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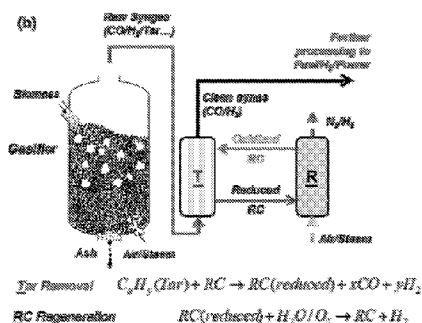
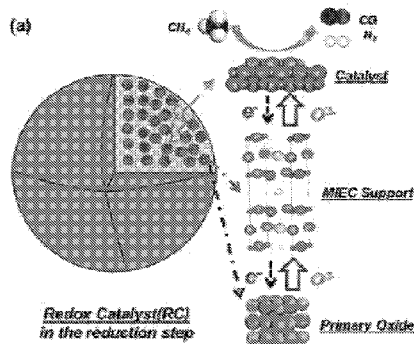
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(54) Title: MIXED-CONDUCTOR ENHANCED COMPOSITE AND CORE-SHELL OXIDES FOR CYCLIC REDOX PRODUCTION OF FUELS AND CHEMICALS



(57) Abstract: Compositions and methods for preparing and using ceramic mixed ionic-electronic conductor (MIEC) enhanced transition metals and metal oxides in composite or core-shell forms are disclosed. The presently disclosed compositions are stable at high temperatures and can carry as much as about 20 weight % oxygen.

Fig. 1



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MIXED-CONDUCTOR ENHANCED COMPOSITE AND CORE-SHELL OXIDES
FOR CYCLIC REDOX PRODUCTION OF FUELS AND CHEMICALS

CROSS-REFERENCE TO RELATED APPLICATIONS

- 5 This application claims the benefit of U.S. Provisional Application No. 61/923,939, filed January 6, 2014, which is incorporated herein by reference in its entirety.

FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

- 10 This invention was made with government support under 556106 awarded by the National Science Foundation (NSF). The government has certain rights in the invention.

BACKGROUND

- 15 Chemical looping combustion (CLC) and chemical looping gasification (CLG) represent promising technologies for capturing carbon dioxide (CO₂) emissions from fossil fuels with reduced energy penalty. These processes utilize the transfer of oxygen from air and/or water to the fuel through cyclic redox operations of solid oxygen carriers. Similar cyclic redox processes include the steam-iron process, solar-
20 thermal water-splitting processes, and a number of redox catalyst-based selective oxidation processes, e.g., the DuPont redox maleic anhydride production process.

- An important aspect of these cyclic redox processes is the selection of oxygen carrier (or redox catalyst) materials with adequate reactivity. Oxides of transition metals (e.g., Mn, Fe, Co, Ni, V, Mo, and Cu), their mixtures, and natural minerals
25 have been used as oxygen carriers in CLC. High reactivity during redox reactions over a long term and the ability to fully or partially convert the fuel are sought-after characteristics. In addition, thermal stability, mechanical strength, and resistance to agglomeration also are important. Two methods for achieving the desired characteristics of stability, strength, reactivity, and selectivity are known. One
30 method is to mix the oxygen carrier with an inert support, such as TiO₂, SiO₂, ZrO₂, Al₂O₃ or MgAl₂O₄, followed with thermal treatment.

 To date, however, an effective strategy to design oxygen carrier/redox catalysts with optimum performance in terms of stability, strength, reactivity, and

selectivity is still lacking.

SUMMARY

In some aspects, the presently disclosed subject matter provides a redox
5 catalyst comprising an oxygen carrying material, a mixed ionic-electronic conductive (MIEC) support, and a catalytically-active surface.

In other aspects, the presently disclosed subject matter provides a core-shell redox catalyst comprising: (i) metal oxide core; (ii) a mixed ionic-electronic conductive (MIEC) shell; and (iii) a plurality of surface catalytic sites.

10 In yet other aspects, the presently disclosed subject matter provides a redox catalyst comprising a mixed ionic-electronic conductive (MIEC) oxide that acts both as an oxygen carrying material and a catalyst.

In particular aspects, the presently disclosed oxides can be generally used for cyclic redox conversion of commodity fuels, such as natural gas, coal, biomass, and
15 the like, into value-added, environmentally friendly products, such as hydrogen, synthesis gas, electricity, and other chemicals or fuels.

Certain aspects of the presently disclosed subject matter having been stated hereinabove, which are addressed in whole or in part by the presently disclosed subject matter, other aspects will become evident as the description proceeds when
20 taken in connection with the accompanying Examples and Figures as best described herein below.

BRIEF DESCRIPTION OF THE FIGURES

Having thus described the presently disclosed subject matter in general terms,
25 reference will now be made to the accompanying Figures, which are not necessarily drawn to scale, and wherein:

FIGS. 1a and 1b show a schematic diagram of: (a) the Redox Catalyst (RC) in the tar removal step; and (b) the tar removal scheme, which involves cyclic reduction-regeneration of the RC;

30 FIGS. 2a and 2b show a schematic illustration of: (a) the core-shell redox catalyst (RC) comprising: (i) transition metal oxide core; (ii) mixed-conductive shell; (iii) surface catalytic sites; and (b) the proposed methane (CH₄) reforming scheme;

FIG. 3 shows a simplified schematic of the redox reactions of perovskite supported iron oxide composites (other mixed ionic-electronic conductive (MIEC) supports having a structure different from perovskite also can be used);

FIG. 4 shows reactivity comparisons among various composite iron oxides.

5 FeLSF refers to LSF-1 and Sol-Gel refers to LSF-CS-2 in Table 1;

FIG. 5 shows the effect of a perovskite support on the reactivity of composite oxides;

FIG. 6 shows the recyclability and phase stability of the composite oxygen carrier;

10 FIG. 7 shows the physical stability of the CTF oxygen carrier. Left (fresh pellet), center (post 100 cycles at 900 °C), right (center pellet after 100 addition redox cycles at 1,100 °C pellet);

FIG. 8 shows the physical stability of the $\text{Fe}_2\text{O}_3@\text{LSF}$ nano-particle. Left (fresh particle), right (post 10 cycles at 900 °C);

15 FIG. 9 shows a transmission electron microscopy (TEM) image and energy-filtered transmission electron microscopy (EFTEM) elemental mapping of LSF-SG-1;

FIG. 10 shows the structural/compositional stabilities of LSF-SG-1; and

FIG. 11 shows the superior selectivity of the core-shell redox catalyst toward CO generation.

20

DETAILED DESCRIPTION

The presently disclosed subject matter now will be described more fully hereinafter with reference to the accompanying Figures, in which some, but not all embodiments of the inventions are shown. Like numbers refer to like elements throughout. The presently disclosed subject matter may be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will satisfy applicable legal requirements. Indeed, many modifications and other embodiments of the presently disclosed subject matter set forth herein will come to mind to one skilled in the art to which the presently disclosed subject matter pertains having the benefit of the teachings presented in the foregoing descriptions and the associated Figures. Therefore, it is to be understood that the presently disclosed subject matter is not to be

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limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims.

I. MIXED-CONDUCTOR ENHANCED COMPOSITE AND CORE-SHELL
5 OXIDES FOR CYCLIC REDOX PRODUCTION OF FUELS AND
CHEMICALS

The presently disclosed subject matter is generally directed to ceramic mixed
ionic-electronic conductor (MIEC) enhanced transition metals and metal oxides in
either composite or core-shell forms. The presently disclosed mixed-conductor
10 enhanced metal oxides exhibit structural and chemical stability, tunable
thermodynamic properties, superior redox activity, and/or product selectivity.

The presently disclosed subject matter further provides a strategy for
designing and optimizing oxygen carriers and redox catalysts. In some embodiments,
the strategy includes activity enhancement via a composite of primary (transition)
15 metal oxide and a mixed-conductive “support.” In other embodiments, the strategy
includes formation of a primary metal oxide@mixed-conductive oxide core-shell
structure.

A. *Primary Metal Oxide-Mixed Ionic-Electronic Conductive (MIEC) Composite*

In some embodiments, the presently disclosed subject matter provides a redox
20 catalyst comprising an oxygen carrying material, a mixed ionic-electronic conductive
(MIEC) support, and a catalytically-active surface. In certain embodiments, the
oxygen carrying material comprises a metal oxide. In particular embodiments, the
metal oxide comprises a transition metal oxide and mixtures thereof. In some
embodiments, the transition metal oxide comprises an oxide of a transition metal
25 selected from the group consisting of Mn, Fe, Co, Ni, V, Mo, Cu, Zn, Si and mixtures
thereof.

In other embodiments, the metal oxide comprises a spinel oxide having a
formula $A^{2+}B_2^{3+}O_4^{2-}$, wherein A and B are each independently a metal cation. In such
embodiments, the metal cation is selected from the group consisting of magnesium,
30 calcium, strontium, barium, zinc, iron, manganese, aluminum, chromium, titanium,
and silicon.

In yet other embodiments, the MIEC support has a perovskite structure. In
particular embodiments, the MIEC support is selected from the group consisting of

$\text{La}_x\text{Sr}_{1-x}\text{FeO}_3$, $\text{BaCe}_y\text{Fe}_{1-y}\text{O}_3$, $\text{CaTi}_z\text{Fe}_{1-z}\text{O}_3$ ($0.2 < x < 0.8$, $0.2 < y < 0.8$, $0.05 < z < 0.75$). In yet more particular embodiments, the redox catalyst comprises a metal oxide-MIEC composite selected from the group consisting of between 20%-80% Fe_2O_3 , 20%-80% $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$; 20%-80% Fe_2O_3 , 20%-80% $\text{BaCe}_{0.7}\text{Fe}_{0.3}\text{O}_3$; and 20%-80% Fe_2O_3 ,
 5 20%-80% $\text{CaTi}_{0.85}\text{Fe}_{0.15}\text{O}_3$, wherein 20%-80% includes 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, and 80%, and any integer or fractional integer in between. In even yet more particular embodiments, the redox catalyst comprises a metal oxide-MIEC composite selected from the group consisting of 50% Fe_2O_3 , 50% $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$; 50% Fe_2O_3 , 50% $\text{BaCe}_{0.7}\text{Fe}_{0.3}\text{O}_3$; and 50% Fe_2O_3 , 50%
 10 $\text{CaTi}_{0.85}\text{Fe}_{0.15}\text{O}_3$.

In some embodiments, the redox catalyst is prepared by a method selected from the group consisting of a solid state reaction (SSR) and a sol-gel method.

A number of primary oxide and MIEC materials can be used to synthesize the presently disclosed oxygen carriers and redox catalysts. For example, a primary oxide
 15 comprising at least one of Fe, Mn, Co, Cu, Ni, V, Mo, Bi, Zn, Si and mixtures thereof (e.g., Fe-Mn, Fe-Co, Ni-Fe, Cu-Fe) can be used. Further, spinel oxides comprising Fe, Ni, Cu, Co, Al, and Mg, also can be used as the primary oxide.

Spinel oxides are a class of minerals of the general formula $\text{A}^{2+}\text{B}_2^{3+}\text{O}_4^{2-}$ which crystallize in the cubic (isometric) crystal system, with the oxide anions arranged in a
 20 cubic close-packed lattice and the cations A and B occupying some or all of the octahedral and tetrahedral sites in the lattice. A and B can be divalent, trivalent, or quadrivalent cations, including magnesium, zinc, iron, manganese, aluminum, chromium, titanium, and silicon. Although the anion is normally oxide, the analogous thiospinel structure, where the oxygen atom is replaced with a sulfur atom also is
 25 included in the spinel minerals. A and B also can be the same metal under different charges, such as the case in magnetite, Fe_3O_4 (as $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4^{2-}$).

Members of the spinel group include, but are not limited to, aluminum spinels, such as spinel (MgAl_2O_4), gahnite (ZnAl_2O_4), and hercynite (FeAl_2O_4); iron spinels, such as cuprospinel (CuFe_2O_4), franklinite ($(\text{Fe}, \text{Mn}, \text{Zn})(\text{Fe}, \text{Mn})_2\text{O}_4$), jacobsonite
 30 (MnFe_2O_4), hercynite ($\text{Fe}^{+2}\text{Al}_2\text{O}_4$), magnesioferrite, ($\text{MgFe}_2^{+3}\text{O}_4$), magnetite (Fe_3O_4), greigite (Fe_3S_4), trevorite (NiFe_2O_4), ulvöspinel (TiFe_2O_4), and zinc ferrite ($(\text{Zn}, \text{Fe})\text{Fe}_2\text{O}_4$); chromium spinels, such as chromite (FeCr_2O_4) and magnesiochromite (MgCr_2O_4); and other compounds having a spinel structure, such as ringwoodite

((Mg,Fe)₂SiO₄), and the thiospinels and selenospinel, which can be synthesized, or in some instances occur in nature.

More particularly, in some embodiments, the MIEC support can have one of the following structures: perovskite, fluorite, La₂Cu_{1-x}Co_xO_{4-δ}, and K₂NiF₄-type structures. Generally, a perovskite structure includes any material with the same type of crystal structure as calcium titanium oxide (CaTiO₃), which also is referred to as the "perovskite structure" and is denoted A^{2/3+}B^{3/4+}X²⁻₃ with the X²⁻ atom, e.g., O²⁻, in the face centers. The general chemical formula for perovskite compounds is ABX₃, where 'A' and 'B' are two cations of different sizes, and X is an anion that bonds to both. The 'A' atoms typically are larger than the 'B' atoms.

The perovskite structure is adopted by many oxides that have the chemical formula ABO₃. In a perovskite structure, the ideal cubic-symmetry structure has the B cation in 6-fold coordination, surrounded by an octahedron of anions and the A cation in 12-fold cuboctahedral coordination. Naturally occurring compounds having this structure include perovskite, loparite ((Ce,Na,Ca)(Ti,Nb)O₃), and the silicate perovskites, e.g., (Mg,Fe)SiO₃ and CaSiO₃.

In particular embodiments, with regard to the perovskite structure, a general formula of A_xA'_{1-x}B_yB'_{1-y}O_{3-δ} is preferred. In general, both x and y vary between 0-1. A and A' can be selected from alkali earth, alkali, and/or rare earth group metals. Preferred A/A' metals include Ca, Ba, Sr, La, Pr, Sm, K, Na, and Li. B and B' can be selected from alkali earth and transition metals. Preferred B/B' metals include Ti, Fe, Mn, Co, Ni, Cu, Mg, Zr, Ce, Bi, V, Mo, W, Pt, Pd, Ru, Zn, and Rh. Redox performances of several preferred configurations of the redox catalysts/oxygen carriers are given herein below.

In particular embodiments, perovskite having a general formula of A_xA'_{1-x}B_yB'_{1-y}O_{3-δ} can act as a standalone oxygen carrier and catalyst for redox applications. Preferred A/A' metals include Ca, Ba, Sr, La, and preferred B/B' metals include Ti, Fe, Ni, Mn, and Ce.

B. Primary Metal Oxide@Mixed-Conductive Oxide Core-Shell Structure

In some embodiments, the presently disclosed subject matter provides a core-shell redox catalyst comprising: (i) metal oxide core; (ii) a mixed ionic-electronic conductive (MIEC) shell; and (iii) a plurality of surface catalytic sites. In certain embodiments, the metal oxide core comprises a transition metal oxide and mixtures

thereof. In some embodiments, the transition metal oxide comprises an oxide of a transition metal selected from the group consisting of Mn, Fe, Co, Ni, V, Mo, Cu, Zn, and mixtures thereof.

In other embodiments, the metal oxide comprises a spinel oxide having a formula $A^{2+}B_2^{3+}O_4^{2-}$, wherein A and B are each independently a metal cation. In such 5 embodiments, the metal cation is selected from the group consisting of magnesium, zinc, iron, manganese, aluminum, chromium, titanium, and silicon.

In yet other embodiments, the MIEC shell has a perovskite structure. In particular embodiments, the MIEC shell is selected from the group consisting of In 10 particular embodiments, the MIEC support is selected from the group consisting of $La_xSr_{1-x}FeO_3$, $BaCe_yFe_{1-y}O_3$, $CaTi_zFe_{1-z}O_3$ ($0.2 < x < 0.8$, $0.2 < y < 0.8$, $0.05 < z < 0.75$). In yet more particular embodiments, the redox catalyst comprises a metal oxide-MIEC composite selected from the group consisting of between 20%-80% Fe_2O_3 , 20%-80% $La_{0.7}Sr_{0.3}FeO_3$; 20%-80% Fe_2O_3 , 20%-80% $BaCe_{0.7}Fe_{0.3}O_3$; and 20%-80% Fe_2O_3 , 15 20%-80% $CaTi_{0.85}Fe_{0.15}O_3$, wherein 20%-80% includes 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, and 80%, and any integer or fractional integer in between. In even yet more particular embodiments, the redox catalyst comprises a metal oxide-MIEC composite selected from the group consisting of 50% Fe_2O_3 , 50% $La_{0.7}Sr_{0.3}FeO_3$; 50% Fe_2O_3 , 50% $BaCe_{0.7}Fe_{0.3}O_3$; and 50% Fe_2O_3 , 50% 20 $CaTi_{0.85}Fe_{0.15}O_3$.

In some embodiments, the redox catalyst is prepared by a method selected from the group consisting of a solid state reaction (SSR) and a sol-gel method. In further embodiments, the core-shell redox catalyst further comprises an active metal.

C. *Applications of the Presently Disclosed Redox Catalysts*

25 The presently disclosed oxides can be generally used for cyclic redox conversion of commodity fuels, such as natural gas, coal, biomass, and the like, into value-added, environmentally friendly products, such as hydrogen, synthesis gas, electricity, and other chemicals or fuels.

i. Conversion of Biomass Tar

30 In some embodiments, the presently disclosed methods include a strategy to convert biomass tar (FIG. 1). In representative embodiments as depicted in FIG. 1, the presently disclosed redox catalyst for use in tar conversion combines three components: (i) an oxygen carrying material (primary metal oxide) for lattice oxygen

(O^{2-}) storage; (ii) a mixed ionic-electronic conductive (MIEC) “support” which facilitates O^{2-} and electron/hole conduction; and (iii) a catalytically active surface for tar conversion.

To participate in tar oxidation reactions, O^{2-} is shuttled from the primary oxide to the catalyst surface via the MIEC support. As used herein, MIEC supports are materials that conduct both ions (σ_i) and electronic (σ_{el}) charge carriers (electrons and/or holes). MIECs typically refer to those materials in which σ_i and σ_{el} do not differ by more than two orders of magnitude. MIECs also can refer to materials in which σ_i and σ_{el} are not too low ($\sigma_i, \sigma_{el} \geq 10^{-5} \text{ Scm}^{-1}$). MIECs also can include materials that conduct matter (ions and/or atoms) and electronic charge carriers, which includes ionic and metallic bonding in solids and a variety of structures including, but not limited to, a crystalline structure, glasses, and polymers.

In the tar oxidation reactions, the electrons released by O^{2-} on the catalyst surface are conducted back to the primary oxide to maintain charge balance and to facilitate primary oxide reduction. In a subsequent regeneration step, oxygen consumed in the tar removal step is replenished by air/ H_2O (FIG. 1b). Each redox catalyst particle can be considered as a large collection of MIEC membrane reactors at a nanoscale. Compared to conventional membrane reactors, the presently disclosed mixed ionic-electronic conductive (MIEC)-primary oxide composite redox catalyst can be more robust and flexible, since a dense membrane layer is unnecessary.

Without wishing to be bound to any one particular theory, it is believed that since the primary oxide is surrounded by MIEC on a nanoscale, all O^{2-} stored in the primary oxide is accessible to the redox reactions. The embedded O^{2-} can improve the catalyst activity. Moreover, coke formation, a major contributor to tar removal catalyst deactivation, is not thermodynamically favored on the presently disclosed redox catalyst due to its active lattice oxygen. The same concept can be used to prepare composite oxygen carriers for CLG and CLC.

Accordingly, in some embodiments, the presently disclosed subject matter provides a method for converting biomass to syngas, the method comprising: (a) gasifying the biomass to produce a raw syngas comprising CO , H_2 , and biomass tar of the formula C_xH_y ; (b) contacting the raw syngas with a redox catalyst comprising one of: (i) an oxygen carrying material, a mixed ionic-electronic conductive (MIEC) support, and a catalytically-active surface; (ii) a metal oxide core; a mixed ionic-

electronic conductive (MIEC) shell; and a plurality of surface catalytic sites; and (iii) a mixed conductive catalyst having a perovskite structure and a general formula of $A_xA'_{1-x}B_yB'_{1-y}O_{3-\delta}$, wherein A/A' metals are selected from the group consisting of Ca, Ba, Sr, and La, and B/B' metals are selected from the group consisting of Ti, Fe, Ni, Mn, and Ce; thereby reducing the redox catalyst and converting the biomass tar of formula C_xH_y to xCO and yH_2 ; and (c) contacting the reduced redox catalyst with H_2O/O_2 to regenerate the redox catalyst and to produce H_2 and/or heat.

ii. Conversion of Methane into Syngas

In other embodiments, the presently disclosed subject matter provides a strategy to convert methane into syngas, a fuel gas mixture consisting primarily of hydrogen, carbon monoxide, and also, in some cases, carbon dioxide (FIG. 2).

In representative embodiments as depicted in FIG. 2, the presently disclosed redox catalyst combines three components: (i) an oxygen carrying core (primary metal oxide) for lattice oxygen (O^{2-}) storage; (ii) a mixed ionic-electronic conductive (MIEC) shell, which facilitates O^{2-} and electron/hole conduction and serves as the catalyst substrate; and (iii) an (optional) active metal for methane reforming. To participate in reforming reactions, O^{2-} is shuttled from the primary oxide to the catalyst surface by the MIEC shell. Meanwhile, the electrons released by O^{2-} on the surface are conducted back to the primary oxide to maintain charge balance and to facilitate primary oxide reduction. In a subsequent regeneration step, oxygen consumed for methane oxidation is replenished by air (FIG. 1b).

Under such an arrangement, each core-shell redox catalyst particle can be considered as a nano-scale MIEC membrane reactor. Compared to conventional membrane reactors, the presently disclosed core-shell redox catalyst can be more robust and flexible since the functionality of the redox catalyst does not rely on large, defect-free membrane layers. Enclosed by a rigid, stable MIEC shell, the redox catalyst will be highly resistant toward sintering.

Moreover, the MIEC shell allows full accessibility of the ample active O^{2-} stored at the nano-scale primary oxide core (up to 20 wt% oxygen storage). The embedded, active O^{2-} can improve the reforming activity of the catalyst. Moreover, it can inhibit carbon formation and sulfur poisoning of the redox catalyst thermodynamically, making the catalyst less susceptible to deactivation. Methane partial oxidation enabled by the redox catalyst also produces a syngas stream with a

H₂:CO molar ratio of approximately 2:1, which is ideal for liquid fuel synthesis via the Fischer-Tropsch process.

Accordingly, in some embodiments, the presently disclosed subject matter provides a method for generating syngas from methane, the method comprising:

5 contacting methane or light hydrocarbons with a redox catalyst comprising: (i) an oxygen carrying material, a mixed ionic-electronic conductive (MIEC) support, and a catalytically-active surface; (ii) a metal oxide core; a mixed ionic-electronic conductive (MIEC) shell; and a plurality of surface catalytic sites; and (iii) a mixed

10 conductive catalyst with a perovskite structure and a general formula of $A_xA'_{1-x}B_yB'_{1-y}O_{3-\delta}$, wherein A/A' metals are selected from the group consisting of Ca, Ba, Sr, and La, and B/B' metals are selected from the group consisting of Ti, Fe, Ni, Mn, and Ce; thereby reducing the redox catalyst and converting the methane or light hydrocarbons, thereby reducing the redox catalyst and producing CO and H₂; and (b) contacting the reduced redox catalyst with H₂O/O₂ to regenerate the redox catalyst and to produce

15 H₂ and/or heat.

iii. Oxidation of Syngas into Carbon Dioxide and Splitting of Water to Form Hydrogen

Referring now to FIG. 3, another representative example for developing a presently disclosed composite oxygen carrier is provided, where catalyst modification

20 to the surface is not performed. The process involves complete oxidation of a fuel to generate carbon dioxide. The reduced metal oxide is then regenerated with air to produce heat. It also can be used to split water, making hydrogen.

Although specific terms are employed herein, they are used in a generic and

25 descriptive sense only and not for purposes of limitation. Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this presently described subject matter belongs.

Following long-standing patent law convention, the terms “a,” “an,” and “the”

30 refer to “one or more” when used in this application, including the claims. Thus, for example, reference to “a subject” includes a plurality of subjects, unless the context clearly is to the contrary (e.g., a plurality of subjects), and so forth.

Throughout this specification and the claims, the terms “comprise,”
“comprises,” and “comprising” are used in a non-exclusive sense, except where the
context requires otherwise. Likewise, the term “include” and its grammatical variants
are intended to be non-limiting, such that recitation of items in a list is not to the
5 exclusion of other like items that can be substituted or added to the listed items.

For the purposes of this specification and appended claims, unless otherwise
indicated, all numbers expressing amounts, sizes, dimensions, proportions, shapes,
formulations, parameters, percentages, quantities, characteristics, and other numerical
values used in the specification and claims, are to be understood as being modified in
10 all instances by the term “about” even though the term “about” may not expressly
appear with the value, amount or range. Accordingly, unless indicated to the
contrary, the numerical parameters set forth in the following specification and
attached claims are not and need not be exact, but may be approximate and/or larger
or smaller as desired, reflecting tolerances, conversion factors, rounding off,
15 measurement error and the like, and other factors known to those of skill in the art
depending on the desired properties sought to be obtained by the presently disclosed
subject matter. For example, the term “about,” when referring to a value can be
meant to encompass variations of, in some embodiments, $\pm 100\%$ in some
embodiments $\pm 50\%$, in some embodiments $\pm 20\%$, in some embodiments $\pm 10\%$, in
20 some embodiments $\pm 5\%$, in some embodiments $\pm 1\%$, in some embodiments $\pm 0.5\%$,
and in some embodiments $\pm 0.1\%$ from the specified amount, as such variations are
appropriate to perform the disclosed methods or employ the disclosed compositions.

Further, the term “about” when used in connection with one or more numbers
or numerical ranges, should be understood to refer to all such numbers, including all
25 numbers in a range and modifies that range by extending the boundaries above and
below the numerical values set forth. The recitation of numerical ranges by endpoints
includes all numbers, e.g., whole integers, including fractions thereof, subsumed
within that range (for example, the recitation of 1 to 5 includes 1, 2, 3, 4, and 5, as
well as fractions thereof, e.g., 1.5, 2.25, 3.75, 4.1, and the like) and any range within
30 that range.

EXAMPLES

The following Examples have been included to provide guidance to one of ordinary skill in the art for practicing representative embodiments of the presently disclosed subject matter. In light of the present disclosure and the general level of skill in the art, those of skill can appreciate that the following Examples are intended to be exemplary only and that numerous changes, modifications, and alterations can be employed without departing from the scope of the presently disclosed subject matter. The synthetic descriptions and specific examples that follow are only intended for the purposes of illustration, and are not to be construed as limiting in any manner to make compounds of the disclosure by other methods.

EXAMPLE 1

Preparation of the Presently Disclosed Composites

To evaluate the performance of the MIEC-primary oxide composite, eleven perovskites and perovskite-supported ferrites were prepared. The nominal compositions of these single-phase and composite oxides are summarized in Table 1. Fe₂O₃-LSF (LaSrFe) composites were investigated, since previous studies had confirmed high redox activity of a similar oxygen carrying material. BaCeFe (BCF) and CaTiFe (CTF) perovskites were selected due to their varying ionic and electronic conductivities. Both solid state reaction (SSR) and sol-gel methods were used to synthesize the oxides. Both methods allow the formation of a mixed matrix between the (primary) iron oxide and perovskite support.

To investigate the effect of iron oxide particle sizes, a composite sample (CTF-2) can be prepared using larger precursor particles, i.e., between 38 μm and 53 μm Fe₂O₃ and CTF perovskite particles.

Table 1. Summary of the Mixed and Composite Oxides Prepared.	
Sample No.	Composition (wt%)
LSF-0	100% La _{0.7} Sr _{0.3} FeO ₃
BCF-0	100% BaCe _{0.7} Fe _{0.3} O ₃
CTF-0	100% CaTi _{0.85} Fe _{0.15} O ₃
CTF-SG-0	100% CaTi _{0.85} Fe _{0.15} O ₃
LSF-1	50% Fe ₂ O ₃ , 50% La _{0.7} Sr _{0.3} FeO ₃

BCF-1	50% Fe ₂ O ₃ , 50% BaCe _{0.7} Fe _{0.3} O ₃
CTF-1	50% Fe ₂ O ₃ , 50% CaTi _{0.85} Fe _{0.15} O ₃
CTF-2	50% Fe ₂ O ₃ , 50% CaTi _{0.85} Fe _{0.15} O ₃
CTF-SG-1	50% Fe ₂ O ₃ , 50% CaTi _{0.85} Fe _{0.15} O ₃
LSF-CS-1	Fe ₂ O ₃ @LSF Core-Shell with Sol-Gel method
LSF-CS-2	Fe ₂ O ₃ @LSF Core-Shell with hydrothermal method

To synthesize pure perovskites via the SSR method, stoichiometric amounts of precursors were measured and mixed using a planetary ball-mill (XBM4X, Columbia International) for 6 hours with a rotation speed of 250 rpm. The homogeneous mixture was subsequently pelletized using a hydraulic press (YLJ-15T, MTI Corporation) under 15 MPa to 20 MPa and annealed in air at 1200 °C for 8 hours in a Tube Furnace (GSL-1500-X50, MTI Corporation). The calcined pellets were then crushed and sieved into particles of between 150 μm to 250 μm for further characterization. A high calcination temperature was used to ensure adequate solid state reactions. The synthesis procedure for composite, perovskite supported ferrites is identical to that for single phase perovskites.

The sol-gel method also was used to synthesize CTF and CTF supported Fe₂O₃. To prepare single phase CTF, stoichiometric amounts of citric acid, EDTA, and NH₃·H₂O were mixed to form a transparent solution. Calculated amounts of Ca(NO₃)₂·4H₂O (Sigma Aldrich) and Fe(NO₃)₃·9H₂O (Sigma Aldrich) were subsequently added to the citric-EDTA-NH₃·H₂O solution under constant stirring at 50 °C to form solution "A". The ratio among citric acid: EDTA acid:total metal ions is 1.6:1.0:1.0, and the pH value was kept at 7-9. To introduce the titanium precursor, a stabilized titanium solution, comprising calculated amounts of tetrabutyl titanate, ethanol, acetic acid, and lactic acid, was introduced into the solution "A". The mixture was then heated to 80 °C and kept for 2 hours under stirring at 650 rpm to form a gel. The gel was then dried at 120 °C for 6 hours followed with calcination at 800 °C for 8 hours to obtain the CTF perovskite powder. The CTF supported Fe₂O₃ was prepared using a similar approach. The primary difference in this method was the addition of iron oxide in the form of Fe₂O₃ nanoparticles (Sigma Aldrich) into solution "A". This step allowed a separate hematite phase to be embedded into the CTF perovskite support.

EXAMPLE 2

Characterization of the Presently Disclosed Composites

5 The performance of LSF-1 and LSF-SG-1 was compared with that of typical iron oxide based composites supported with alumina, spinel, and yttrium-stabilized-zirconia (FIG. 4). As shown in FIG. 4, the LSF-1 composite and LSF-SG-1 core-shell were two orders of magnitude more active than conventional supported oxygen carriers. In addition, they were more resistant toward coke formation. Comparing the reactivity among the three perovskite supported oxygen carriers, CTF-1 exhibited the
10 highest activity (FIG. 5). FIG. 6 further exhibits the redox stability and phase stability of the CTF oxygen carriers. In addition to the formulation illustrated in Table 1, a wide variety of A/A', B/B' metal types and compositions listed hereinabove were investigated (data not shown). Most of the composites have been found to exhibit satisfactory activity and stability.

15 In addition to redox and phase stabilities, structural stability also is very important for redox materials. Both the core-shell structure and composite structure were found to enhance the mechanical/structural stability of the redox materials. FIGS. 7 and 8 illustrate the stability of the redox material after high temperature redox cycles. As can be seen from FIG. 7, the redox material was stable even under an
20 extremely high temperature of 1,100 °C. In addition, FIG. 8 indicates the stability of individual Fe₂O₃@LSF core-shell nano-particles at 900 °C. FIG. 9 illustrates the morphology of another type of Fe₂O₃@LSF core-shell nano-particles (LSF-SG-1). The structural stability of the nano-particles and their selectivity toward CO versus CO₂ is given in FIGS. 10, 11, and Table 2.

Table 2. Performances for methane partial oxidation among various synthesized composite and coreshell- LSF-Fe ₂ O ₃ redox catalysts.					
	Perovskite: Iron Oxide (1:1)				
Material	LSF:Fe/Prax	LSFPt:Fe/Prax	LSF Core Shell	LSF/Iron Composite	LSFPt Fe Core Shell
H ₂ Selectivity	60%	100%	100%	72%	74%
CO Selectivity	87%	89%	88%	83%	83%

In summary, the strategies and compositions outlined in FIGS. 1-3 are proven to be highly stable and active for cyclic redox operations. The materials can also be tailored with high selectivity toward partial oxidation products. They can also carry more than 20 wt% lattice oxygen, making them ideal redox catalyst/oxygen carrier for a variety of applications. It also has been shown that a variety of mixed-oxides can be used as the primary oxide for the abovementioned applications with tunable redox properties.

REFERENCES

All publications, patent applications, patents, and other references mentioned in the specification are indicative of the level of those skilled in the art to which the presently disclosed subject matter pertains. All publications, patent applications, patents, and other references are herein incorporated by reference to the same extent as if each individual publication, patent application, patent, and other reference was specifically and individually indicated to be incorporated by reference. It will be understood that, although a number of patent applications, patents, and other references are referred to herein, such reference does not constitute an admission that any of these documents forms part of the common general knowledge in the art.

EP 2640509 A2 for Catalyst for Hydrogen Production, to J. Alouisius and Z. Pieterse, published Sept. 25, 2013.

Although the foregoing subject matter has been described in some detail by way of illustration and example for purposes of clarity of understanding, it will be understood by those skilled in the art that certain changes and modifications can be practiced within the scope of the appended claims.

THAT WHICH IS CLAIMED:

1. A redox catalyst comprising an oxygen carrying material, a mixed ionic-electronic conductive (MIEC) support, and a catalytically-active surface.
5
2. The redox catalyst of claim 1, wherein the oxygen carrying material comprises a metal oxide.
3. The redox catalyst of claim 2, wherein the metal oxide comprises a
10 transition metal oxide and mixtures thereof.
4. The redox catalyst of claim 3, wherein the transition metal oxide comprises an oxide of a transition metal selected from the group consisting of Mn, Fe, Co, Ni, V, Mo, Cu, Zn, Si, and mixtures thereof.
15
5. The redox catalyst of claim 2, wherein the metal oxide comprises a spinel oxide having a formula $A^{2+}B_2^{3+}O_4^{2-}$, wherein A and B are each independently a metal cation.
6. The redox catalyst of claim 5, wherein the metal cation is selected
20 from the group consisting of magnesium, calcium, strontium, barium, zinc, iron, manganese, aluminum, chromium, titanium, and silicon.
7. The redox catalyst of claim 1, wherein the MIEC support has a
25 perovskite structure.
8. The redox catalyst of claim 1, wherein the MIEC support is selected from the group consisting of $La_xSr_{1-x}FeO_3$, $BaCe_yFe_{1-y}O_3$, and $CaTi_zFe_{1-z}O_3$, wherein $0.2 < x < 0.8$, $0.2 < y < 0.8$, and $0.05 < z < 0.75$.
30
9. The redox catalyst of claim 1, comprising a metal oxide-MIEC composite selected from the group consisting of 20%-80% Fe_2O_3 , 20%-80%

$\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$; 20%-80% Fe_2O_3 , 20%-80% $\text{BaCe}_{0.7}\text{Fe}_{0.3}\text{O}_3$; and 20%-80% Fe_2O_3 ,
20%-80% $\text{CaTi}_{0.85}\text{Fe}_{0.15}\text{O}_3$,

10. The redox catalyst of claim 1, wherein the redox catalyst is prepared
5 by a method selected from the group consisting of a solid state reaction (SSR) and a sol-gel method.

11. A core-shell redox catalyst comprising: (i) metal oxide core; (ii) a
mixed ionic-electronic conductive (MIEC) shell; and (iii) a plurality of surface
10 catalytic sites.

12. The core-shell redox catalyst of claim 11, wherein the metal oxide core
comprises a transition metal oxide and mixtures thereof.

13. The core-shell redox catalyst of claim 12, wherein the transition metal
oxide comprises an oxide of a transition metal selected from the group consisting of
15 Mn, Fe, Co, Ni, V, Mo, Cu, Zn, and mixtures thereof.

14. The core-shell redox catalyst of claim 11, wherein the metal oxide
20 comprises a spinel oxide having a formula $\text{A}^{2+}\text{B}_2^{3+}\text{O}_4^{2-}$, wherein A and B are each independently a metal cation.

15. The core-shell redox catalyst of claim 14, wherein the metal cation is
selected from the group consisting of magnesium, zinc, iron, manganese, aluminum,
25 chromium, titanium, and silicon.

16. The core-shell redox catalyst of claim 11, wherein the MIEC shell
comprises a perovskite structure.

17. The core-shell redox catalyst of claim 11, wherein the MIEC shell is
30 selected from the group consisting of $\text{La}_x\text{Sr}_{1-x}\text{FeO}_3$, $\text{BaCe}_y\text{Fe}_{1-y}\text{O}_3$, and $\text{CaTi}_z\text{Fe}_{1-z}\text{O}_3$,
wherein $0.2 < x < 0.8$, $0.2 < y < 0.8$, and $0.05 < z < 0.75$.

18. The core-shell redox catalyst of claim 11, wherein the redox catalyst is prepared by a method selected from the group consisting of a solid state reaction (SSR) and a sol-gel method.
- 5
19. The core-shell redox catalyst of claim 11, further comprising an active metal.
20. A mixed-conductive redox catalyst having a perovskite structure and a
10 general formula of $A_xA'_{1-x}B_yB'_{1-y}O_{3-\delta}$, wherein A/A' metals are selected from the group consisting of Ca, Ba, Sr, and La, and B/B' metals are selected from the group consisting of Ti, Fe, Ni, Mn, and Ce.
21. A method for converting biomass to syngas, the method comprising:
- 15 (a) gasifying the biomass to produce a raw syngas comprising CO, H₂, and biomass tar of the formula C_xH_y;
- (b) contacting the raw syngas with a redox catalyst comprising one of:
- (i) an oxygen carrying material, a mixed ionic-electronic
conductive (MIEC) support, and a catalytically-active surface;
- 20 (ii) a metal oxide core; a mixed ionic-electronic conductive (MIEC) shell; and a plurality of surface catalytic sites; and
- (iii) a mixed conductive catalyst having a perovskite structure and a general formula of $A_xA'_{1-x}B_yB'_{1-y}O_{3-\delta}$, wherein A/A' metals are selected from the group consisting of Ca, Ba, Sr, and La, and
25 B/B' metals are selected from the group consisting of Ti, Fe, Ni, Mn, and Ce;
- thereby reducing the redox catalyst and converting the biomass tar of formula C_xH_y to xCO and yH₂; and
- (c) contacting the reduced redox catalyst with H₂O/O₂ to regenerate the
30 redox catalyst and to produce H₂ and/or heat.
22. A method for generating syngas from methane, the method comprising:

- (a) contacting methane or light hydrocarbons with a redox catalyst comprising:
- (i) an oxygen carrying material, a mixed ionic-electronic conductive (MIEC) support, and a catalytically-active surface;
 - 5 (ii) a metal oxide core; a mixed ionic-electronic conductive (MIEC) shell; and a plurality of surface catalytic sites; and
 - (iii) a mixed conductive catalyst with a perovskite structure and a general formula of $A_xA'_{1-x}B_yB'_{1-y}O_{3-\delta}$, wherein A/A' metals are selected from the group consisting of Ca, Ba, Sr, and La, and
 - 10 B/B' metals are selected from the group consisting of Ti, Fe, Ni, Mn, and Ce;
- thereby reducing the redox catalyst and converting the methane or light hydrocarbons, thereby reducing the redox catalyst and producing CO and H₂; and
- (b) contacting the reduced redox catalyst with H₂O/O₂ to regenerate the
- 15 redox catalyst and to produce H₂ and/or heat.

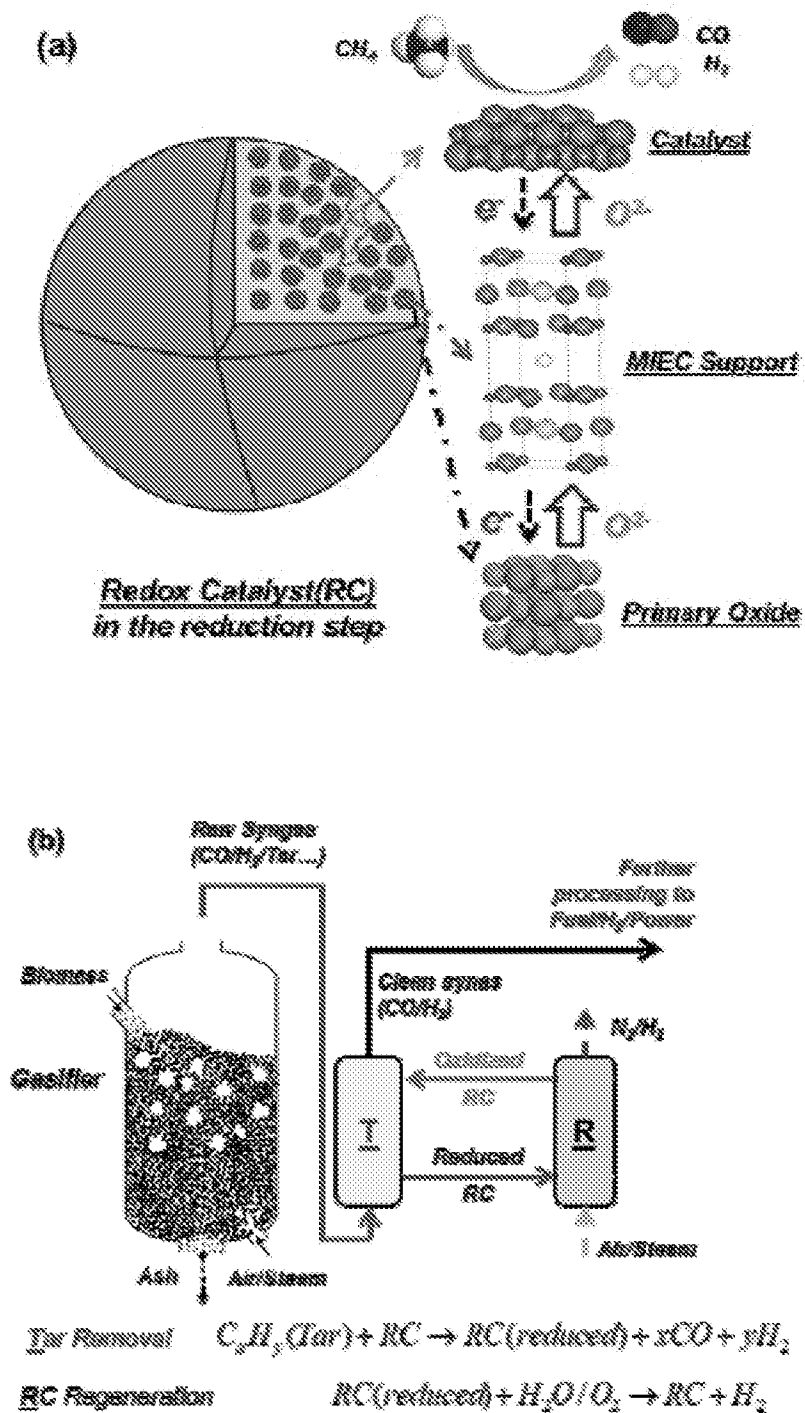
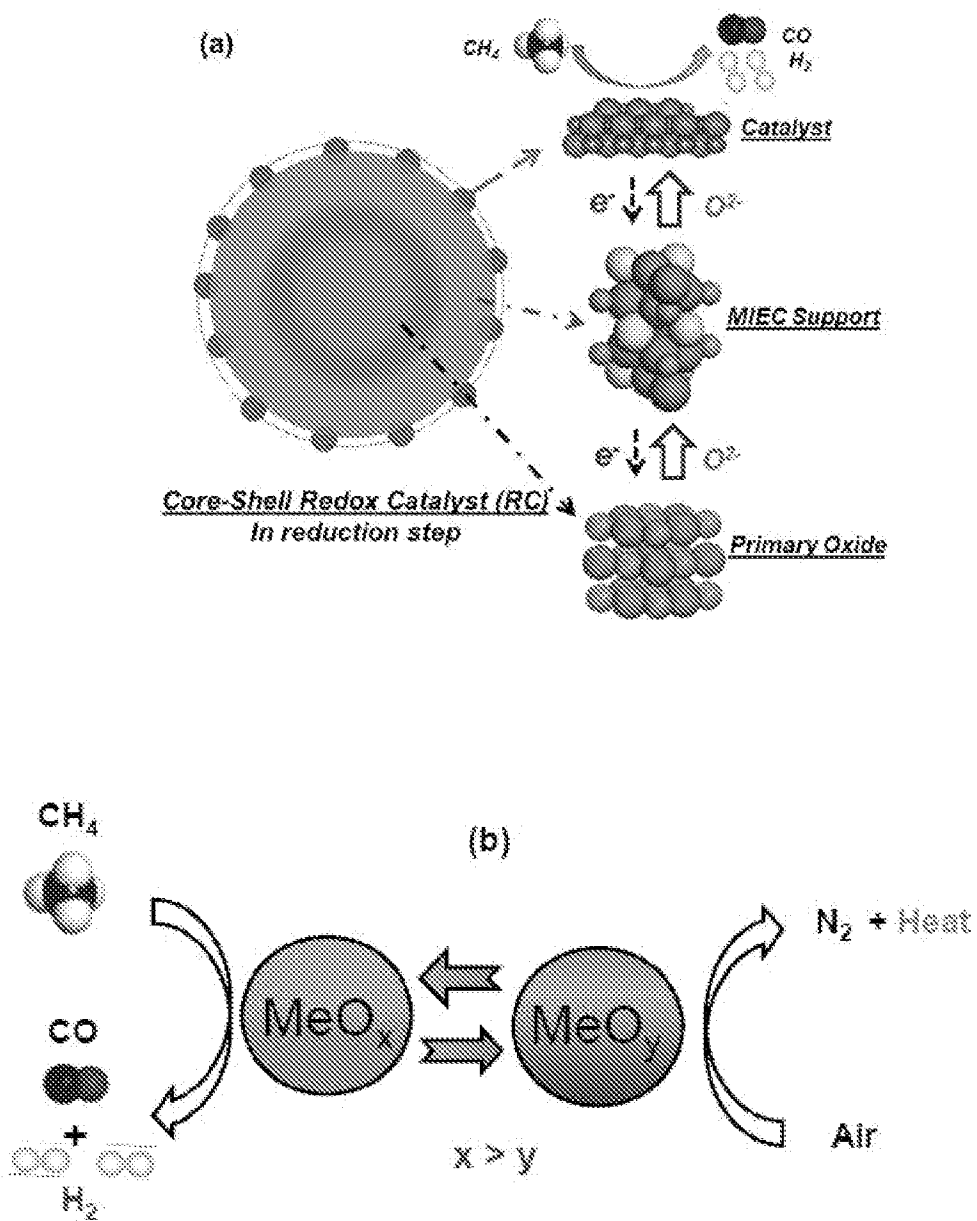
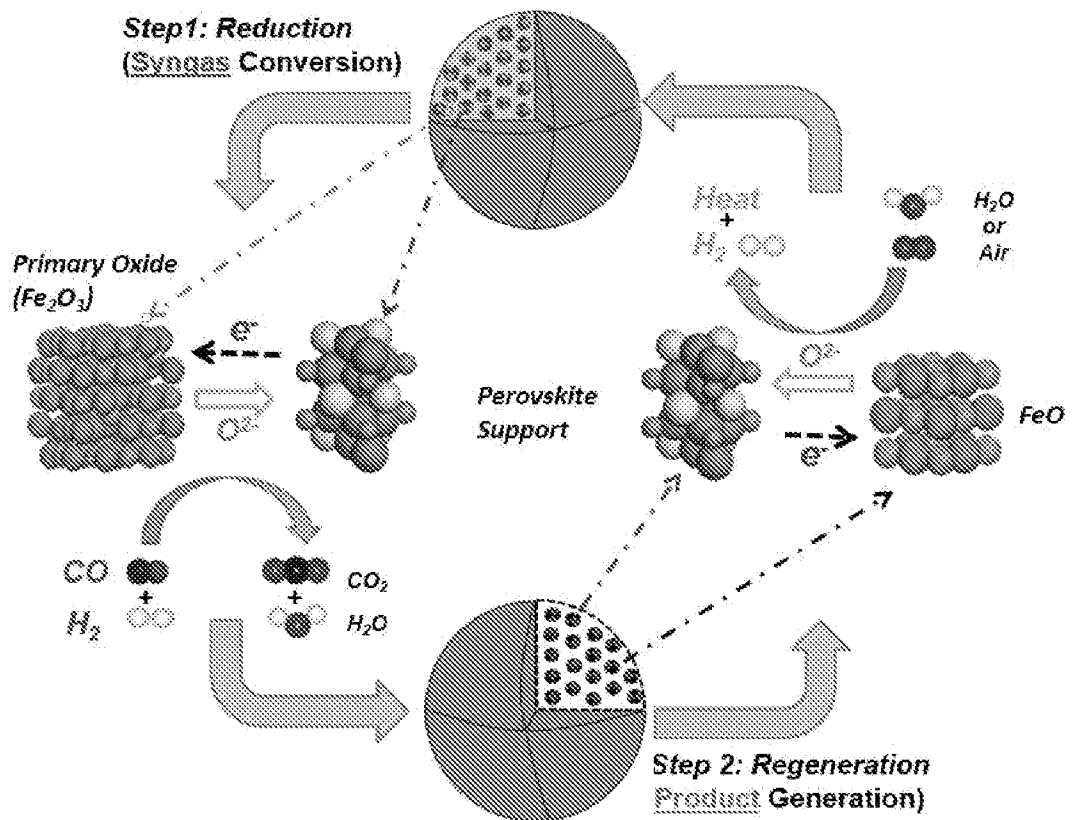


Fig. 1

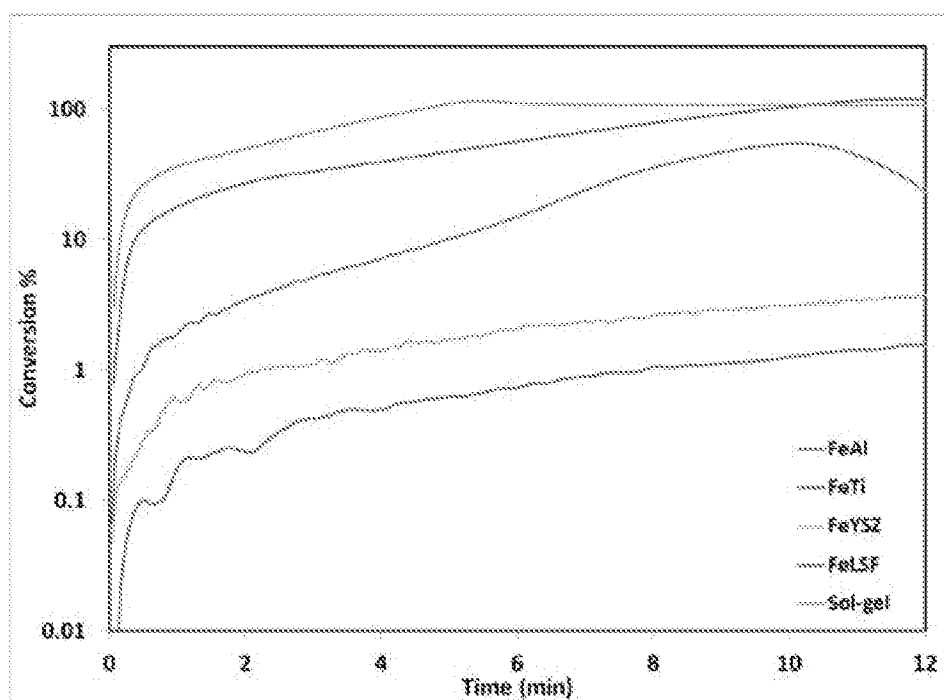
2/11

**Fig. 2**

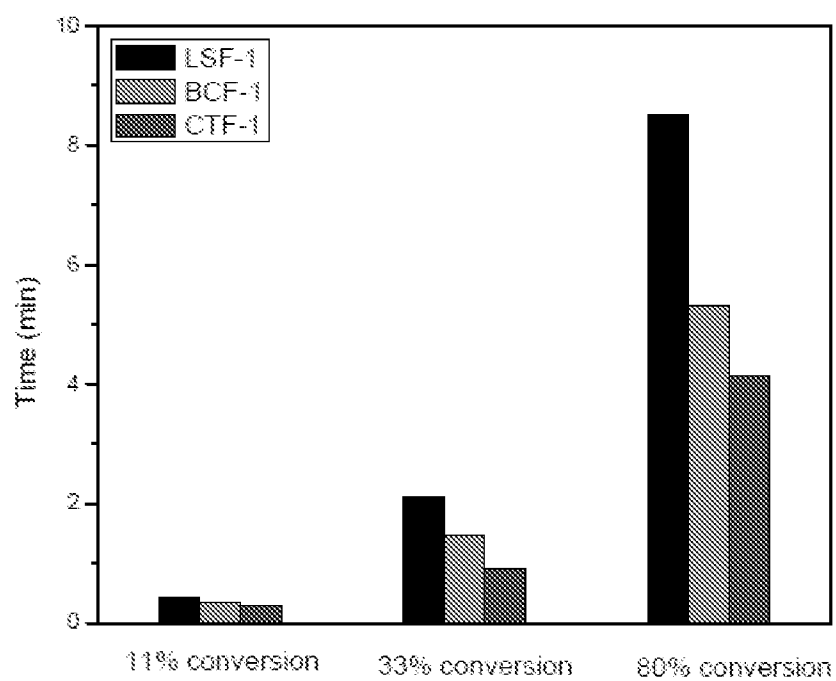
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*Fig. 3*

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*Fig. 4*

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***Fig. 5***

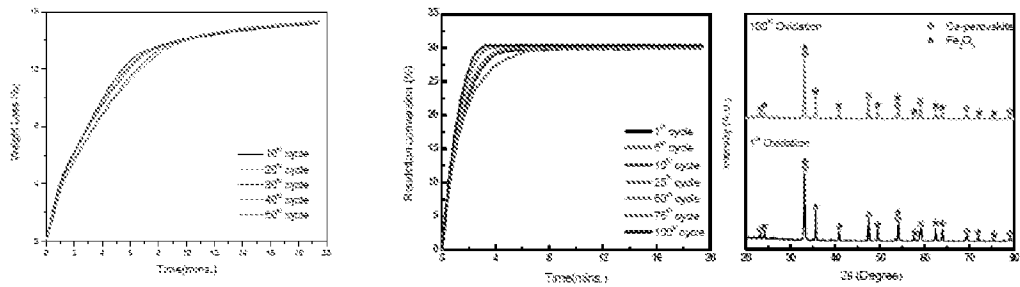


Fig. 6

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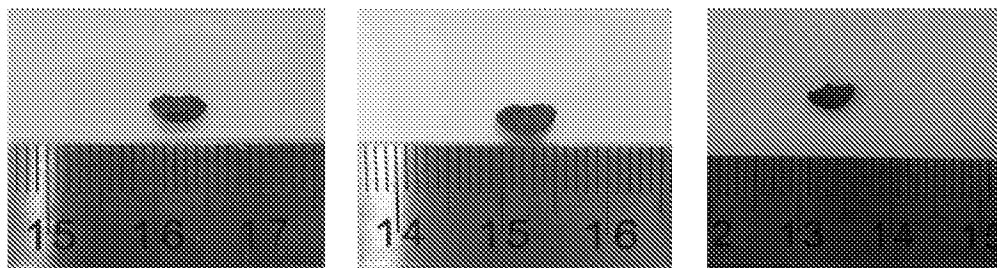


Fig. 7

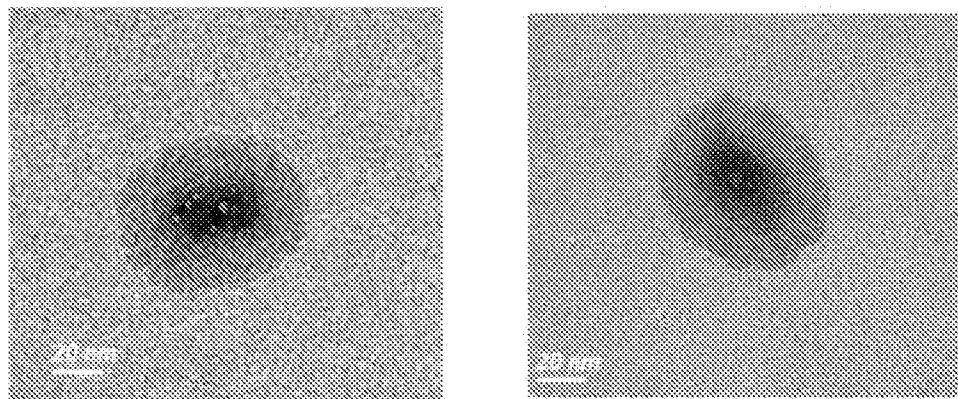


Fig. 8

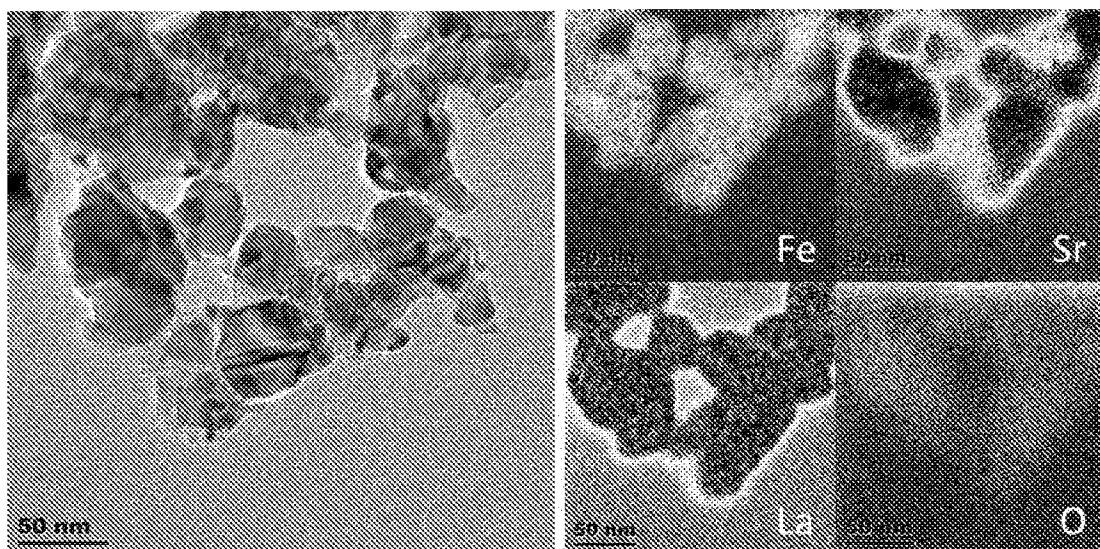
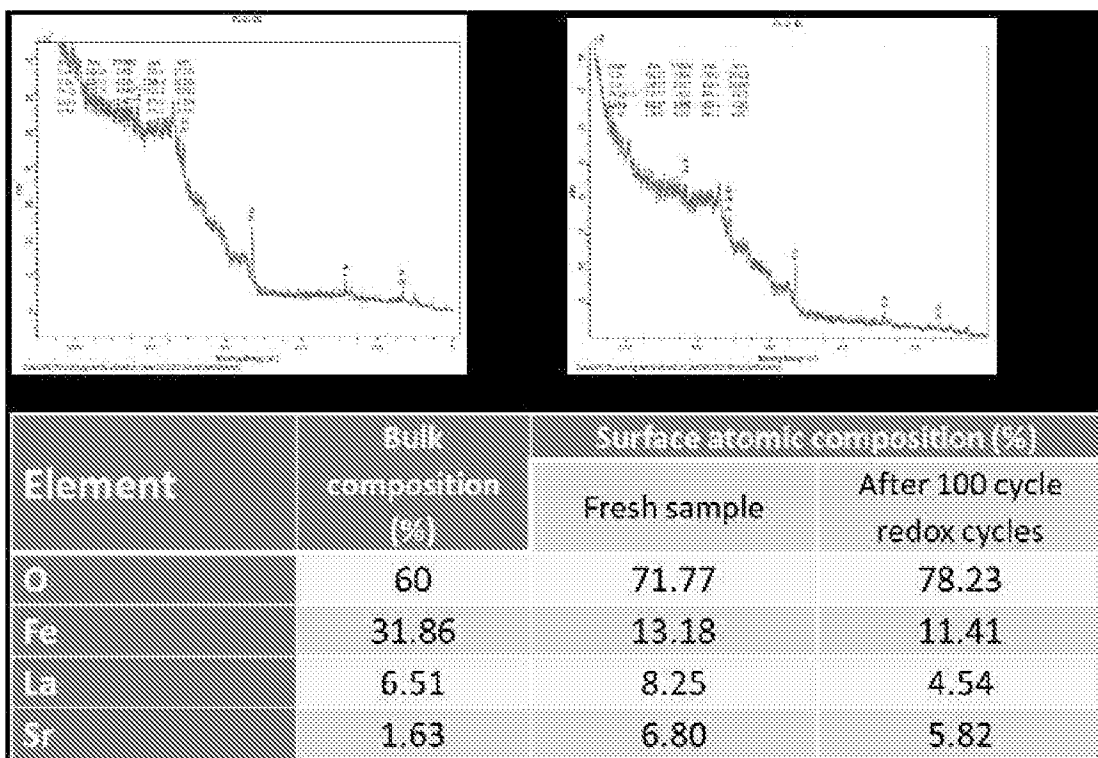
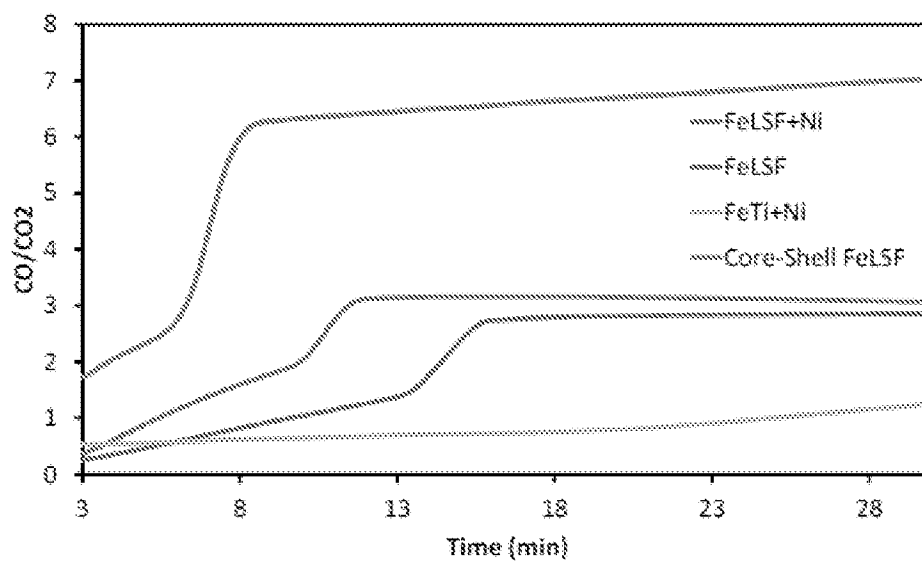


Fig. 9

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***Fig. 10***

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*Fig. 11*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/010280**A. CLASSIFICATION OF SUBJECT MATTER****B01D 53/94(2006.01)i**

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)

B01D 53/94

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & keywords: redox catalyst, oxygen carrying, mixed ionic-electronic conductive(MIEC), transition metal oxide, perovskite, core-shell, syngas, methane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GALINSKY, N. L. et al., "Iron Oxide with Facilitated O ₂ - Transport for Facile Fuel Oxidation and CO ₂ Capture in a Chemical Looping Scheme", ACS Sustainable Chem. Eng. 2013, 1, pp. 364-373, 2 February 2013 See abstract; line 1, left column of page 370; lines 2-6, left column of page 365; experimental section.	1-10, 20
Y		12-18
A		11, 19, 21, 22
X	SHAFIEFARHOOD, A. et al., "Core-Shell Redox Catalyst for Chemical Looping Reforming of Methane", AIChE, 2013 Annual Meeting, Particle Technology Forum, 11 May 2013 See first and third paragraphs.	1, 2, 11, 19, 21, 22
Y		12-18
A		3-10, 20
A	KHINE, M.S.S. et al., "Syngas production by catalytic partial oxidation of methane over (La _{0.7} A _{0.3})BO ₃ (A=Ba, Ca, Mg, Sr, and B=Cr or Fe) perovskite oxides for portable fuel cell applications", International Journal of Hydrogen Energy, 38, (2013) pp. 13300-13308, 22 August 2013 See abstract; 2. experimental.	1-22

☒ 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

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Date of the actual completion of the international search

12 May 2015 (12.05.2015)

Date of mailing of the international search report

14 May 2015 (14.05.2015)

Name and mailing address of the ISA/KR

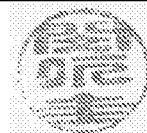
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2015/010280

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WEI, L. et al., "Synthesis of Diphenyl Carbonate over the Magnetic Catalysts Pd/La _{1-x} Pb _x MnO ₃ (x=0.2-0.7)", Chin. J. Chem. Eng., Vol. 21, No. 1, January 2013 See abstract; 2. Experimental.	1-22
A	MIMS, C. A. et al., "Modes of surface exchange in La _{0.2} Sr _{0.8} Cr _{0.2} Fe _{0.8} O _{3-d} ", Solid State Ionics 176 (2005) pp. 319-323, January 2005 See abstract; 2. experimental.	1-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/010280Patent document
cited in search reportPublication
datePatent family
member(s)Publication
date

None