} = 1.5 min reduction with 5.1 6 vol% C_2H_4 in balance N_2, (ii) 2 min purge with N_2, (iii) t_{ox} = 15 min oxidation with air, (iv) 2 min purge with N_2. The EO line in the top chart overlaps the $C0_2$ line at 10 minutes and then forms the lower peaks at each time thereafter. In the second and third charts the EO line appears to be simply noise.

Figure 6 shows the selectivity and conversion percentages for 15 wt% Ag/$SrFe_{0\cdot9}Mno.i0_{3-\delta}$ in Example 2.

Figure 7 shows the selectivity and conversion percentages for 15 wt% Ag/[$SrFe0_{3-\delta}$ + $Sr_3Fe_20_{7-s}$] in Example 2.

Figure 8 shows the selectivity and conversion percentages for 15 wt% Ag + 600 ppmw CsCI/$SrFe0_3$ in Example 2.

Figures 9A and 9B show the conversion profiles and selectivity for the first sample in Example 3.

Figures 10A and 10B show the conversion profiles and selectivity for the second sample in Example 3.

Figures 11A and 11B show the conversion profiles and selectivity for the second sample in Example 3.

Figures 12A and 12B show the conversion profiles and selectivity for the first sample in Example 4.

Figures 13A and 13B show the conversion profiles and selectivity for the second sample in Example 4.

In an embodiment of Figure 1, the following steps are conducted. In step (i), ethene is added to the reaction vessel and ethylene oxide is obtained as the product. This depleted the oxygen from the carrier. In step (ii) nitrogen is introduced to flush out any residual ethene or ethylene oxide. In step (iii) air is flowed through the chamber to regenerate the carrier. In step (iv) nitrogen is flowed through the chamber to flush out any residual gaseous oxygen.

The invention will now be described in relation to a specific non-limiting examples. In particular, the following discussion will focus on the production of ethylene oxide in a chemical looping reactor. Nonetheless, it should be appreciated that the invention may be applied equally to other oxidation processes as discussed herein.

Example 1

Ethylene oxide (EO) is an industrially significant chemical intermediate, with a global production of 26 million tonnes in 201 3. It is used as a feedstock in the synthesis of polymers, antifreeze, surfactants, solvents *etc.* The predominant technology for its production is based solely on the epoxidation of ethylene with air or purified oxygen. Silver is the only catalyst used because no other material has been found that performs competitively.

A key intermediate species in the reaction mechanism is the oxygen adatom (O_a), which is the selective oxygen species responsible for the epoxidation and, depending on its electrophilicity, combustion. In the conventional process, where ethylene and gaseous oxygen are co-fed to the reactor, O_a is generated from the dissociative adsorption of 0_2, *i.e.* from the gas phase.

There have been no reports of O_a being directly supplied from a solid oxidant, and this is probably because of the challenging requirements imposed on such a solid oxidant. There is a kinetic challenge, because solid state conduction of oxide ions is typically slow at these reaction temperatures of 200 - 300°C. There is also a thermodynamic challenge, which is indicated by the high partial pressures of 0_2 typically used, which may be up to 2 bar.

Theoretical and experimental evidence suggest the existence of surface silver oxide phases at these temperatures and pressures. The inventors realised that the solid oxidant needs to have a high oxygen chemical potential, μ_{02}, to stabilise these active phases, or at the very least, to ensure a sufficiently high surface coverage of O_a. Such a high μ_{02} in this temperature range is rare among solid oxides. Lastly, the solid oxidant needs to be regenerable without significant loss of oxygen-storage capacity and kinetic activity.

The inventors identified $SrFe0_3$ as a potential oxygen carrier for chemical looping combustion. It was found that $SrFe0_3$ was able to reversibly release gaseous 0_2 over many cycles at low temperatures (-673 K, $p0_2 = 0.15$ bar), which demonstrates its high μ_{02}. Crucially, $SrFe0_3$ does not carbonate significantly. Carbonation would deactivate the oxygen carrier, which is a problem that affects other materials with high μ_{02} such as $Sr0_2/SrO$ and $Ba0_2/BaO$. Resistance against carbonation is necessary because significant levels of $C0_2$ may be generated from side reactions during epoxidation.

The inventors realised that these favourable properties allow the advantageous interfacing of $SrFe0_3$ with Ag; $SrFe0_3$ can then supply oxygen to Ag as bulk or subsurface oxygen (O_{ss}), where the oxygen can then diffuse to the silver surface to be presented as O_a to effect the epoxidation in the absence of gaseous 0_2. The catalyst can then be regenerated in air in a separate step to complete the chemical looping cycle.

It is advantageous to perform selective oxidations using a solid oxidant, in the absence of $0_{2(g)}$, because this avoids flammable mixtures and renders a safer process. Furthermore, this can reduce separation costs by avoiding the need to separate diluting N_2 (either from purifying oxygen or from purifying the products). Lastly, improved selectivities may be achieved by the removal of gaseous oxygen.

The following examples demonstrate that the epoxidation may be performed in the absence of $0_{2(g)}$ by using a solid oxygen carrier. The aim is not to show competitive selectivities, so common promoters were not used *{e.g.* Cs and Cl), but rather to demonstrate the concept. The addition of such promoters would be expected to increase the yields to commercially acceptable levels.

A catalyst, composed of 15 wt% Ag supported on $SrFe0_3$, was evaluated in a packed bed reactor *(n.b.* here, the nonstoichiometric perovskite $SrFe0_{3-\delta}$ is abbreviated as $SrFe0_3$ for brevity).

A typical experiment is shown in Figure 2, where the selectivity and conversion achieved by the catalyst decayed gradually with cycling, before approaching an asymptote. This decay is probably caused by the slow rate of regeneration of the catalyst. The EO line overlaps the $C0_2$ line at 10 minutes and then forms the lower peaks at each time thereafter.

This is supported by the results in Figure3, which show the effect of varying the duration of reduction and oxidation. When the duration of oxidation was increased from t_{ox} = 7.5 min to 30 min, both the selectivity and conversion were maintained at higher values. A similar improvement was observed when the duration of reduction was decreased from t_{red} = 3 min to 1 min. The decrease in conversion is probably caused by the depletion of oxygen species, owing to the catalyst gradually becoming more reduced with cycling. Accumulation of coke, indicated by slight elevations in the concentration of $C0_2$ (on the order of 10 ppm) during oxidation with air, may also have caused the decaying activity. The decrease in selectivity may be explained by the depletion of subsurface oxygen species, O_{ss}, when the catalyst was reduced. The decrease in abundance of O_{ss} causes the degree of electrophilicity of O_a to decrease, which resulted in the observed decrease in selectivity.

The regenerability of the 15 wt% Ag/$SrFe0_3$ catalyst was examined further by calcining the cycled sample *ex situ* in static air at 400°C for 2 h, before subjecting them to the same ten cycles. This was repeated three times, shown in Figure 4. It can be seen that this treatment fully regenerated both the selectivity and activity of the catalyst, which confirms that the oxidation step is probably the rate-limiting step in the cycle. Additionally, coke should have been more effectively removed. Figure 4 also shows that the selectivity gradually improved over time, which may be explained by sintering of the Ag particles. The activity and selectivity of Ag particles increases with their size up to 100 nm, and improves markedly over the range of 20 - 50 nm. This also demonstrates the stability of the catalyst to the thermal cycling required for use in such a chemical looping process.

Scanning electron microscopy (SEM) images of the fresh and cycled catalysts show that Ag particles as small as 50 nm present on the fresh catalyst were no longer present on the cycled catalyst.

Generally, over the course of one cycle, the instantaneous selectivity of the carrier decreased as it became more reduced. The trend is consistent with the proposed picture earlier, that reduction of the catalyst led to a gradual depletion of O_a and O_{ss}, which resulted in the decreasing selectivity. Interestingly, the first cycle after each calcination step always exhibited a maximum in selectivity and conversion *(n.b.* the early maxima for subsequent cycles are probably artefacts of the response time of the gas analyser, or noise). This gradual improvement in the selectivity during the first cycle may be due to carbon deposition which selectively poisoned unselective sites.

The performance of Ag/$SrFe0_3$ was in stark contrast with those of (i) 15 wt% Ag/Al_20_3 and (ii) a heterogeneous mixture of particles of 15 wt% Ag/Al_20_3 with particles of $SrFe0_3$, shown in Figure 5. The 15 wt% Ag/Al_20_3 catalyst yielded only barely detectable levels of EO (-1 0 ppm) with instantaneous selectivities of up to -30% in the first cycle, and no more detectable EO in subsequent cycles. The production of $C0_2$ also quickly fell to insignificant levels (< 30 ppm). This is because neither Ag nor Al_20_3 can carry enough oxygen over from the preceding oxidation step in the cycle, so the subsequent reaction with ethylene became starved of oxygen.

With the addition of separate particles of $SrFe0_3$ to the bed, only $C0_2$ was produced. This is because the perovskite could not generate O_a by itself nor did it supply any oxygen to Ag/Al_20_3, which prevented epoxidation from occurring and so only combustion occurred. This also shows that some $C0_2$ evolved in the reaction with Ag/$SrFe0_3$ must have originated from reaction with the $SrFe0_3$ surface that was not covered with Ag, therefore the selectivity could be improved simply by increasing the coverage of $SrFe0_3$ with Ag.

The experiment with bare $SrFe0_3$ also eliminates the possibility of $SrFe0_3$ supplying oxygen to Ag *via* gaseous transport at this temperature. Hence, the performance of 15 wt% Ag/$SrFe0_3$ must have originated from the intimate physical contact between Ag and $SrFe0_3$, so that either (i) solid state oxygen conducted from $SrFe0_3$ to Ag, as hypothesised, or (ii) the oxygen storage capacity of Ag became enhanced.

However, because of the magnitude of the effect, the latter seems unlikely; if one assumes that all of the oxygen in the products originated solely from Ag, then the bulk chemical state of the silver phase would be written as $AgO_{0.08}$ (for the first cycle with t_{red} = 3 min), which is far higher than the limit of solubility (0:Ag molar ratio ~ 10^{-6}). The mechanism of (i) may be exploited in catalyst-oxygen carrier systems other than Ag-$SrFe0_3$ shown herein and would be applicable to selective oxidations other than epoxidation of ethylene.

The Ag/Al_20_3 and Ag/$SrFe0_3$ catalysts were also examined in a co-feeding mode, where the feed was a premixed stream of 0_2 (4 vol%) and C_2H_4 (4 vol%), with 200 mL/min total flow and 1.0 g catalyst (half the catalyst loading compared to the chemical looping experiments). After 5 h of time on stream, Ag/Al_20_3 achieved a conversion of 1.6% at a selectivity of 27%, whilst Ag/$SrFe0_3$ achieved a conversion of 6% at a selectivity of 5.7% Whilst the selectivities and conversions shown were worse than the performance of the conventional co-feeding operation, we note that there are many degrees of freedom available to optimise the performance of both, or separately, the catalyst and the oxygen carrier, in addition to the operating parameters.

No such optimisation was undertaken in producing these results. It is noteworthy that the instantaneous performance near the start of chemical looping operation briefly surpassed the co-feeding operation, and that this could be reliably reproduced with a long regenerating treatment at elevated temperatures in air - we speculate that tuning the material properties for faster reoxidation to sustain this early transient will be particularly important.

Example 2

Three additional samples were prepared. In samples 1 and 2, only the oxygen carrier was modified (same Ag loading, same impregnation method, same reactor conditions) compared to Example 1.

The first sample had manganese doped into the oxygen carrier (90:10 Fe:Mn mole ratio). This sample demonstrated improved selectivity, conversion and regenerability (i.e. cyclic stability).

The second sample was supposed to have an oxygen carrier consisting of 100 wt% $SrFe0_3$, but the batch was impure and was found to contain ~7 wt% $Sr_3Fe_20_7$, in addition to $SrFe0_3$.

This lead to a startlingly improved performance (an order of magnitude improvement in the concentration of EO) which is due to the presence of this impure phase $Sr_3Fe_20_7$.

The third sample had a final catalyst which was Ag impregnated with 600 ppmw CsCl. A small improvement in selectivity and conversion was found but not as much as could be expected. We suspect much bigger improvements if the loading of promoter is optimised.

Example 3

Three additional samples were prepared. Only the oxygen carrier was modified (same Ag loading, same impregnation method, same reactor conditions) compared to Example 1.

The first sample had copper doped into the oxygen carrier (80:20 Fe:Cu mole ratio) to provide 15 wt% Ag/$SrFe_{0.8}Cuo_{.2}0_{3-\delta}$. The results are shown in Figure 9A and 9B. This sample had copper doped into the support material $SrFe0_3$ (80:20 Fe:Cu mole ratio). In comparison to the undoped $SrFe0_3$, the results give increase in conversion, while selectivity is preserved at the same level.

Second sample was 15 wt% Ag/$Sr_3Fe_20_{7-\delta}$. The results are shown in Figure 10A and 10B. In this sample the support material was $Sr_3Fe_20_7$. This sample results gave increase in conversion and decrease in selectivity in comparison to the results with $SrFe0_3$.

Third sample was a mixture of 15 wt% Ag/[$Sr_3Fe_20_7$:$SrFe0_3$] (50%wt:50%wt). The results are shown in Figure 11A and 11B. In this sample the support material was a mixture of $SrFe0_3$ and $Sr_3Fe_20_7$, with a weight ratio of 1:1. This gave a significant increase in selectivity of EO production; however, the ethylene conversion decreased.

Example 4

Four additional samples were prepared. Only the oxygen carrier was modified (same Ag loading, same impregnation method, same reactor conditions) compared to Example 1.

The first sample was 15wt% silver on a CuO oxygen carrier. The results are shown in Figure 12A and 12B. The experiments were carried out with 4 g of catalysts, at 230-300°C. The conversion is low, but likely can be improved. The activity was much less (20 ppm) than for

$SrFeO_3$ (500 ppm). Nevertheless, the amount of oxygen in the epoxide was more than the solubility of O in Ag, which proves that CuO was donating oxygen.

The second sample was 15 wt% Ag/$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$. The results are shown in Figure 13A and 13B. The experiments were carried out with 2 g of catalysts, at 230-290°C. The selectivity and conversion are not impressive, but we would expect both to improve after finding an optimal experimental condition or adding combustion inhibitors.

Third and fourth samples were tested, but did not successfully give ethylene oxide. These demonstrate the importance of the solid-state oxygen carrier selection based on oxidation state changes at the operation temperature. These samples were 15 wt% Ag/ Bi_2O_3 and 15 wt% Ag/ CeO_2. For the 15 wt% Ag/ Bi_2O_3 there was no activity, neither for epoxidation or complete combustion. No combustion products observed. For 15 wt% Ag/ CeO_2, CO_2 was produced, but no CO or epoxide was detected.

Unless otherwise stated, all percentages herein are by weight and all pressures are absolute, rather than gauge. All disclosures of comprising language are intended to also encompass closed, consisting language, unless indicated to the contrary. In particular, the solid-state-oxygen carriers disclosed herein may consist of the specific species disclosed.

Although preferred embodiments of the invention have been described herein in detail, it will be understood by those skilled in the art that variations may be made thereto without departing from the scope of the invention or of the appended claims.

Claims:

1. A method for the selective oxidation of an organic molecule in a chemical looping reactor comprising a packed bed or fluidised bed, the packed bed or fluidised bed having a bed material comprising one or more catalytic composites comprising a solid-state-oxygen carrier as a primary oxygen source, the solid-state-oxygen carrier having an oxidation catalyst on a surface thereof, wherein the composite is for selective oxidation of an organic molecule in the absence of a secondary oxygen source,

the method comprising repeating the following steps:

(i) contacting the packed bed or fluidised bed with a fluid flow comprising the organic molecule to thereby oxidise the organic molecule;

(ii) then optionally flushing the packed bed or fluidised bed with a flow of an inert gas;

(iii) then regenerating the packed bed or fluidised bed with a flow of an oxygen-containing gas;

(iv) then optionally flushing the packed bed or fluidised bed with a flow of an inert gas.

2. The method according to claim 1, wherein the solid-state-oxygen carrier comprises $SrFe0_3$ and/or $SrCo0_3$ and/or $Sr_3Fe_20_7$ and/or CuO.

3. The method according to claim 1 or claim 2, wherein the composite is in particulate form, having a mean particle size of from 10 microns to 10mm, preferably from 100 microns to 1mm.

4. The method according to any of the preceding claims, wherein the solid-state-oxygen carrier is doped with a catalyst promoter species.

5. The method according to any of the preceding claims, wherein the oxidation catalyst is a catalytic metal.

6. The method according to claim 5, wherein the catalytic metal comprises copper, silver, or gold or a combination of two or more thereof.

7. The method according to any of the preceding claims, wherein:

(i) the oxidation catalyst forms an oxygen-permeable membrane coating on the solid-state-oxygen carrier; or

(ii) the oxidation catalyst is present on the surface of the solid-state-oxygen carrier in one or more discrete regions.

8. The method according to any of the preceding claims, wherein the ratio of oxidation catalyst to solid-state-oxygen carrier by weight in the catalytic composite is from 1:99 to 1:4.

9. The method according to any of the preceding claims, wherein the fluid flow comprising the organic molecule introduced into the packed bed or fluidised bed is substantially free of molecular oxygen.

10. The method according to any of the preceding claims, wherein the method is performed without any gaseous oxygen being added in step (i).

11. The method according to any of the preceding claims, wherein the flow of inert gas comprises N_2 and/or $C0_2$.

12. The method according to any of the preceding claims, wherein the method further comprises recovering a product fluid flow from the packed bed or fluidised bed in step (i) to obtain the oxidised organic molecule and, optionally, purifying the product fluid flow.

13. The method according to any of the preceding claims, wherein the method further comprises:

(a) monitoring a fluid flow from the packed bed or fluidised bed in step (i) to determine when the solid-state-oxygen carrier is in an oxygen-depleted state, and/or

(b) monitoring a fluid flow from the packed bed or fluidised bed in step (iii) to determine when the solid-state-oxygen carrier is in an oxygen-replenished state.

14. The method according to any of the preceding claims, wherein step (i) is conducted at a packed bed or fluidised bed temperature of from 150 to 900°C, preferably from 150 to 600°C.

15. The method according to any of the preceding claims, wherein the gaseous flow of the organic molecule further comprises one or more reaction promoters.

16. The method according to any of the preceding claims, wherein the fluid flow comprising the organic molecule is a gaseous flow comprising the organic molecule.

17. The method according to any of the preceding claims, for the production of alkylene oxide from an olefin, wherein the fluid flow comprising the organic molecule comprises the olefin.

18. The method according to any of claims 1 to 16, for the production of ethylene oxide from ethene, wherein the fluid flow comprising the organic molecule comprises ethene.

19. The method according to any of claims 1 to 16, for the production of formaldehyde from methanol, wherein the fluid flow comprising the organic molecule comprises methanol.

20. The method according to any of claims 1 to 16, for the production of propylene oxide from propene, wherein the fluid flow comprising the organic molecule comprises propene.

21. The method according to any of claims 1 to 16, for the production of acrolein from propene, wherein the fluid flow comprising the organic molecule comprises propene.

22. The method according to any of claims 1 to 16, for the production of maleic anhydride from butane, wherein the fluid flow comprising the organic molecule comprises butane.

23. Use of a catalytic composite comprising a solid-state-oxygen carrier comprising $SrFe0_3$ and/or $SrCo0_3$ and/or $Sr_3Fe_20_7$ as a primary oxygen source, the solid-state-oxygen carrier having an oxidation catalyst on a surface thereof, to selectively oxidise an organic molecule in the absence of a secondary oxygen source.

24. Use of a catalytic composite for the selective oxidation of an organic molecule in a chemical looping reactor comprising a packed bed or fluidised bed comprising the catalytic composite,

wherein the catalytic composite comprises a solid-state-oxygen carrier as a primary oxygen source, the solid-state-oxygen carrier having an oxidation catalyst on a surface thereof, wherein the composite is for selective oxidation of an organic molecule in the absence of a secondary oxygen source,

the use comprising repeating the following steps:

(i) contacting the packed bed or fluidised bed with a fluid flow comprising the organic molecule to thereby oxidise the organic molecule;

(ii) then optionally flushing the packed bed or fluidised bed with a flow of an inert gas;

(iii) then regenerating the packed bed or fluidised bed with a flow of an oxygen-containing gas;

(iv) then optionally flushing the packed bed or fluidised bed with a flow of an inert gas, and

preferably wherein:

a) the use is for the selective oxidation of an olefin to an alkylene oxide, wherein the fluid flow comprising the organic molecule comprises the olefin; or

b) the use is for the selective oxidation of ethene to ethylene oxide, wherein the fluid flow comprising the organic molecule comprises ethene;

c) the use is for the selective oxidation of methanol to formaldehyde, wherein the fluid flow comprising the organic molecule comprises methanol;

d) the use is for the selective oxidation of propene to propylene oxide, wherein the fluid flow comprising the organic molecule comprises propene;

e) the use is for the selective oxidation of propene to acrolein, wherein the fluid flow comprising the organic molecule comprises propene;

f) the use is for the selective oxidation of butane to maleic anhydride, wherein the fluid flow comprising the organic molecule comprises butane.

25. The use according to claim 24, wherein the catalytic composite comprises $SrFe0_3$ and/or $SrCo0_3$ and/or $Sr_3Fe_20_7$ and/or CuO.

Figure 1

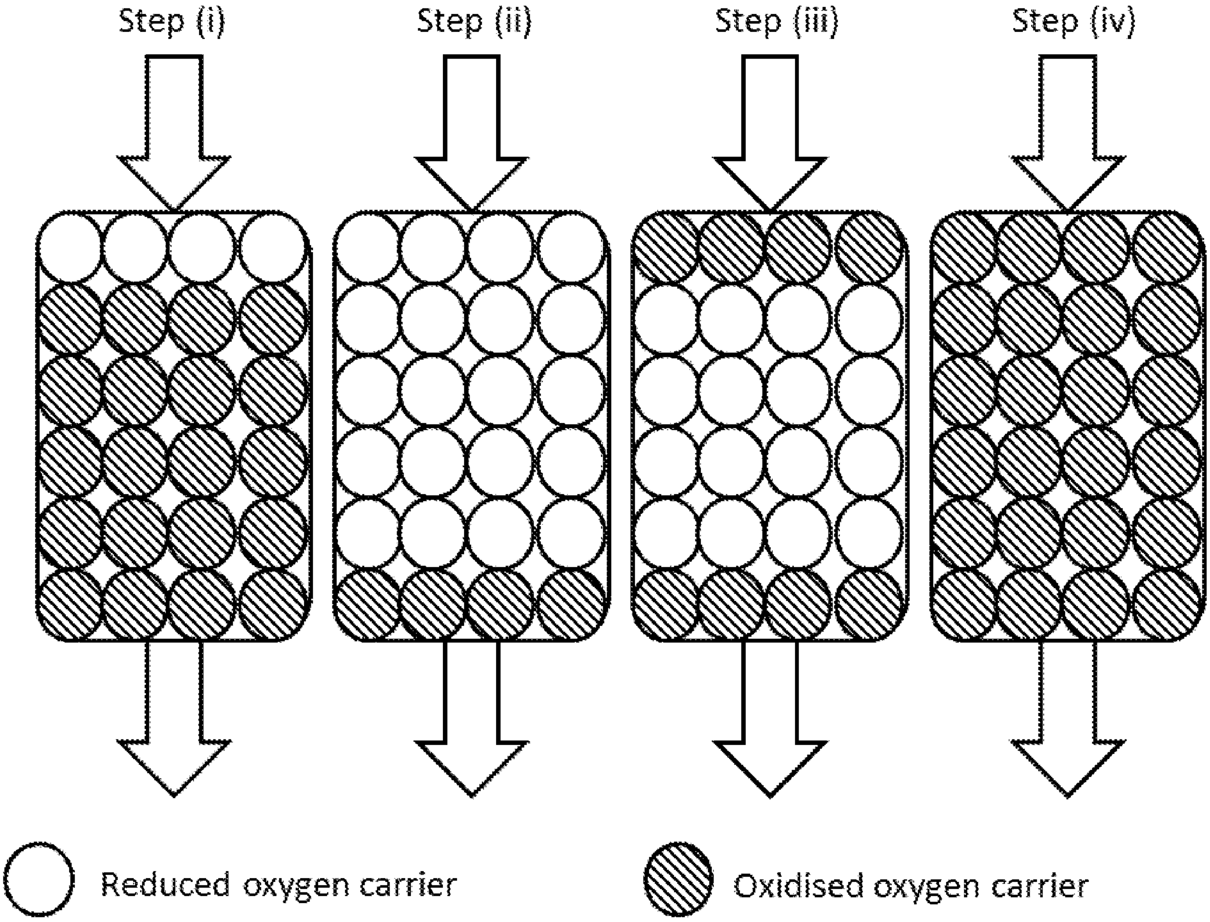

Step (i)
Step (ii)
Step (iii)
Step (iv)
Reduced oxygen carrier
Oxidised oxygen carrier

Figure 2

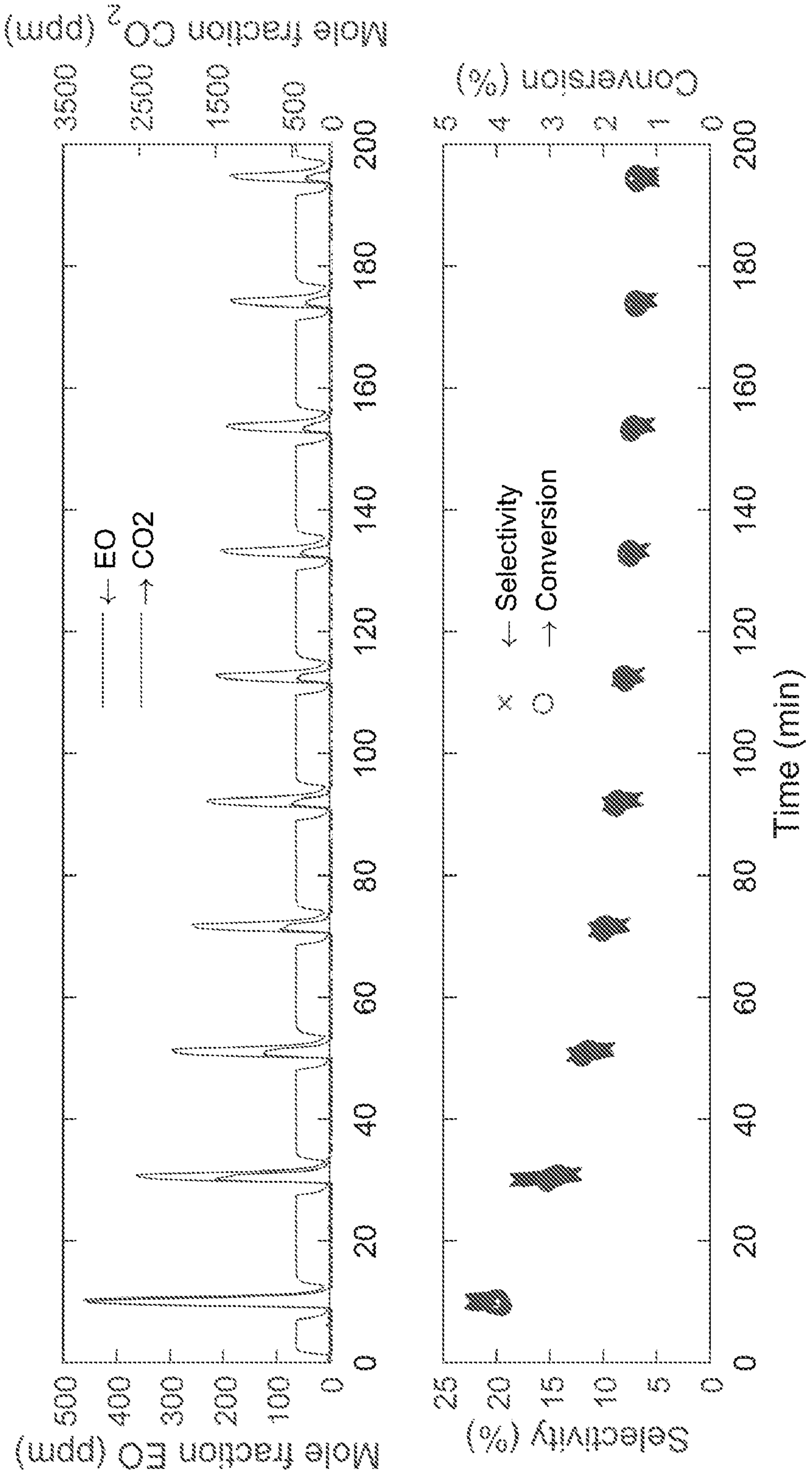

Mole fraction EO (ppm)
0
100
200
300
400
500
Mole fraction CO$_2$ (ppm)
0
500
1500
2500
3500
← EO
→ CO2
Selectivity (%)
0
5
10
15
20
25
Conversion (%)
0
1
2
3
4
5
× ← Selectivity
○ → Conversion
Time (min)
0
20
40
60
80
100
120
140
160
180
200

Figure 3

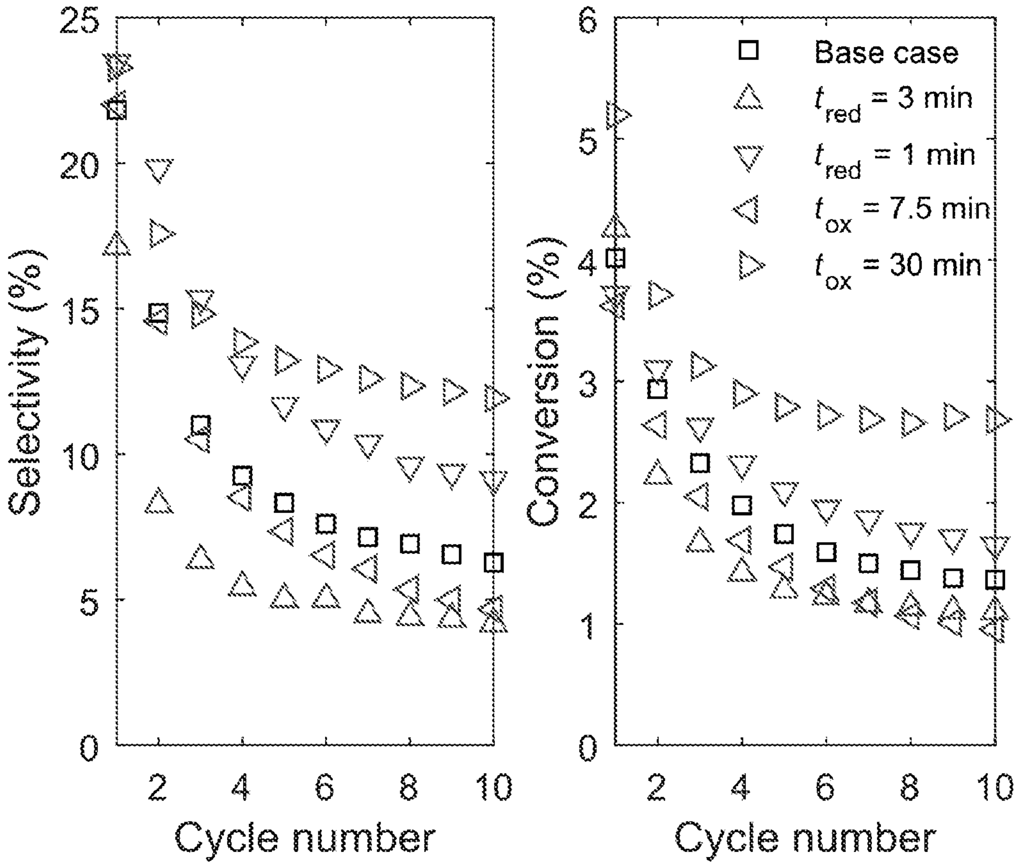

Selectivity (%)
25
20
15
10
5
0
2
4
6
8
10
Cycle number
Conversion (%)
6
5
4
3
2
1
0
□ Base case
△ t_{red} = 3 min
▽ t_{red} = 1 min
◁ t_{ox} = 7.5 min
▷ t_{ox} = 30 min

Figure 4

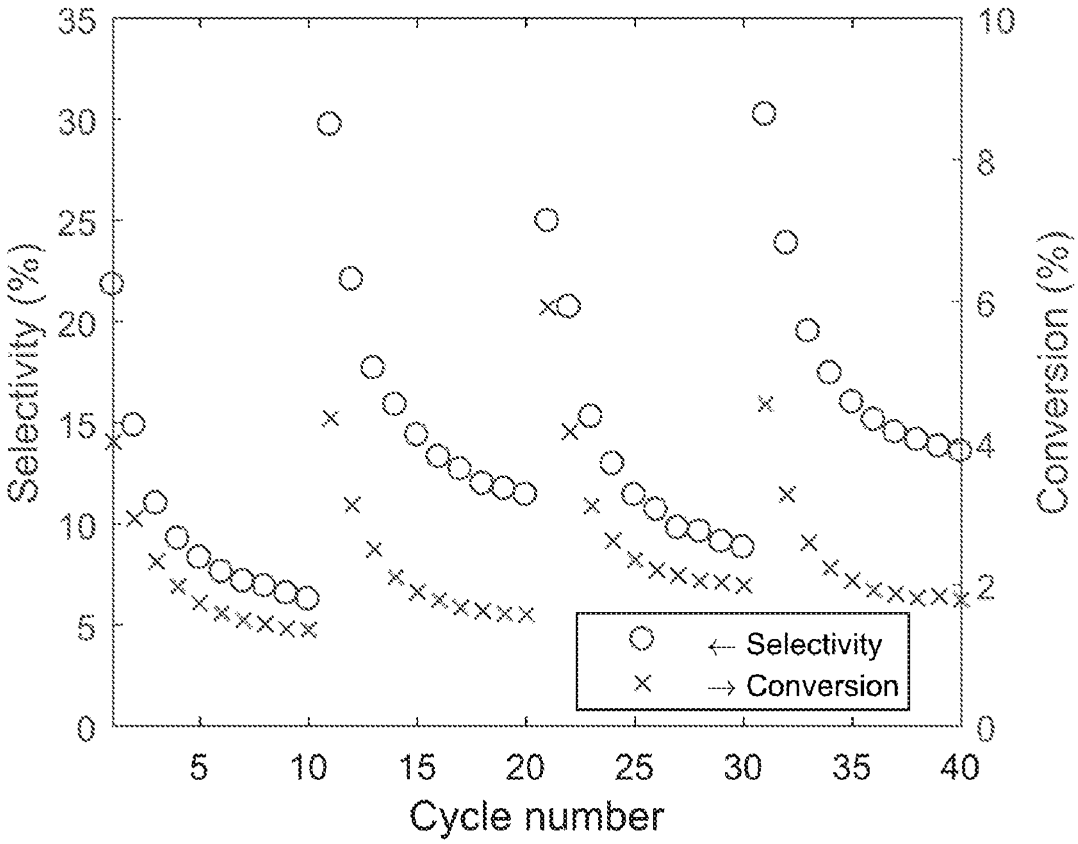

Selectivity (%)
Conversion (%)
Cycle number
35
30
25
20
15
10
5
0
10
8
6
4
2
0
5
10
15
20
25
30
35
40
← Selectivity
→ Conversion

Figure 5

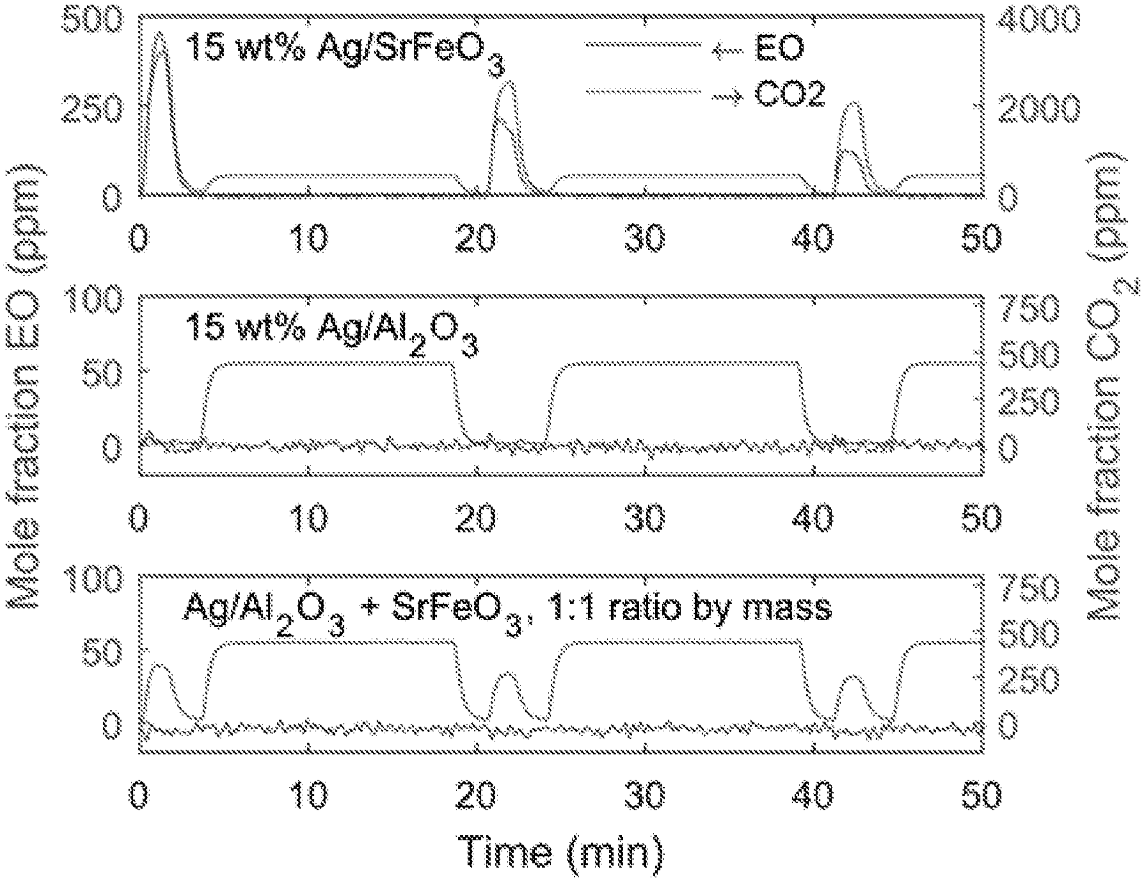


Figure 6

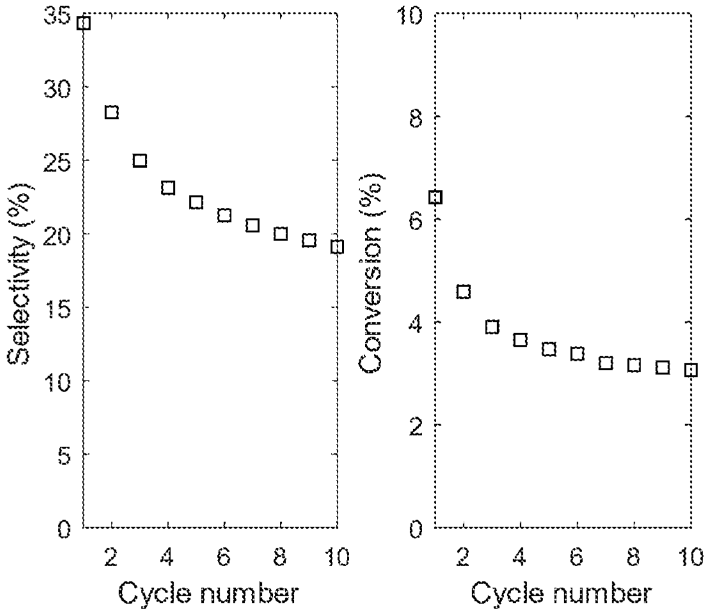


Figure 7

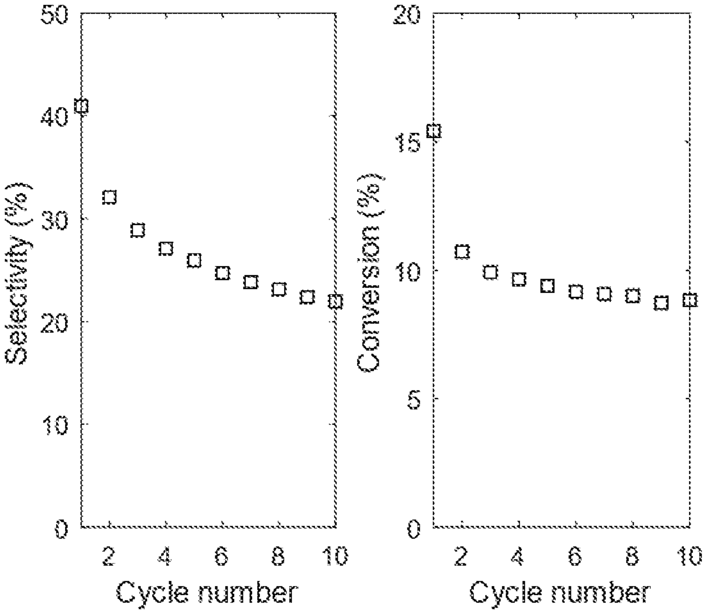


Figure 8

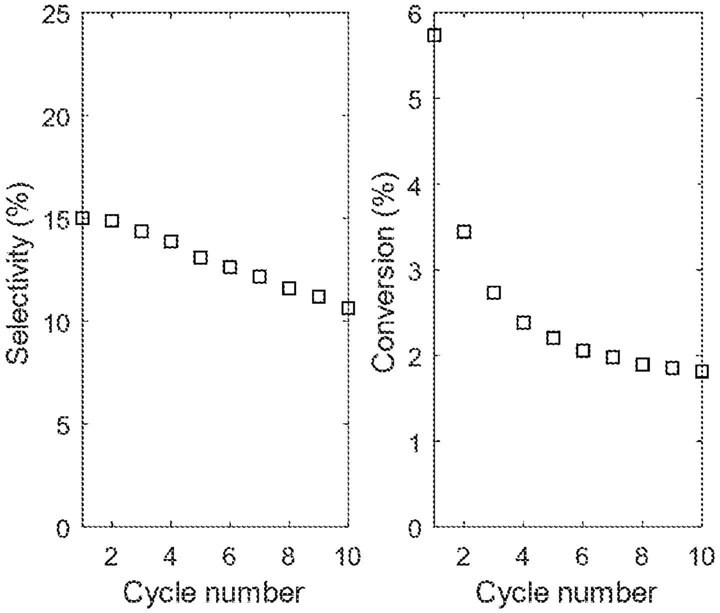


Figure 9A

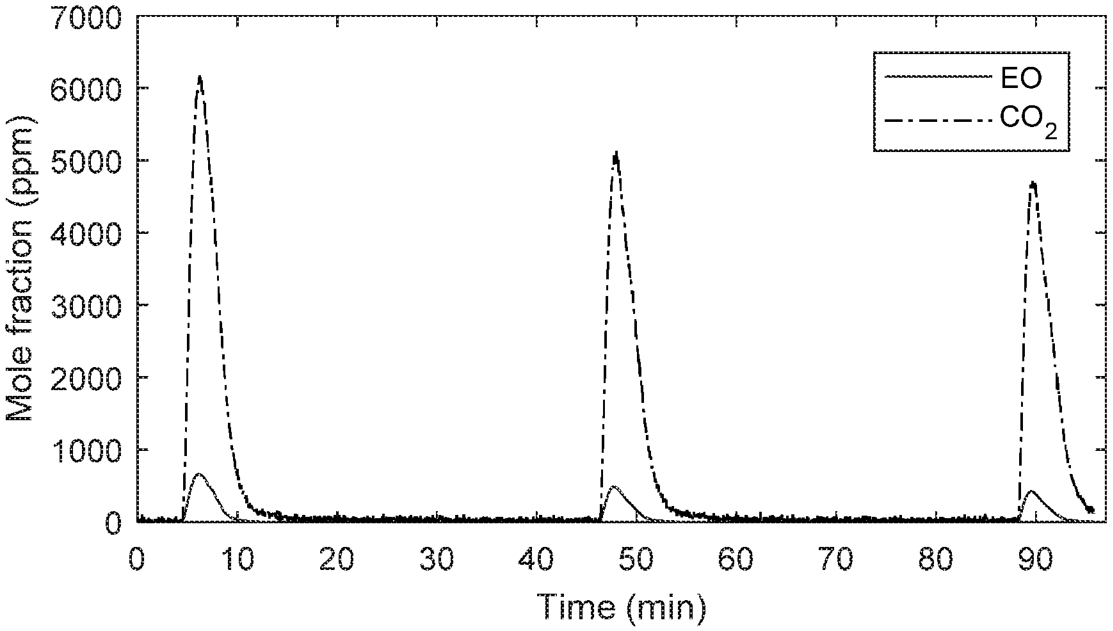


Figure 9B

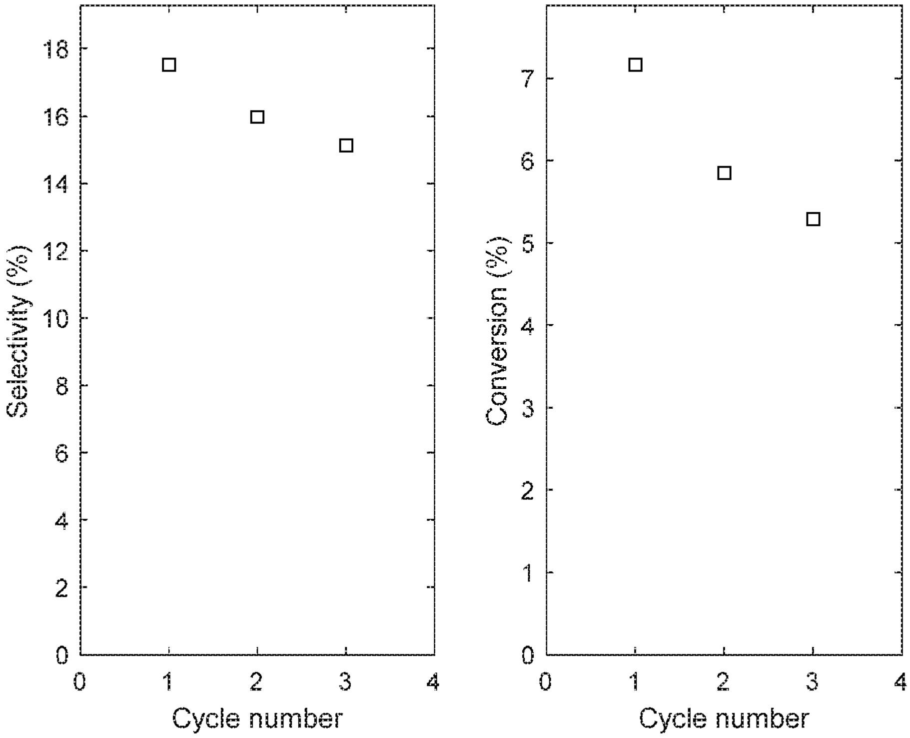


Figure 10A

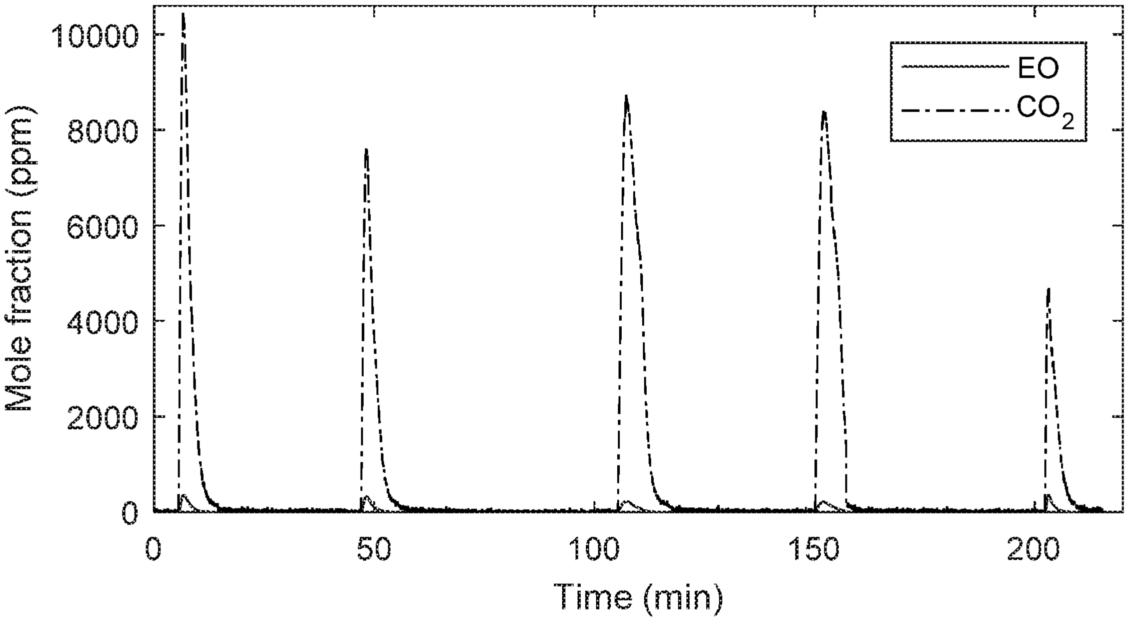


Figure 10B

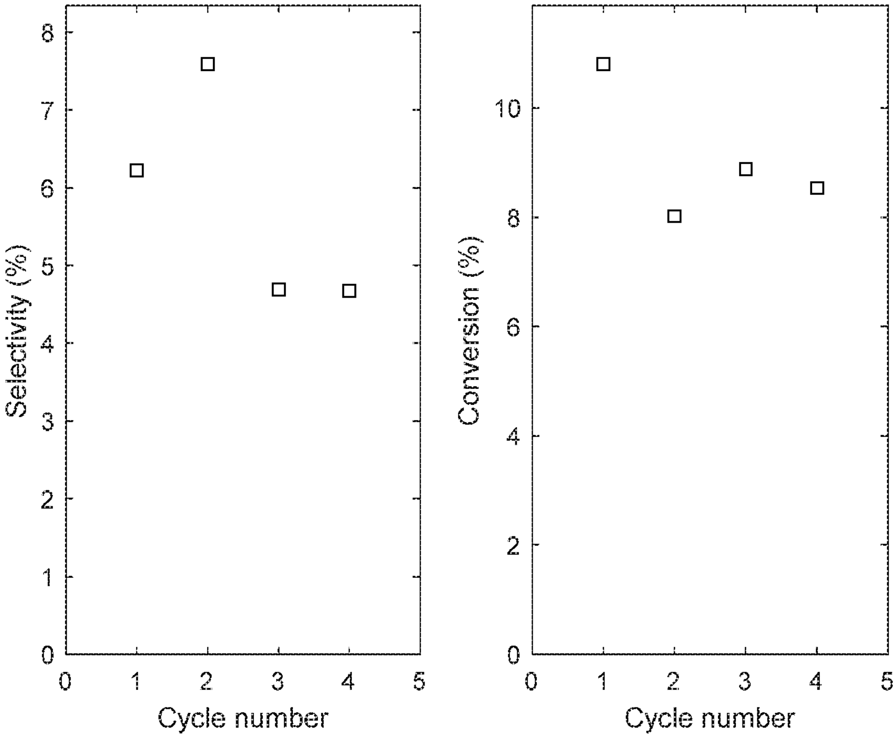


Figure 11A

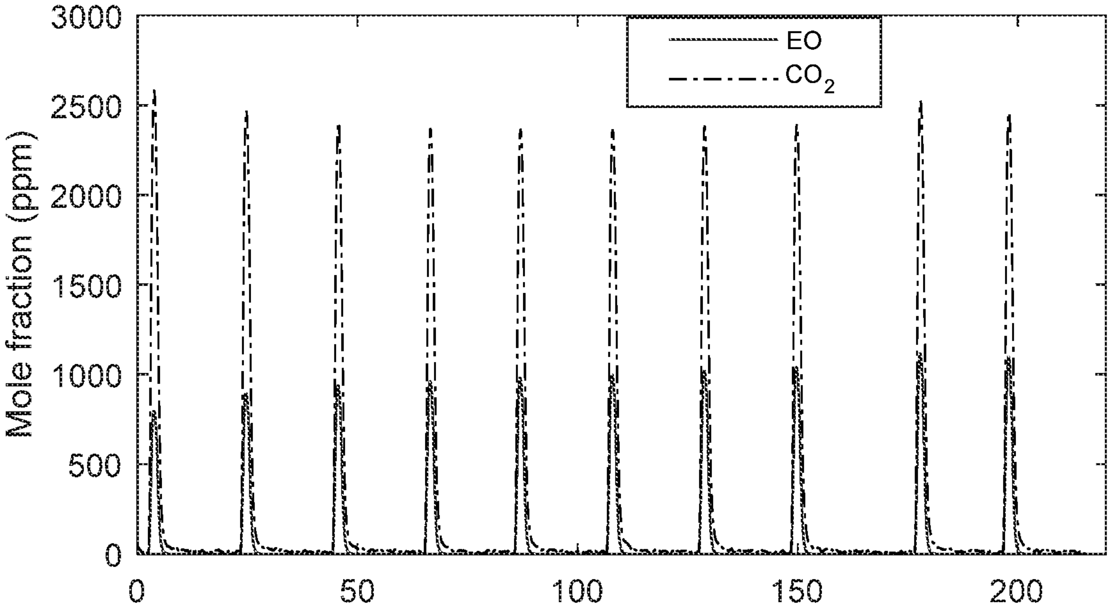


Figure 11B

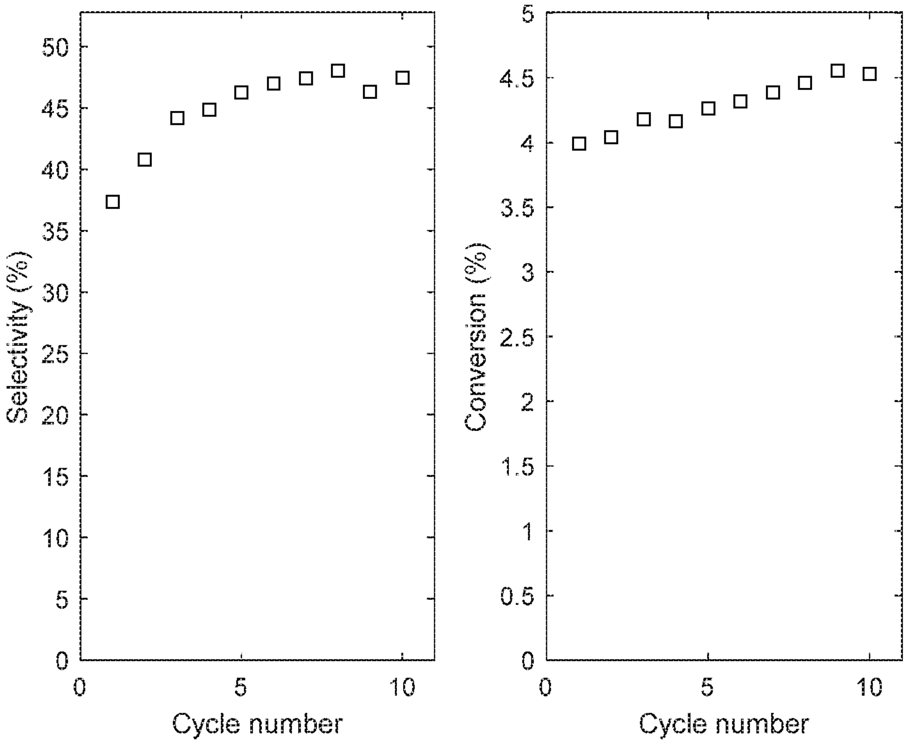


Figure 12A

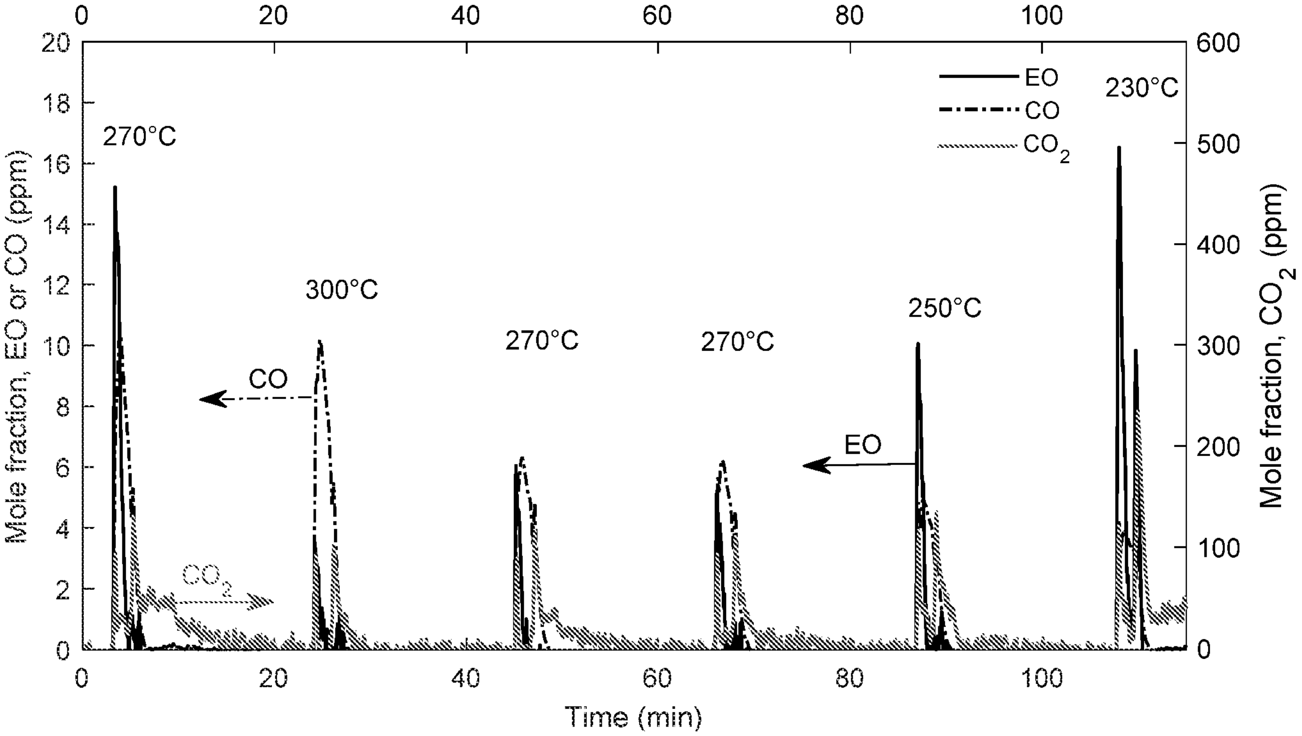


Figure 12B

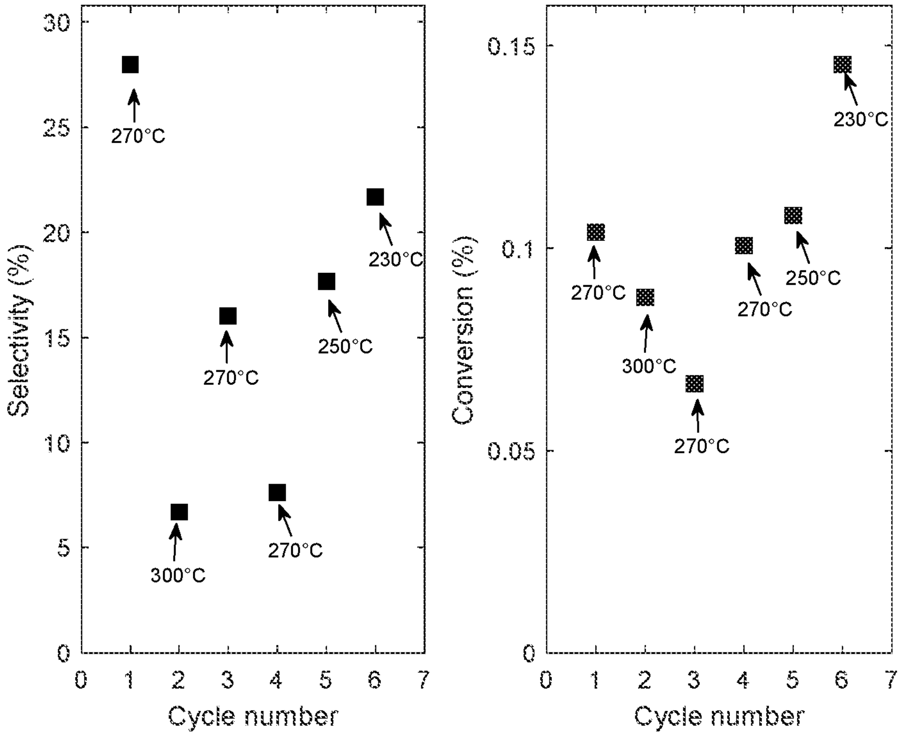


Figure 13A

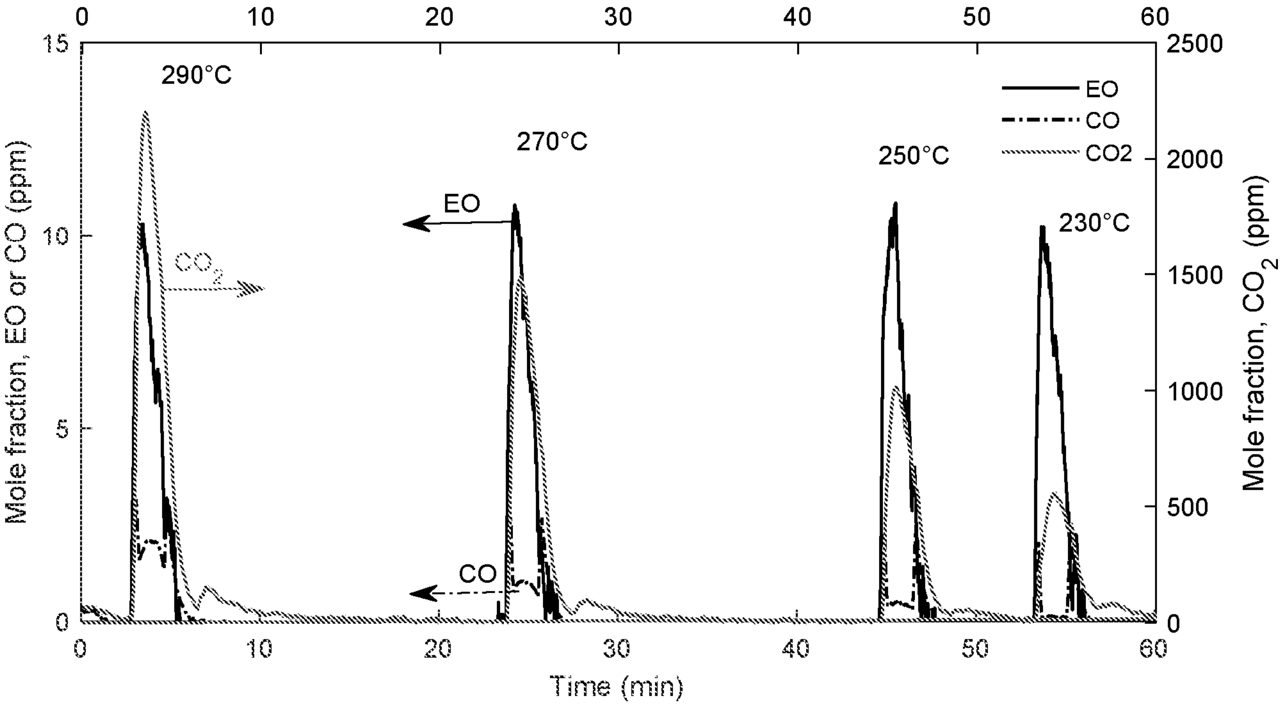
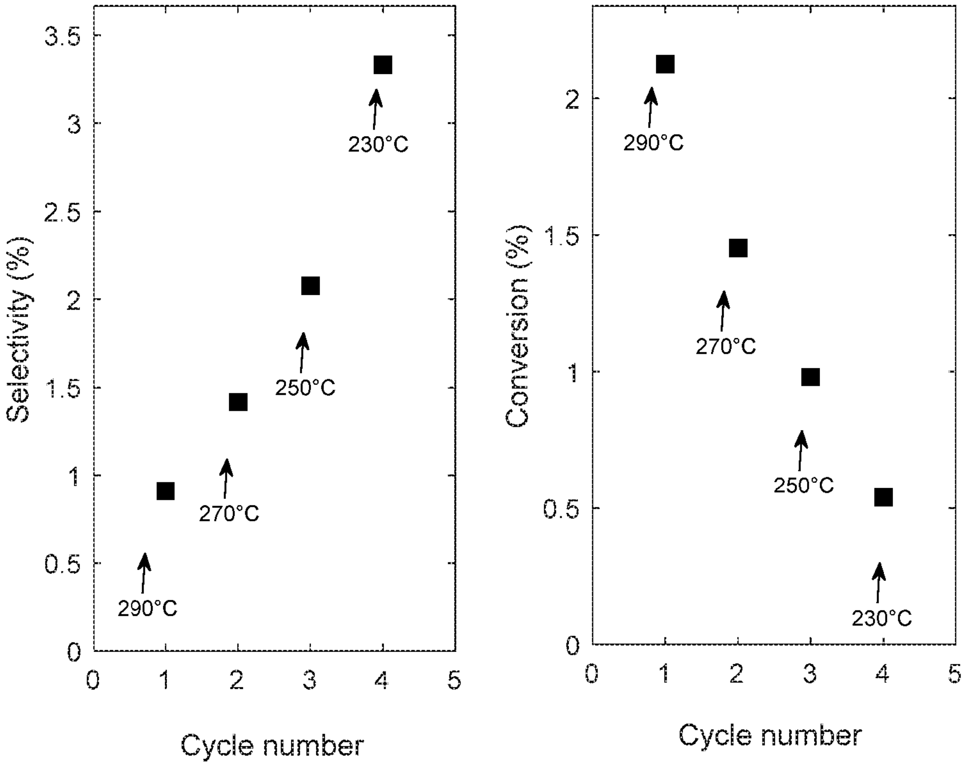


Figure 13B



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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2018/052470

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J38/12 B01J38/14 B01J38/22 B01J23/94 B01J23/00
B01J23/50 B01J23/52 B01J23/96 C07D301/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, BIOSIS, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	ZHEN GUO ET AL: "Recent advances in heterogeneous selective oxidation catalysis for sustainable chemistry", CHEMICAL SOCIETY REVIEWS, vol. 43, no. 10, 2014, page 3480, XP055528383, UK ISSN: 0306-0012, DOI: 10.1039/c3cs60282f abstract page 3517, left-hand column, last paragraph - page 3518, left-hand column, paragraph 1; figures 9, 29	1,3-22, 24 2,25

-/- ·

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 3 December 2018	Date of mailing of the international search report 11/12/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Nazario, Luis

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/036902 A2 (ELTRON RES & DEV INC [US]; WHITE JAMES H [US]; SCHUTTE ERICK J [US]; R) 27 March 2008 (2008-03-27) abstract page 3, lines 10-21 page 5, lines 12-20 page 10, lines 19-21 claims 20, 21; example 13 -----	1,3-5, 7-11, 13-22,24
X	US 6 765 101 BI (BHASIN MADAN MOHAN [US] ET AL) 20 July 2004 (2004-07-20) abstract column 1, lines 9-14 column 2, lines 11-20 page 2, lines 26-60 page 3, line 32 - page 4, line 23 column 6, lines 16-65 column 10, line 48 - column 11, line 55; claims; figure 1 -----	1-6, 8-22,24, 25
X	W0 2010/103669 AI (NIPPON STEEL MATERIALS CO LTD [JP]; UEMURA KENICHI [JP]; NAGAI T0RU [J) 16 September 2010 (2010-09-16)	23
Y	abstract; claims; example 1 -----	2,25
X	EP 0 091 814 AI (ENGELHARD CORP [US]) 19 October 1983 (1983-10-19)	23
Y	abstract page 1, lines 9-15 page 4, line 28 - page 5, line 32 claims; examples -----	2,25
Y	CN 105 195 185 A (UNIV WUHAN TECH) 30 December 2015 (2015-12-30) abstract -----	2,25

International application No.
PCT/GB2018/052470

INTERNATIONAL SEARCH REPORT

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: 1-25

The following groups have been found:

1.1. claims: 1-22, 24, 25

Independent claims 1 and 24 (and claims 2-22 and 25) relate to methods or uses for selective oxidation of an organic molecule in a chemical looping reactor having a packed or fluidised bed of a catalyst comprising a solid-state-oxygen carrier and an oxidation catalyst. There is no secondary source of oxygen.

1.2. claim: 23

Independent claim 23 relates to the use of a catalytic composite comprising SrFe03 and/or SrCoO and/or Sr3Fe207 as primary source of oxygen and having a oxidation catalyst supported thereon to selectively oxidise an organic molecule in the absence of a secondary oxygen source.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2018/052470

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2008036902 A2	27-03-2008	AU 2007299691 A1	27-03-2008
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