coking resistance, as coke deposition on catalyst surfaces can lead to a drop in catalytic activity and selectivity.

[0007] It is an object of the invention to at least partially satisfy the above needs.

Summary ~~of Invention~~

[0008] The present inventors have identified that catalysts comprising a catalytic element, for example, metallic nickel, disposed on a ceria-based substrate lead to a significant improvement in catalytic performance when used to catalyse the methanation reaction of a feedstock, and in particular, a feedstock including sulfur, when compared with conventional catalysts.

[0009] Accordingly, in an ~~first~~ aspect, the ~~present invention~~ there is provide~~ds~~ a catalyst, comprising a catalytic element disposed on a substrate, wherein said substrate has formula $Ce_{1-x}M_xO_2$, wherein x is between about 0 and about 0.3, optionally between about 0.01 and about 0.3, and wherein M, if present, is a metallic element other than Ce, when used for catalysing a methanation reaction.

[00010] The following options may be used in conjunction with the ~~first~~ above defined aspect either individually or in any suitable combination.

[00011] The catalytic element may be a metal. The metal may be a transition metal, e.g., it may be selected from the group consisting of Co, Fe, Pt, Ru, Rh, Pd, Ni and Ir. Therefore, the catalytic element may be Co, Fe, Pt, Ru, Rh, Pd, Ni or Ir. In particular, the catalytic element may be metallic, e.g., it may be metallic nickel, or may be metallic cobalt, or metallic palladium, or metallic platinum, or metallic iron, or metallic rhodium, or metallic ruthenium, or metallic iridium. In some instances it may be a mixture or alloy of any two or more of these metals, or may be a mixture or alloy of any one of these metals with some other metal.

[00012] The substrate may be particulate. The particles of the substrate may have a mean particle diameter of less than about 0.5 μm or less than about 100 nm.

[00013] In the substrate of formula $Ce_{1-x}M_xO_2$, x may be between about 0.01 and about 0.25, or may be between about 0.1 and about 0.2. For example, in the substrate of formula $Ce_{1-x}M_xO_2$, x may be about 0.01, or may be about 0.05, or may be about 0.1, or may be about 0.15, or may be

about 0.2. In some embodiments, x = 0. In other embodiments x > 0, optionally > 0.01 or > 0.1. The metallic element, M, may be a lanthanoid, or it may be a transition metal, or it may be an alkaline earth metal, e.g., the metallic element may be a transition metal. The transition metal may be Y. The metallic element may alternatively be a lanthanoid. The lanthanoid may be selected from the group consisting of Sm and Gd. It may be Sm or it may be Gd. The metallic element may be an alkaline earth, e.g., Ca. The metallic element may have a greater affinity for sulfur than for oxygen and/or may enhance the sulfur adsorption ability of the catalyst.

[00014] In one embodiment, the substrate is $Ce_{0.9}Sm_{0.1}O_2$. In another embodiment, the substrate is $Ce_{0.9}Gd_{0.1}O_2$. In a further embodiment, the substrate is $Ce_{0.9}Ca_{0.1}O_2$. In yet a further embodiment, the substrate is $Ce_{0.85}Y_{0.15}O_2$. In yet a further embodiment, the substrate is $Ce_{0.85}Sm_{0.15}O_2$.

[00015] The catalyst may include regions, commonly discrete or unconnected regions, of a catalytic element disposed on a surface of the substrate. The catalyst may include a catalytic element dispersed on a surface of the substrate, e.g., uniformly or non-uniformly dispersed. The catalyst may include between about 1% and about 40% of a catalytic element by weight, e.g., may include between about 5% and about 20% of a catalytic element by weight. The specific surface area of the substrate may be between about 10 and about 300 m^2/g, e.g., between about 50 and about 300 m^2/g.

[00016] In one embodiment, the present ~~invention~~ disclosure provides a catalyst, comprising a catalytic element selected from the group consisting of metallic Co, Fe, Pt, Ru, Rh, Pd, Ni or Ir, disposed on a substrate, wherein said substrate has formula $Ce_{1-x}M_xO_2$, wherein x is between about 0 and about 0.3, optionally between about 0.01 and about 0.3, and wherein M, if present, is a metallic element other than Ce, when used for catalysing a methanation reaction.

[00017] In another embodiment, the present disclosure~~invention~~ provides a catalyst, comprising metallic nickel disposed on a substrate, wherein said substrate has formula $Ce_{1-x}M_xO_2$, wherein x is between about 0 and about 0.3, optionally between about 0.01 and about 0.3, and wherein M, if present, is a metallic element other than Ce, when used for catalysing a methanation reaction.

[00018] In another embodiment the present disclosure~~invention~~ provides a catalyst including between about 1% and about 40% of a catalytic element selected from the group consisting of metallic Co, Fe, Pt, Ru, Rh, Pd, Ni or Ir by weight of the catalyst disposed on a surface of a substrate,

wherein said substrate has formula CeO_2, when used for catalysing a methanation reaction; wherein said substrate is particulate and the particles have a mean particle diameter of less than about 0.5 μm.

[00019] In another embodiment, the present disclosure~~invention~~ provides a catalyst, comprising a catalytic element selected from the group consisting of metallic Co, Fe, Pt, Ru, Rh, Pd, Ni or Ir disposed on a substrate, wherein said substrate has formula $Ce_{1-x}M_xO_2$, wherein x is between about 0.1 and about 0.3 and wherein M is a metallic element selected from the group consisting of a lanthanoid, a transition metal and an alkaline earth metal, when used for catalysing a methanation reaction.

[00020] In another embodiment, the present disclosure~~invention~~ provides a catalyst, comprising discrete regions of a catalytic element disposed on a substrate, wherein said substrate has formula $Ce_{1-x}M_xO_2$, wherein x is between about 0.1 and about 0.3 and wherein M is a metallic element selected from the group consisting of Y, Sm, Gd and Ca, when used for catalysing a methanation reaction.

[00021] In another embodiment, the present disclosure~~invention~~ provides a catalyst, comprising a catalytic element disposed on a substrate, wherein said substrate has formula $Ce_{1-x}M_xO_2$, wherein x is between about 0.1 and about 0.3 and wherein M is a metallic element that enhances the sulfur adsorption ability of the catalyst, when used for catalysing a methanation reaction; wherein said substrate has a specific surface area of between about 10 and about 300 m^2/g; and wherein said substrate is particulate and the particles have a mean particle diameter of less than about 0.5 μm.

[00022] In another embodiment, the present disclosure~~invention~~ provides a catalyst, comprising between about 1% and about 40% by weight of the catalyst of a catalytic element, wherein the catalytic element is metallic nickel, disposed in discrete regions on a surface of a substrate, wherein said substrate has formula $Ce_{1-x}M_xO_2$, wherein x is between about 0.1 and about 0.3 and wherein M is a metallic element selected from the group consisting of a lanthanoid, a transition metal and an alkaline earth metal, when used for catalysing a methanation reaction; wherein said substrate is particulate and the particles have a mean particle diameter of less than about 0.5 μm.

[00023] In another embodiment, the present disclosure~~invention~~ provides a catalyst, comprising metallic nickel disposed on a substrate, wherein said substrate has formula $Ce_{0.9}M_{0.1}O_2$, (i.e., x is 0.1),

and wherein M is a metallic element selected from the group consisting of Y, Sm, Gd and Ca, when used for catalysing a methanation reaction.

[00024] In another embodiment, the present disclosure~~invention~~ provides a catalyst, comprising between about 1% and about 40% by weight of the catalyst of metallic nickel disposed on a surface of a substrate, wherein said substrate has formula $Ce_{0.9}Gd_{0.1}O_2$, (i.e., x is 0.1), when used for catalysing a methanation reaction; wherein said substrate has a specific surface area of between about 10 and about 300 m^2/g; and wherein said substrate is particulate and the particles have a mean particle diameter of less than about 0.5 μm.

[00025] In another embodiment, the present disclosure~~invention~~ provides a catalyst, comprising metallic nickel disposed on a substrate, wherein said substrate has formula $Ce_{1-x}Ca_xO_2$, wherein x is between about 0.01 and about 0.3, when used for catalysing a methanation reaction.

[00026] In another embodiment, the present ~~invention~~disclosure provides a catalyst, comprising metallic nickel disposed on a substrate, wherein said substrate has formula $Ce_{1-x}Gd_xO_2$, wherein x is between about 0.01 and about 0.3, when used for catalysing a methanation reaction.

[00027] In another embodiment, the present ~~invention~~disclosure provides a catalyst, comprising between about 1% and about 40% by weight of the catalyst of metallic nickel disposed on a surface of a substrate, wherein said substrate has formula $Ce_{0.9}Ca_{0.1}O_2$, (i.e., x is 0.1), when used for catalysing a methanation reaction; wherein said substrate has a specific surface area of between about 10 and about 300 m^2/g; and wherein said substrate is particulate and the particles have a mean particle diameter of less than about 0.5 μm.

[00028] In another embodiment, the present ~~invention~~disclosure provides a catalyst, comprising between about 1% and about 40% by weight of the catalyst of metallic nickel disposed on a surface of a substrate, wherein said substrate has formula $Ce_{0.9}Sm_{0.1}O_2$, (i.e., x is 0.1), when used for catalysing a methanation reaction; wherein said substrate has a specific surface area of between about 10 and about 300 m^2/g; and wherein said substrate is particulate and the particles have a mean particle diameter of less than about 0.5 μm.

[00029] According to another ~~second~~ aspect ~~of the invention,~~ there is provided the use of a catalyst ~~according to the first aspect~~as defined above for catalysing a methanation reaction.

[00030] In one embodiment, the present ~~invention~~disclosure provides use of a catalyst comprising between about 1% and about 40% of a catalytic element selected from the group consisting of metallic Co, Fe, Pt, Ru, Rh, Pd, Ni or Ir by weight of the catalyst disposed on a surface of a substrate, wherein said substrate has formula $Ce_{1-x}M_xO_2$, wherein x is between about 0.1 and about 0.3 and wherein M is a metallic element selected from the group consisting of a lanthanoid, a transition metal and an alkaline earth metal, for catalysing a methanation reaction.

[00031] In another embodiment, the present ~~invention~~disclosure provides use of a catalyst, comprising metallic nickel disposed on a substrate, wherein said substrate has formula $Ce_{0.9}M_{0.1}O_2$, (i.e., x is 0.1), and wherein M is a metallic element selected from the group consisting of Y, Sm, Gd and Ca, for catalysing a methanation reaction.

[00032] According to another ~~third~~ aspect ~~of the invention,~~ there is provided the use of a catalyst ~~according to the first aspect~~as defined above, said use being for reducing the carbon monoxide content of a gas mixture including carbon monoxide and hydrogen.

[00033] According to another ~~fourth~~ aspect ~~of the invention,~~ there is provided a method for methanation of a feedstock including carbon monoxide and hydrogen, said method comprising contacting the feedstock with a catalyst ~~according to the first aspect above~~as defined above.

[00034] The following options may be used in conjunction with the ~~fourth~~ above aspect either individually or in any suitable combination.

[00035] The feedstock may additionally include carbon dioxide gas. The feedstock may additionally include steam. The feedstock may include coal gasification effluent and biomass gasification effluent. The feedstock may alternatively include coal gasification effluent or biomass gasification effluent.

[00036] The feedstock may additionally include a sulfur-containing gas or vapour. The sulfur-containing gas or vapour may be present at a concentration of about 0.1 to about 5000 ppm. The sulfur-containing gas or vapour may include any one or more of hydrogen sulfide, carbonyl sulfide, sulfur dioxide and an organic thiol.

[00037] The molar ratio of hydrogen to carbon monoxide in the feedstock may be between about 4:1 and about 1:1.

[00038] Contacting may include passing the feedstock through a packed bed reactor comprising the catalyst, or it may comprise passing the feedstock through a fluidised bed reactor. The pressure of the feedstock during the contacting may be between about 1 bar and about 40 bar. The contacting may be conducted at a temperature of at least about 250 °C. The contacting may be conducted at a temperature of between about 250 and about 750 °C. The temperature and feedstock flow rate, e.g., gas hourly space velocity, during the contacting may be sufficient to achieve equilibrium conversion of carbon oxides to methane.

[00039] The flow rate, e.g., gas hourly space velocity (GHSV) of the feedstock may be between about 1000 h^{-1} and about 100 000 h^{-1}.

[00040] In one embodiment, the present ~~invention~~disclosure provides a method for methanation of a feedstock including carbon monoxide and hydrogen, said method comprising contacting the feedstock with a catalyst ~~according to the first aspect~~as defined above, wherein the feedstock additionally includes a sulfur-containing gas or vapour present at a concentration of about 0.1 to about 5000 ppm and wherein the contacting is conducted at a temperature of at least about 250 °C.

[00041] In another embodiment, the present ~~invention~~disclosure provides a method for methanation of a feedstock including carbon monoxide, hydrogen and carbon dioxide, said method comprising contacting the feedstock with a catalyst ~~according to the first aspect~~as defined above, wherein the feedstock additionally includes a sulfur-containing gas or vapour present at a concentration of about 0.1 to about 5000 ppm and wherein the contacting is conducted at a temperature of between about 250 and about 750 °C.

[00042] In another embodiment, the present ~~invention~~disclosure provides a method for methanation of a feedstock including carbon monoxide and hydrogen, wherein the molar ratio of hydrogen to carbon monoxide in the feedstock is between about 4:1 and about 1:1, said method comprising contacting the feedstock with a catalyst ~~according to the first aspect~~as defined above, wherein the feedstock additionally includes a sulfur-containing gas or vapour present at a concentration of about 0.1 to about 5000 ppm and wherein the contacting is conducted at a temperature of between about 250 and about 750 °C wherein the pressure of the feedstock during contacting is between about 1 bar and about 40 bar.

[00043] In another embodiment, the present ~~invention~~disclosure provides a method for methanation of a feedstock including carbon monoxide and hydrogen, said method comprising contacting the

feedstock with a catalyst comprising metallic nickel disposed on a substrate, wherein said substrate has formula $Ce_{1-x}M_xO_2$, wherein x is between about 0.1 and about 0.3 and wherein M is a metallic element selected from the group consisting of a lanthanoid, a transition metal and an alkaline earth metal, wherein the feedstock includes coal gasification effluent or biomass gasification effluent and further includes a sulfur-containing gas or vapour at a concentration of about 0.1 to about 5000 ppm.

[00044] In another embodiment, the present ~~invention~~disclosure provides a method for methanation of a feedstock including carbon monoxide and hydrogen, said method comprising contacting the feedstock with a catalyst comprising metallic nickel disposed on a substrate, wherein said substrate has formula $Ce_{0.9}M_{0.1}O_2$, (i.e., x is 0.1), and wherein M is a metallic element selected from the group consisting of Sm, Gd and Ca, wherein said substrate has a specific surface area of between about 10 and about 300 m^2/g; and wherein said substrate is particulate and the particles have a mean particle diameter of less than about 0.5 μm, wherein the feedstock includes coal gasification effluent or biomass gasification effluent and further includes a sulfur-containing gas or vapour at a concentration of about 0.1 to about 5000 ppm.

[00045] According to another embodiment ~~fifth aspect~~ of the disclosure~~invention~~, there is provided a method for reducing the carbon monoxide content of a gas mixture including carbon monoxide and hydrogen, said method comprising contacting the feedstock with a catalyst ~~according to the first aspect~~as defined above.

[00046] According to another ~~sixth~~ aspect ~~of the invention~~, there is provided the use of a substrate of formula $Ce_{1-x}M_xO_2$, wherein x is between about 0 and about 0.3, optionally between about 0.01 and about 0.3, and wherein M, if present, is a metallic element other than Ce, for reducing poisoning of a catalytic element by a sulfur-containing gas or vapour.

[00047] According to another ~~seventh~~ aspect ~~of the invention~~, there is provided a method for reducing poisoning of a catalytic element by a sulfur-containing gas or vapour, said method comprising depositing said catalytic element on a substrate, wherein said substrate has formula $Ce_{1-x}M_xO_2$, wherein x is between about 0 and about 0.3, optionally between about 0.01 and about 0.3, and wherein M, if present, is a metallic element other than Ce.

[00048] The following options may be used in conjunction with the ~~seventh aspect~~above aspect either individually or in any suitable combination.