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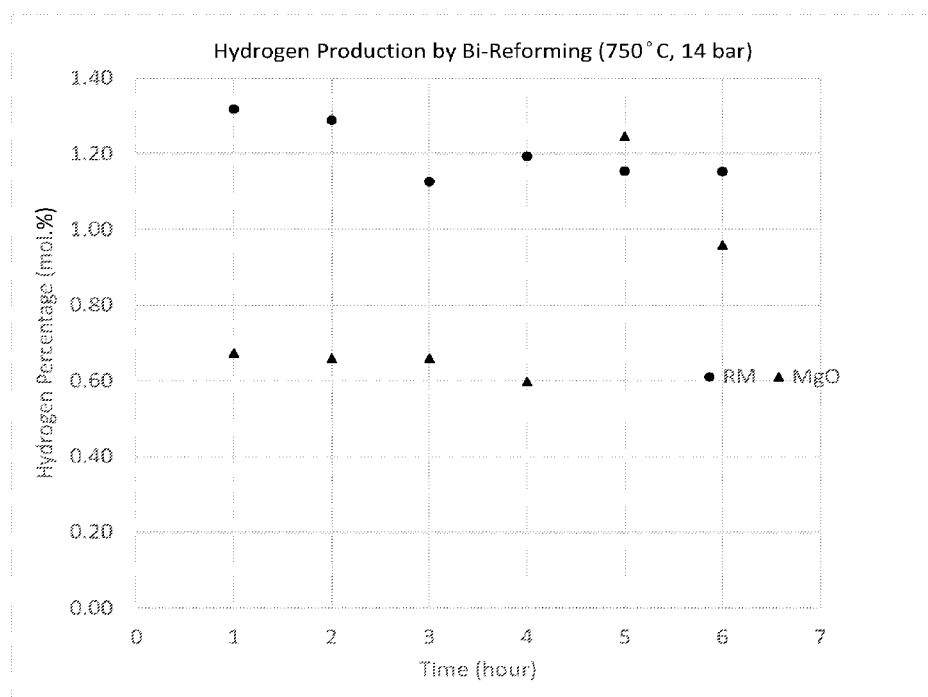


FIG. 1

(57) Abstract: Methods for bi-reforming with a red mud catalyst support composition, one method including providing a methane feed in the presence of carbon dioxide and steam to react over the red mud catalyst support composition at increased temperature and increased pressure to produce synthesis gas comprising H₂ and CO, the composition comprising red mud material produced from an alumina extraction process from bauxite ore.



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PCT PATENT APPLICATION
CATALYST CARRIER FOR BI-REFORMING PROCESSES

BACKGROUND

Field

[0001] Embodiments of the disclosure relate to catalyst carrier compositions for use in reforming processes. In particular, certain embodiments of the disclosure relate to catalyst carrier compositions for and methods of bi-reforming.

Description of the Related Art

[0002] Bi-reforming is a green method for the production of synthesis gas (syngas, H₂ and CO), since it utilizes the two greenhouse gases of CH₄ and CO₂ as reactants. In addition, it can offer certain advantages over dry reforming and steam reforming with respect to catalyst deactivation and final product ratio. The general chemical equation representing bi-reforming is shown below.



[0003] Bi-reforming technology combines dry reforming and steam reforming of methane to produce syngas. Unlike dry reforming, bi-reforming produces a syngas that is both flexible (with variability in the CO₂/H₂O ratio) and meets the 2/1 H₂/CO ratio required by many higher-value products, for example, higher oxygenates. In addition, the presence of steam provides a higher oxidant level in bi-reforming that addresses the inevitable and typically intolerable carbon deposition in dry reforming.

[0004] However, one of the main challenges of bi-reforming is to develop catalysts and supports

that are resistant to high temperatures and the presence of a more oxidative environment due to steam. Suitable catalysts for bi-reforming should be resistant to high temperatures and the presence of a more oxidative environment due to steam addition. Methane reforming can quickly deactivate catalysts due to coke formation on the surface of catalysts. In addition, high temperatures for methane conversion can lead to catalyst deactivation by coking or sintering. Nickel catalyst with aluminum oxide and magnesium oxide as supports is used for methane reforming.

[0005] However, present catalyst technology is insufficient in some processes to provide cost-effective and durable means for bi-reforming.

SUMMARY OF THE INVENTION

[0006] Applicant has recognized a need for catalyst carrier compositions comprising red mud to be applied in systems and processes for bi-reforming. Red mud catalyst carrier compositions for use in bi-reforming are disclosed. The red mud catalyst carrier compositions in some embodiments contain Fe, Al, Si, Na, Ca, and Ti oxides from red mud, and the compositions act as a base support for catalytically active compositions, for example added metals and metal oxides. A factor in designing suitable reforming catalysts is the catalyst support or base material, which can have an active catalytic role in a catalytic reaction or be merely inert. In embodiments of the present disclosure, red mud acts as a catalyst carrier. Disclosed compositions are useful as a catalyst carrier in bi-reforming processes for the conversion of methane to syngas, according to Equation 1. Utilization of red mud in bi-reforming processes provides the concurrent advantages of utilizing a waste material (red mud) and producing useful H₂, while also using two greenhouse gases (CO₂ and CH₄) as reactants.

[0007] Red mud is a caustic waste material produced from bauxite ore processing for alumina extraction, and is utilized here as a catalyst carrier for bi-reforming processes. Surprisingly and unexpectedly, without being specifically designed as a catalyst or carrier (for example using specific zeolitic structure), red mud waste material can be readily used as a catalyst support. Red mud generally includes a mixture of transition metals such as Ti, Fe, and Al, which make it an advantageous catalyst in addition to or alternative to catalyst carrier for bi-reforming processes, for example once modified with nickel in addition to or alternative to other metals, such as transition metals and their oxides.

[0008] Embodiments disclosed here apply red mud as a catalyst support or base material, while offering some catalytic activity itself for bi-reforming of methane, optionally followed by a water-gas shift reaction to produce additional H₂.

[0009] Therefore, disclosed here is a method for bi-reforming with a red mud catalyst support composition, the method including providing a methane feed in the presence of carbon dioxide and steam to react over the red mud catalyst support composition at increased temperature and increased pressure to produce synthesis gas comprising H₂ and CO, the composition comprising: red mud material produced from an alumina extraction process from bauxite ore. In some embodiments, the composition further comprises at least one added catalytic metal, the added

catalytic metal not being present in an unmodified form of the red mud material produced from the alumina extraction process from bauxite ore. Still in other embodiments, the at least one added catalytic metal is a Periodic Table Group 3-12 metal. In certain embodiments, the increased temperature is between about 500 °C to about 1000 °C. In other embodiments, the increased temperature is between about 600 °C to about 800 °C. In yet other embodiments, the increased temperature is between about 700 °C to about 750 °C.

[0010] In other embodiments of the method, the increased pressure is between about 5 bar and about 20 bar. Still in certain other embodiments, the increased pressure is between about 7 bar and about 15 bar. In some embodiments, the increased pressure is about 14 bar. Still in other embodiments, gas hourly space velocity of the methane feed and carbon dioxide feed mixed is between about 1000 h⁻¹ to 10000 h⁻¹, or is about 3,000 h⁻¹ or is about 5000 h⁻¹. In some embodiments, the composition includes at least one component selected from the group consisting of: Fe₂O₃, Al₂O₃, SiO₂, Na₂O, CaO, and TiO₂. Still in other embodiments, a majority of the particles of the composition have a particle size of less than about 70 μm. In some embodiments, a molar ratio of methane:carbon dioxide:steam is about 3:1:2. Still in other embodiments, produced H₂ is at least about 1 mol.% of produced products from the reaction for at least about 5 hours.

[0011] In certain other embodiments, the composition includes between about 20 wt.% and about 30 wt.% Al₂O₃, between about 5 wt.% and about 10 wt.% CaO, between about 15 wt.% and about 25 wt.% Fe₂O₃, between about 5 wt.% and about 15 wt.% Na₂O, between about 15 wt.% and about 25 wt.% SiO₂, and between about 5 wt.% and about 10 wt.% TiO₂.

BRIEF DESCRIPTION OF THE DRAWING

[0012] These and other features, aspects, and advantages of the present disclosure will become better understood with regard to the following descriptions, claims, and accompanying drawing. It is to be noted, however, that the drawing illustrates only several embodiments of the disclosure and is therefore not to be considered limiting of the disclosure's scope as it can admit to other equally effective embodiments.

[0013] FIG. 1 is a graph showing mol.% of H₂ out of the total products produced from bi-reforming of CH₄ for unmodified red mud (RM) used as a catalyst support and for MgO used as a catalyst support.

DETAILED DESCRIPTION OF THE INVENTION

[0014] So that the manner in which the features and advantages of the embodiments of compositions of red mud along with systems and methods for bi-reforming with such compositions, may be understood in more detail, a more particular description of the embodiments of the present disclosure briefly summarized previously may be had by reference to the embodiments thereof, which are illustrated in the appended drawing, which forms a part of this specification. It is to be noted, however, that the drawing illustrates only various embodiments of the disclosure and is therefore not to be considered limiting of the present disclosure's scope, as it may include other effective embodiments as well.

[0015] As noted, red mud is a caustic waste material generated during alumina extraction from bauxite ore. Red mud includes a mixture of transition metals, for example as listed in Table 1.

Table 1. Example composition ranges for global red mud.

Component	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	Na ₂ O	CaO	TiO ₂
Approx. Weight Percentage	30-60 %	10-20 %	3-50 %	2-10 %	2-8 %	10 %

[0016] In one embodiment, a Saudi Arabian red mud sample was evaluated for bi-reforming activities at 750 °C and 14 bar, as shown in FIG. 1. The results are compared to MgO catalyst support material. MgO is a commercially-available catalyst support material known for a variety of reforming processes with a surface area of about 29 m²/g. The MgO was tested as received. FIG. 1 shows that red mud surprisingly and unexpectedly outperforms MgO as a support for bi-reforming catalyst support in terms of hydrogen production (also methane conversion according to Equation 1), especially at high pressure which is a preferred condition for industry application of bi-reforming.

[0017] Saudi Arabian red mud from Ma'aden Aluminium Company, based at Ras Al Khair, Saudi Arabia was used in the test runs. Table 2 shows the weight percent for certain components in the Saudi Arabian red mud composition.

Table 2. Certain component weight percentages in Saudi Arabian red mud (RM)
catalyst/catalyst support composition.

Component	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	Na ₂ O	CaO	TiO ₂
Weight Percentage	18.75 %	25.22 %	18.88 %	11.77 %	7.97 %	6.89 %

[0018] The red mud was tested as-is without further treatment, for example acid or base treatment, for use as a catalyst support with a Brunauer-Emmett-Teller (BET) surface area of about 16 m²/g.

[0019] Several tests on red mud support catalytic activity and MgO support catalytic activity for bi-reforming were experimentally conducted. Saudi Arabian red mud was tested as received as a catalyst support without any modifications, and it was placed in a micromeritics® PID Eng & Tech brand microactivity reactor designed for catalyst activity and selectivity analysis, and similar tests were performed for the MgO catalyst support. The results are compared, for example, in FIG. 1. Results show that red mud support catalytic activity for bi-reforming is advantageously improved over MgO support catalytic activity for bi-reforming.

[0020] Experimental conditions in the bi-reforming reactor included temperature at about 750 °C and pressure at about 14 bar. In some embodiments, gas hourly space velocity (GHSV) of the mixed feed is between about 1000 h⁻¹ and 10000 h⁻¹, or GHSV can be between about 3000 h⁻¹ to about 8000 h⁻¹, or about 7362 h⁻¹. The test was conducted for 6 hours. In some embodiments, the feed was about 50 mol.% methane, 17 mol.% CO₂, and 33 mol.% steam for both catalysts tested. The GHSV was calculated for the mixed feed. For bi-reforming, the feed composition can comprise, consist essentially of, or consist of CH₄, CO₂, and steam. Based in part on thermodynamics, a suitable molar ratio of methane:carbon dioxide:steam is about 3:1:2. GHSV generally measures the flow rate of the feed gases divided by the catalyst volume, which indicates the residence time of the reactants on the catalyst.

[0021] FIG. 1 is a graph showing mol.% of H₂ out of the total products produced from bi-reforming of CH₄ for unmodified red mud used as a catalyst support and for MgO used as a catalyst support. Hydrogen production illustrated in FIG. 1 shows that untreated red mud produced hydrogen at nearly double the rate of MgO for most of the experiment.

[0022] The singular forms “a,” “an,” and “the” include plural referents, unless the context clearly

dictates otherwise. The term “about” when used with respect to a value or range refers to values including plus and minus 5% of the given value or range.

[0023] In the drawings and specification, there have been disclosed example embodiments of the present disclosure, and although specific terms are employed, the terms are used in a descriptive sense only and not for purposes of limitation. The embodiments of the present disclosure have been described in considerable detail with specific reference to these illustrated embodiments. It will be apparent, however, that various modifications and changes can be made within the spirit and scope of the disclosure as described in the foregoing specification, and such modifications and changes are to be considered equivalents and part of this disclosure.

CLAIMS

That claimed is:

1. A method for bi-reforming with a red mud catalyst support composition, the method comprising the steps of:

providing a methane feed in the presence of carbon dioxide and steam to react over the red mud catalyst support composition at increased temperature and increased pressure to produce synthesis gas comprising H₂ and CO, the composition comprising:

red mud material produced from an alumina extraction process from bauxite ore.

2. The method according to claim 1, where the composition further comprises at least one added catalytic metal, the added catalytic metal not being present at greater than 1 wt.% in an unmodified form of the red mud material produced from the alumina extraction process from bauxite ore.

3. The method according to claim 2, where the at least one added catalytic metal is a Periodic Table Group 3-12 metal.

4. The method according to any one of claims 1 to 3, where the increased temperature is between 500 °C to 1000 °C.

5. The method according to any one of claims 1 to 3, where the increased temperature is between 600 °C to 800 °C.

6. The method according to any one of claims 1 to 3, where the increased temperature is 750 °C.

7. The method according to any one of claims 1 to 6, where the increased pressure is between 5 bar and 20 bar.

8. The method according to any one of claims 1 to 6, where the increased pressure is between 10 bar and 15 bar.

9. The method according to any one of claims 1 to 6, where the increased pressure is 14 bar.

10. The method according to any one of claims 1 to 9, where gas hourly space velocity of the methane feed in the presence of carbon dioxide and steam is between 1000 h⁻¹ to 10000 h⁻¹.

11. The method according to any one of claims 1 to 10, where the composition includes at least one component selected from the group consisting of: Fe_2O_3 , Al_2O_3 , SiO_2 , Na_2O , CaO , and TiO_2 .
12. The method according to any one of claims 1 to 11, where a majority of the particles of the composition have a particle size of less than 70 μm .
13. The method according to any one of claims 1 to 12, where a molar ratio of methane:carbon dioxide:steam is 3:1:2.
14. The method according to any one of claims 1 to 13, where produced H_2 is at least 1 mol.% of produced products from the reaction for at least 5 hours.
15. The method according to any one of claims 1 to 14, where the composition includes between 20 wt.% and 30 wt.% Al_2O_3 , between 5 wt.% and 10 wt.% CaO , between 15 wt.% and 25 wt.% Fe_2O_3 , between 5 wt.% and 15 wt.% Na_2O , between 15 wt.% and 25 wt.% SiO_2 , and between 5 wt.% and 10 wt.% TiO_2 .

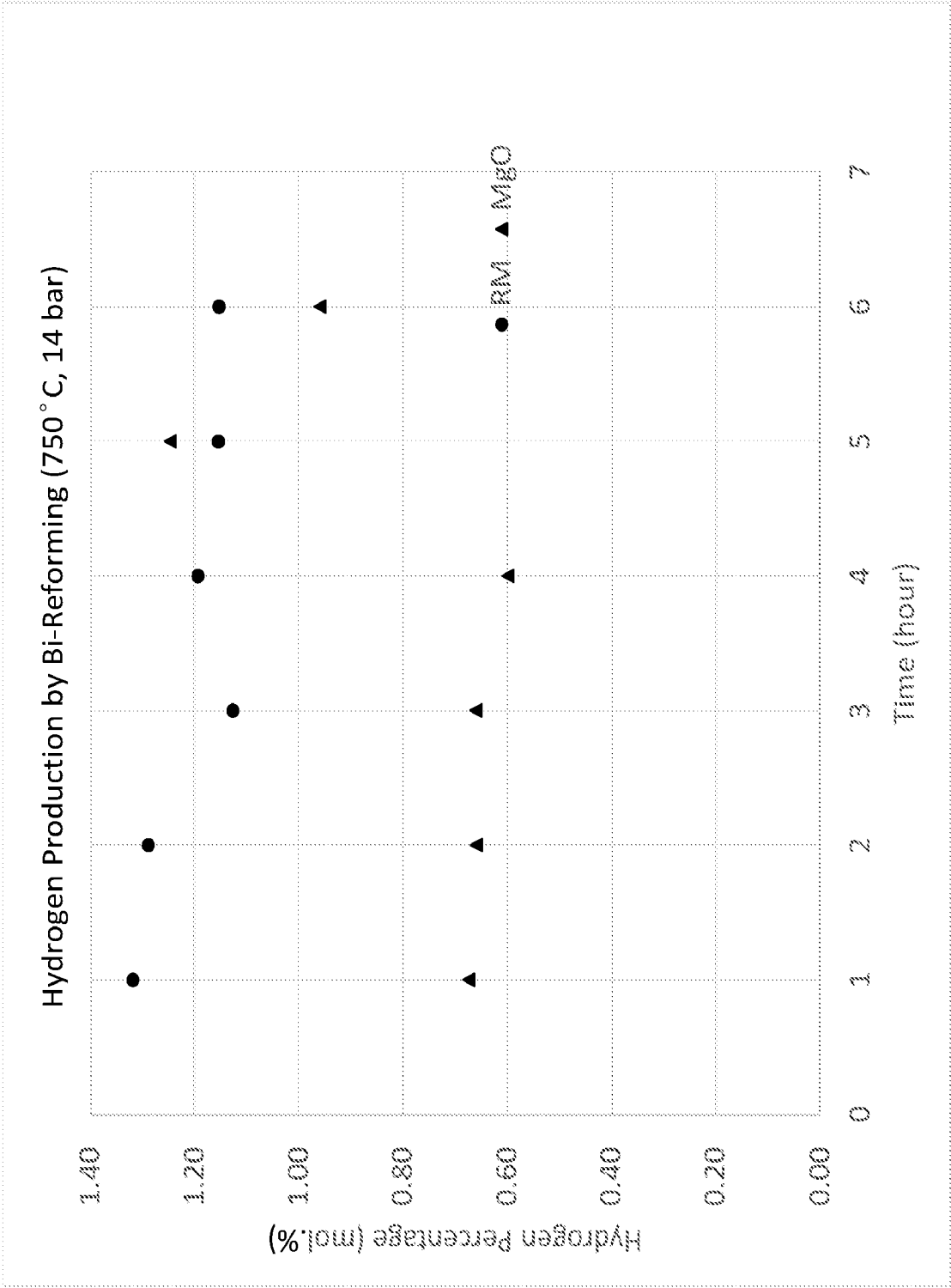


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/38 B01J35/02 C01B3/40
ADD. B01J23/78

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)
C01B B01J

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)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RU 2 542 177 C1 (FEDERAL NOE G BJUDZHETNOE UCHREZHDENIE NATSIONAL NYJ I SKIJ TS KURCHAT) 20 February 2015 (2015-02-20)	1-12, 14, 15
A	paragraph [0017] - paragraphs [0018], [0022]; figure 1; table 3	13
A	GB 714 284 A (ZSIGMOND DE GALOCSY) 25 August 1954 (1954-08-25) page 2 - page 3	1-15
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Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2021/015196

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	MATHUR V K ET AL: "Ore catalysts in two-stage coal liquefaction", FUEL, IPC SIENCE AND TECHNOLOGY PRESS , GUILDFORD, GB, vol. 65, no. 6, 1 June 1986 (1986-06-01), pages 790-796, XP025421628, ISSN: 0016-2361, DOI: 10.1016/0016-2361(86)90071-2 [retrieved on 1986-06-01] page 785; table 5 -----	1-15
A	WO 00/00285 A1 (COMMW SCIENT IND RES ORG [AU]; HOANG MANH [AU]) 6 January 2000 (2000-01-06) page 5, line 5 - line 15; claims 1,3 -----	1-15
A	US 2019/308183 A1 (AGBLEVOR FOSTER [US] ET AL) 10 October 2019 (2019-10-10) claims 1-7 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2021/015196

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US 2019308183	A1	10-10-2019	NONE	
