(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
05 August 2021 (05.08.2021)

WIPO | PCT

(10) International Publication Number
WO 2021/154864 A1

(51) International Patent Classification:
C01B 3/38 (2006.01) *C01B 3/40* (2006.01)
B01J 23/84 (2006.01)

(21) International Application Number:
PCT/US2021/015303

(22) International Filing Date:
27 January 2021 (27.01.2021)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
16/775,135 28 January 2020 (28.01.2020) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(54) Title: CATALYST COMPOSITIONS HAVING ENHANCED ACIDITY FOR DRY REFORMING PROCESSES

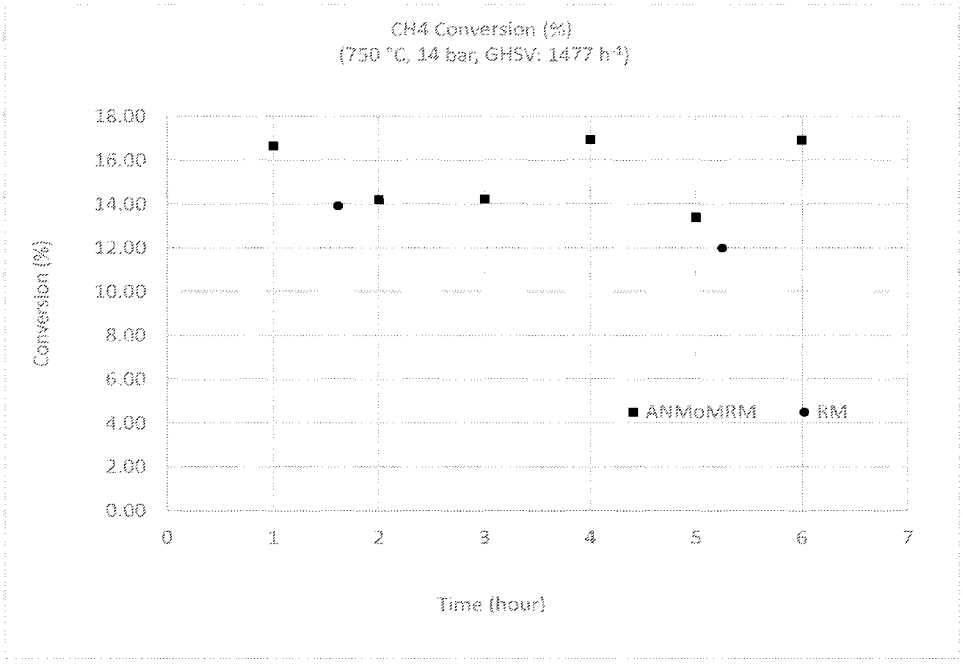


FIG. 1

(57) Abstract: Modified red mud catalyst compositions, methods for production, and methods for use, a composition including red mud material produced from an alumina extraction process from bauxite ore; nickel oxide, the nickel oxide present at between about 5 wt.% to about 40 wt.% of the modified red mud catalyst composition; and a Periodic Table Group VIB metal oxide, the Group VIB metal oxide present at between about 1 wt.% and about 30 wt. % of the modified red mud catalyst composition.

WO 2021/154864 A1

[Continued on next page]

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

CATALYST COMPOSITIONS HAVING ENHANCED ACIDITY FOR DRY REFORMING PROCESSES

BACKGROUND

Field

[0001] Embodiments of the disclosure relate to catalyst compositions for use in reforming processes. In particular, certain embodiments of the disclosure relate to Periodic Table Group VIB metal oxide containing catalyst compositions for and methods of dry reforming.

Description of the Related Art

[0002] Dry reforming simultaneously utilizes two greenhouse gases, CH_4 and CO_2, to produce synthesis (syn) gas (CO and H_2). However, one challenge of dry reforming is the lack of available, durable, and cost-effective catalyst. Dry reforming generally applies a catalyst, increased temperature, and increased pressure in a process generally according to Equation 1.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \text{Eq. 1}$$

[0003] Dry reforming generally is not as common as steam reforming, and one use is in processes that require a high proportion of CO versus H_2 in the produced synthesis gas. The thermodynamics of dry reforming are similar to those of steam reforming. One difference of dry reforming from steam reforming is dry reforming's tendency for coking, increased by a lack of steam to remove carbon deposits. In some applications like mixed reforming or bi-reforming (a combination of steam and dry reforming), steam is added for effective reduction or removal of coke. Since coking

can quickly deactivate Ni catalysts, Rh and Ru catalysts are used in some dry reforming applications.

[0004] Present catalyst technology is insufficient in some processes to provide cost-effective means for dry reforming.

SUMMARY OF THE INVENTION

[0005] Applicant has recognized a need for compositions of Periodic Table Group VIB (Group VIB) metal oxide containing modified red mud to be applied in systems and processes for dry reforming. Enhanced-acidity Group VIB catalyst compositions are disclosed, in some embodiments further including nickel. The enhanced-acidity Group VIB catalysts also contain in some embodiments Fe, Al, Si, Na, Ca, and Ti oxides from red mud. In embodiments of the present disclosure, red mud acts as a catalyst in addition to or alternative to a catalyst carrier. Disclosed compositions are useful as a catalyst in dry reforming processes for the conversion of methane to syngas, according to Equation 1. Utilization of red mud in dry reforming processes provides the concurrent advantages of utilizing a waste material (red mud), converting CO_2 (a greenhouse gas), and producing H_2.

[0006] Red mud is a caustic waste material produced from bauxite ore processing for alumina extraction, and is utilized here as a catalyst for a dry reforming process. Surprisingly and unexpectedly, without being specifically designed as a catalyst (for example using specific zeolitic structure), red mud waste material can be readily modified for use as a catalyst. Dry reforming is considered to be a green method for the production of syngas (H_2 and CO), since it utilizes as reactants two greenhouse gases, CH_4 and CO_2. Despite that, widespread adoption of dry reforming processes has been stymied due in part to the lack of commercially-available durable and efficient catalysts. Red mud generally includes a mixture of transition metals such as Ti, Fe, and Al, which make it an advantageous catalyst for dry reforming processes, for example once modified with nickel and molybdenum.

[0007] Embodiments disclosed here apply red mud as an active catalyst support, promotor, in addition to or alternative to catalyst to produce hydrogen through dry reforming of methane.

[0008] Therefore, disclosed here is a modified red mud catalyst composition including red mud material produced from an alumina extraction process from bauxite ore; nickel oxide, the nickel oxide present at between about 5 wt.% to about 40 wt.% of the modified red mud catalyst composition; and a Periodic Table Group VIB metal oxide, the Group VIB metal oxide present at between about 1 wt.% and about 30 wt. % of the modified red mud catalyst composition. In some embodiments, the Group VIB metal oxide comprises at least one metal selected from the group consisting of: chromium, molybdenum, and tungsten. In other embodiments, 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. Still in other embodiments, a majority of the particles of the composition have a particle size of less than about 70 μm. In certain other embodiments, the nickel oxide is present at between about 10 wt.% to about 30 wt.% of the modified red mud catalyst composition. Still in other embodiments, the nickel oxide is present at between about 15 wt.% to about 25 wt.% of the modified red mud catalyst composition. In some embodiments, the nickel oxide is present at about 23 wt.% of the modified red mud catalyst composition.

[0009] In other embodiments of the composition, the Group VIB metal oxide is present at between about 1 wt.% to about 20 wt.% of the modified red mud catalyst composition. In some embodiments, the Group VIB metal oxide is present at between about 1 wt.% to about 10 wt.% of the modified red mud catalyst composition. Still in other embodiments, the Group VIB metal oxide is present at about 5 wt.% of the modified red mud catalyst composition. In yet other embodiments, the Brunauer-Emmett-Teller (BET) surface area of the modified red mud catalyst composition is between about 50 m^2/g and about 90 m^2/g.

[0010] Additionally disclosed here are methods for producing the modified red mud catalyst compositions, one method including dissolving red mud material produced from an alumina extraction process from bauxite ore in water to produce a red mud solution; neutralizing the pH of the red mud solution using an acid; preparing a nickel-containing solution; preparing a Periodic Table Group VIB metal oxide-containing solution; mixing the red mud solution, the nickel-containing solution, and the Group VIB metal oxide-containing solution to precipitate the modified red mud catalyst composition; and calcining the modified red mud catalyst composition. In some embodiments, the Group VIB metal oxide comprises at least one metal selected from the group consisting of: chromium, molybdenum, and tungsten. Still in other embodiments, the water comprises deionized water. In certain embodiments, the acid comprises hydrochloric acid.

[0011] In some other embodiments of the methods, the nickel-containing solution comprises nickel nitrate dissolved in ethanol. Still in other embodiments, the Group VIB metal oxide-containing solution comprises ammonium molybdate dissolved in ethanol. In yet other embodiments, the method includes filtering the modified red mud catalyst composition and drying the modified red mud catalyst composition before the step of calcining. In some embodiments, the step of drying occurs at about 100 °C. Still in other embodiments, the step of calcining takes

place for about 4 hours at between about 500 °C to about 700 °C. In yet other embodiments, the step of calcining takes place for about 4 hours at about 600 °C. Still in yet other embodiments, the method includes the step of grinding the modified red mud catalyst composition to a particle size of less than about 70 μm. In some embodiments, the BET surface area of the modified red mud catalyst composition is between about 50 m^2/g and about 90 m^2/g.

[0012] Additionally disclosed here is a method for dry reforming over a modified red mud catalyst composition, the method including providing a methane feed and carbon dioxide feed to react over the modified red mud catalyst composition at increased temperature and increased pressure to produce synthesis gas comprising H_2 and CO, the composition comprising: red mud material produced from an alumina extraction process from bauxite ore; nickel oxide, the nickel oxide present at between about 5 wt.% to about 40 wt.% of the modified red mud catalyst composition; and a Periodic Table Group VIB metal oxide, the Group VIB metal oxide present at between about 1 wt.% and about 30 wt. % of the modified red mud catalyst composition.

[0013] In some embodiments, the Group VIB metal oxide comprises at least one metal selected from the group consisting of: chromium, molybdenum, and tungsten. Still in other embodiments, the increased temperature is between about 500 °C to about 1000 °C. In some embodiments, the increased temperature is between about 600 °C to about 800 °C. In other embodiments, the increased temperature is about 750 °C. In certain embodiments, the increased pressure is between about 5 bar and about 20 bar. In other embodiments, the increased pressure is between about 10 bar and about 15 bar. Still in other embodiments, the increased pressure is about 14 bar. In yet other embodiments, the methane conversion rate is at least about 14% for at least about 6 hours. In yet 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}. Still in other embodiments, 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. In certain embodiments, a majority of the particles of the composition have a particle size of less than about 70 μm. And in other embodiments, the nickel oxide is present at between about 10 wt.% to about 30 wt.% of the modified red mud catalyst composition.

[0014] Still in other embodiments, the nickel oxide is present at between about 15 wt.% to about 25 wt.% of the modified red mud catalyst composition. In certain embodiments, the nickel oxide is present at about 23 wt.% of the modified red mud catalyst composition. In some embodiments,

the Group VIB metal oxide is present at between about 1 wt.% to about 20 wt.% of the modified red mud catalyst composition. Still in other embodiments, the Group VIB metal oxide is present at between about 1 wt.% to about 10 wt.% of the modified red mud catalyst composition. In certain embodiments, the Group VIB metal oxide is present at about 5 wt.% of the modified red mud catalyst composition. In certain other embodiments, a molar ratio of the methane feed to the carbon dioxide feed is between about 1:1 and about 1:1.75. In some embodiments, produced H_2 is at least about 9 mol.% of produced products from the reaction. And in other embodiments, the BET surface area of the modified red mud catalyst composition is between about 50 m^2/g and about 90 m^2/g.

[0015] In some embodiments of the compositions and methods described, modified red mud catalyst compositions with nickel in addition to or alternative to molybdenum or other metals include between about 15 wt.% and about 30 wt.% Al_2O_3, between about 1 wt.% and about 5 wt.% CaO, between about 10 wt.% and about 30 wt.% Fe_2O_3, between about 1 wt.% and about 5 wt.% Na_2O, between about 10 wt.% and about 25 wt.% SiO_2, and between about 1 wt.% and about 10 wt.% TiO_2.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] These and other features, aspects, and advantages of the present disclosure will become better understood with regard to the following descriptions, claims, and accompanying drawings. It is to be noted, however, that the drawings illustrate only several embodiments of the disclosure and are therefore not to be considered limiting of the disclosure's scope as it can admit to other equally effective embodiments.

[0017] FIG. 1 is a graph showing conversion percentage for CH_4 in a dry reforming process for unmodified red mud (RM) used as a catalyst and for acid nickel-molybdenum-modified red mud (ANMoMRM) used as a catalyst.

[0018] FIG. 2 is a graph showing mol.% of H_2 out of the total products produced from dry reforming of CH_4 in a dry reforming process for unmodified red mud used as a catalyst and for ANMoMRM used as a catalyst.

DETAILED DESCRIPTION OF THE INVENTION

[0019] So that the manner in which the features and advantages of the embodiments of compositions of Group VIB metal modified red mud, in some embodiments including nickel, along with systems and methods for dry reforming with such compositions and for producing 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 drawings, which form a part of this specification. It is to be noted, however, that the drawings illustrate only various embodiments of the disclosure and are therefore not to be considered limiting of the present disclosure's scope, as it may include other effective embodiments as well.

[0020] 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_2O_3	Al_2O_3	SiO_2	Na_2O	CaO	TiO_2
Approx. Weight Percentage	30-60 %	10-20 %	3-50 %	2-10 %	2-8 %	10 %

[0021] Red mud was modified with nickel and molybdenum to be utilized and tested as a catalyst for dry reforming as follows. In some embodiments, nickel is not required. In some embodiments, nickel in addition to or alternative to any one of or any combination of chromium, molybdenum, and tungsten can be used to modify red mud. Saudi Arabian red mud from Ma'aden Aluminium Company, based at Ras Al Khair, Saudi Arabia was used to prepare a modified catalyst composition. Table 2 shows the weight percent for certain components in the unmodified Saudi Arabian red mud composition.

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

Component	Fe_2O_3	Al_2O_3	SiO_2	Na_2O	CaO	TiO_2
Weight Percentage	18.75 %	25.22 %	18.88 %	11.77 %	7.97 %	6.89 %

[0022] The untreated red mud exhibited a Brunauer-Emmett-Teller (BET) surface area of about 16 m^2/g.

[0023] Table 3 shows an example composition for one embodiment of produced nickel-molybdenum acid treated red mud for use as a modified catalyst. The unmodified red mud used as a catalyst precursor contained no detectable nickel or molybdenum.

Table 3. Example composition for a produced ANMoMRM used as a catalyst.

Component	Fe_2O_3	Al_2O_3	SiO_2	Na_2O	CaO	TiO_2	NiO	MoO
Weight Percentage	16.76 %	21.43 %	19.56 %	2.81 %	2.76 %	5.36 %	23.7 %	5.06 %

[0024] Because red mud is a highly variable waste material, elemental composition will vary between samples and test results.

[0025] *Catalyst Preparation.* An acid nickel-molybdenum-modified red mud (ANMoMRM) catalyst with 23.7 wt.% nickel oxide and 5.06 wt.% molybdenum oxide was prepared using a homogeneous precipitation process. Using an unmodified red mud catalyst precursor, 20 wt.% of nickel oxide (also referred to as NiO) was targeted to be loaded in the red mud to enhance dry reforming activity, and 23.7 wt.% of nickel oxide was confirmed by X-ray fluorescence (XRF) analysis. Using the unmodified red mud catalyst precursor, 5 wt.% of molybdenum oxide (also referred to as MoO) was targeted to be loaded in the red mud to enhance dry reforming activity, and 5.06 wt.% of molybdenum oxide was confirmed by XRF analysis. Depending on the catalyst application, nickel oxide can be loaded to a red mud precursor from between about 1 wt.% to about 50 wt.%, and molybdenum oxide, in addition to or alternative to other Group VIB metals, can be loaded to a red mud precursor from between about 1 wt.% to about 50 wt.%.

[0026] First, 10 g of Saudi Arabian red mud from Ma'aden Aluminium Company, based at Ras Al

Khair, Saudi Arabia was modified by dissolving dried, unmodified red mud in 100 mL of deionized water, and then the pH was neutralized using 40.5 mL of 37 wt.% hydrochloric acid. Afterward, 10 g of nickel(II) nitrate hexahydrate was dissolved in 50 mL of ethanol. Then, 0.92 grams of ammonium molybdate tetrahydrate was dissolved in 50 mL of ethanol. The three separate solutions were mixed to form a mixed solution. Next, the mixed solution was filtered, filtered solids were dried in an oven at 105 °C, and then calcined at 600 °C for 4 hours. The final ANMoMRM solid product was ground to have a particle size of less than about 70 μm. The step of drying in an oven can last from about 2 to about 24 hours.

[0027] Other nickel-containing compounds and molybdenum-containing compounds can be used in addition to or alternative to nickel nitrate and ammonium molybdate, including any nickel-containing compounds or molybdenum-containing compounds soluble in ethanol or other organic or inorganic alcohols, or in aqueous ammonia. XRF in embodiments of the present disclosure confirmed the presence of nickel and molybdenum oxide loading in the ANMoMRM. Nickel can be combined with red mud to result in nickel(II) oxide, NiO, in addition to or alternative to nickel(III) oxide, Ni_2O_3. Molybdenum can be combined with red mud to result in (molybdenum dioxide, MoO_2) or Molybdenum(VI) oxide (molybdenum trioxide, MoO_3).

[0028] BET surface area analysis showed unmodified red mud surface area was about 16 m^2/g. BET surface area for acid modified red mud was about 170 m^2/g. BET surface area for acid modified red mud with nickel in addition to or alternative to molybdenum loading is, in some embodiments, between about 50 m^2/g and about 90 m^2/g, for example about 63 m^2/g or about 89 m^2/g.

[0029] *Catalyst testing*. Several tests on red mud catalytic activity and ANMoMRM catalytic activity for dry reforming were experimentally conducted. Saudi Arabian red mud was tested as received as a catalyst support without any modifications, and it was placed in an Avantium Flowrence® catalyst testing reactor to perform dry reforming experiments. The Avantium Flowrence® reactor is a flexible, high-throughput catalyst testing system that was operated using about 0.5 g of catalyst samples. The ANMoMRM catalyst was tested in a micromeritics® PID Eng & Tech brand microactivity reactor designed for catalyst activity and selectivity analysis. The results are compared, for example, in FIGS. 1 and 2. Results show that ANMoMRM catalytic activity for dry reforming is advantageously improved over non-modified red mud catalytic

activity for dry reforming.

[0030] FIG. 1 is a graph showing conversion percentage for CH_4 in a dry reforming process for unmodified red mud used as a catalyst and for ANMoMRM used as a catalyst. Effects of nickel and molybdenum addition to red mud were studied. Experimental conditions in the dry reforming reactor included temperature at about 750 °C, pressure at about 14 bar, and gas hourly space velocity (GHSV) at about 1477 h^{-1}. The test was conducted for 6 hours. Catalysts tolerant at high pressure are favored for dry reforming processes. The feed was 50 mol.% methane and 50 mol.% CO_2 for both catalysts tested. The GHSV was calculated for the mixed feed. 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.

[0031] For dry reforming, the feed composition will include CH_4 and CO_2. In some embodiments for dry reforming, a feed will consist essentially of or consist of CH_4 and CO_2. Based on thermodynamics, the molar ratio of the feed for CH_4 to CO_2 can be about 1:1. However, some other embodiments showed that greater CO_2 concentrations up to 1:1.75 (mole CH_4 to mole CO_2) surprisingly and unexpectedly enhanced H_2 production.

[0032] Methane conversion illustrated in FIG. 1 shows ANMoMRM catalyst outperformed its counterpart, the untreated red mud. Methane conversion by ANMoMRM reached up to about 17%, and remained nearly constant at this level during the experiment's duration. On the other hand, unmodified red mud methane conversion maxed out at about 14%, then deteriorated. Slight conversion activity of unmodified red mud could be attributed to the existence of several transition metals within red mud, and the greater conversion rate of ANMoMRM can be attributed to the addition of nickel and molybdenum, and synergies of the nickel and molybdenum with the existing transition metals in the red mud.

[0033] FIG. 2 is a graph showing mol.% of H_2 out of the total products produced from dry reforming of CH_4 in a dry reforming process for unmodified red mud (RM) used as a catalyst and for ANMoMRM used as a catalyst. Hydrogen production illustrated in FIG. 2 shows that untreated red mud produced low amounts of hydrogen, whereas ANMoMRM catalyst produced up to about 11 mol.% hydrogen. Nickel-molybdenum modification of red mud has enhanced the performance significantly for hydrogen production.

[0034] 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.

[0035] 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 modified red mud catalyst composition, the composition comprising:

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

nickel oxide, the nickel oxide present at between 5 wt.% to 40 wt.% of the modified red mud catalyst composition; and

a Periodic Table Group VIB metal oxide, the Group VIB metal oxide present at between 1 wt.% and 30 wt. % of the modified red mud catalyst composition.

2. The composition according to claim 1, where the Group VIB metal oxide comprises at least one metal selected from the group consisting of: chromium, molybdenum, and tungsten.

3. The composition according to claim 1 or claim 2, further comprising at least one component selected from the group consisting of: Fe_2O_3, Al_2O_3, SiO_2, Na_2O, CaO, and TiO_2.

4. The composition according to any one of claims 1 to 3, where a majority of the particles of the composition have a particle size of less than 70 μm.

5. The composition according to any one of claims 1 to 4, where the nickel oxide is present at between 10 wt.% to 30 wt.% of the modified red mud catalyst composition.

6. The composition according to any one of claims 1 to 4, where the nickel oxide is present at between 15 wt.% to 25 wt.% of the modified red mud catalyst composition.

7. The composition according to any one of claims 1 to 4, where the nickel oxide is present at 23 wt.% of the modified red mud catalyst composition.

8. The composition according to any one of claims 1 to 7, where the Group VIB metal oxide is present at between 1 wt.% to 20 wt.% of the modified red mud catalyst composition.

9. The composition according to any one of claims 1 to 7, where the Group VIB metal oxide is present at between 1 wt.% to 10 wt.% of the modified red mud catalyst composition.

10. The composition according to any one of claims 1 to 7, where the Group VIB metal oxide is present at 5 wt.% of the modified red mud catalyst composition.

11. The composition according to any one of claims 1 to 10, where the Brunauer-Emmett-Teller (BET) surface area of the modified red mud catalyst composition is between 50 m^2/g and 90 m^2/g.

12. The composition according to any one of claims 1 to 11, where the composition includes between 15 wt.% and 30 wt.% Al_2O_3, between 1 wt.% and 5 wt.% CaO, between 10 wt.% and 30 wt.% Fe_2O_3, between 1 wt.% and 5 wt.% Na_2O, between 10 wt.% and 25 wt.% SiO_2, and between 1 wt.% and 10 wt.% TiO_2.

13. A method for producing the modified red mud catalyst composition of claim 1, the method comprising the steps of:

dissolving red mud material produced from an alumina extraction process from bauxite ore in water to produce a red mud solution;

neutralizing the pH of the red mud solution using an acid;

preparing a nickel-containing solution;

preparing a Periodic Table Group VIB metal oxide-containing solution;

mixing the red mud solution, the nickel-containing solution, and the Group VIB metal oxide-containing solution to precipitate the modified red mud catalyst composition; and

calcining the modified red mud catalyst composition.

14. The method according to claim 13, where the Group VIB metal oxide comprises at least one metal selected from the group consisting of: chromium, molybdenum, and tungsten.

15. The method according to claim 13 or claim 14, where the water comprises deionized water.

16. The method according to any one of claims 13 to 15, where the acid comprises hydrochloric acid.

17. The method according to any one of claims 13 to 16, where the nickel-containing solution comprises nickel nitrate dissolved in ethanol.

18. The method according to any one of claims 13 to 17, where the Group VIB metal oxide-containing solution comprises ammonium molybdate dissolved in ethanol.

19. The method according to any one of claims 13 to 18, further comprising filtering the modified red mud catalyst composition and drying the modified red mud catalyst composition before the step of calcining.

20. The method according to claim 19, where the step of drying occurs at 100 °C.

21. The method according to any one of claims 13 to 20, where the step of calcining takes place for 4 hours at between 500 °C to 700 °C.

22. The method according to any one of claims 13 to 20, where the step of calcining takes place for 4 hours at 600 °C.

23. The method according to any one of claims 13 to 22, further comprising the step of grinding the modified red mud catalyst composition to a particle size of less than 70 μm.

24. The method according to any one of claims 13 to 23, where the Brunauer-Emmett-Teller (BET) surface area of the modified red mud catalyst composition is between 50 m^2/g and 90 m^2/g.

25. The method according to any one of claims 13 to 24, where the composition includes between 15 wt.% and 30 wt.% Al_2O_3, between 1 wt.% and 5 wt.% CaO, between 10 wt.% and 30 wt.% Fe_2O_3, between 1 wt.% and 5 wt.% Na_2O, between 10 wt.% and 25 wt.% SiO_2, and between 1 wt.% and 10 wt.% TiO_2.

26. A method for dry reforming over a modified red mud catalyst composition, the method comprising the steps of:

providing a methane feed and carbon dioxide feed to react over the modified red mud catalyst composition at increased temperature and increased pressure to produce synthesis gas comprising H_2 and CO, the composition comprising:

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

nickel oxide, the nickel oxide present at between 5 wt.% to 40 wt.% of the modified red mud catalyst composition; and

a Periodic Table Group VIB metal oxide, the Group VIB metal oxide present at between 1 wt.% and 30 wt. % of the modified red mud catalyst composition.

27. The method according to claim 26, where the Group VIB metal oxide comprises at least one metal selected from the group consisting of: chromium, molybdenum, and tungsten.

28. The method according to claim 26 or claim 27, where the increased temperature is between 500 °C to 1000 °C.

29. The method according to claim 26 or claim 27, where the increased temperature is between 600 °C to 800 °C.

30. The method according to claim 26 or claim 27, where the increased temperature is 750 °C.

31. The method according to any one of claims 26 to 30, where the increased pressure is between 5 bar and 20 bar.

32. The method according to any one of claims 26 to 30, where the increased pressure is between 10 bar and 15 bar.

33. The method according to any one of claims 26 to 30, where the increased pressure is 14 bar.

34. The method according to any one of claims 26 to 33, where the methane conversion rate is at least 14% for at least 6 hours.

35. The method according to any one of claims 26 to 34, where gas hourly space velocity of the methane feed and carbon dioxide feed mixed is between 1000 h^{-1} to 10000 h^{-1}.

36. The method according to any one of claims 26 to 35, 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.

37. The method according to any one of claims 26 to 36, where a majority of the particles of the composition have a particle size of less than 70 μm.

38. The method according to any one of claims 26 to 37, where the nickel oxide is present at between 10 wt.% to 30 wt.% of the modified red mud catalyst composition.

39. The method according to any one of claims 26 to 37, where the nickel oxide is present at between 15 wt.% to 25 wt.% of the modified red mud catalyst composition.

40. The method according to any one of claims 26 to 37, where the nickel oxide is present at 23 wt.% of the modified red mud catalyst composition.

41. The method according to any one of claims 26 to 40, where the Group VIB metal oxide is present at between 1 wt.% to 20 wt.% of the modified red mud catalyst composition.

42. The method according to any one of claims 26 to 40, where the Group VIB metal oxide is present at between 1 wt.% to 10 wt.% of the modified red mud catalyst composition.

43. The method according to any one of claims 26 to 40, where the Group VIB metal oxide is present at 5 wt.% of the modified red mud catalyst composition.

44. The method according to any one of claims 26 to 43, where a molar ratio of the methane feed to the carbon dioxide feed is between 1:1 and 1:1.75.

45. The method according to any one of claims 26 to 44, where produced H_2 is at least 9 mol.% of produced products from the reaction.

46. The method according to any one of claims 26 to 45, where the Brunauer-Emmett-Teller (BET) surface area of the modified red mud catalyst composition is between 50 m^2/g and 90 m^2/g.

47. The method according to any one of claims 26 to 46, where the composition includes between 15 wt.% and 30 wt.% Al_2O_3, between 1 wt.% and 5 wt.% CaO, between 10 wt.% and 30 wt.% Fe_2O_3, between 1 wt.% and 5 wt.% Na_2O, between 10 wt.% and 25 wt.% SiO_2, and between 1 wt.% and 10 wt.% TiO_2.

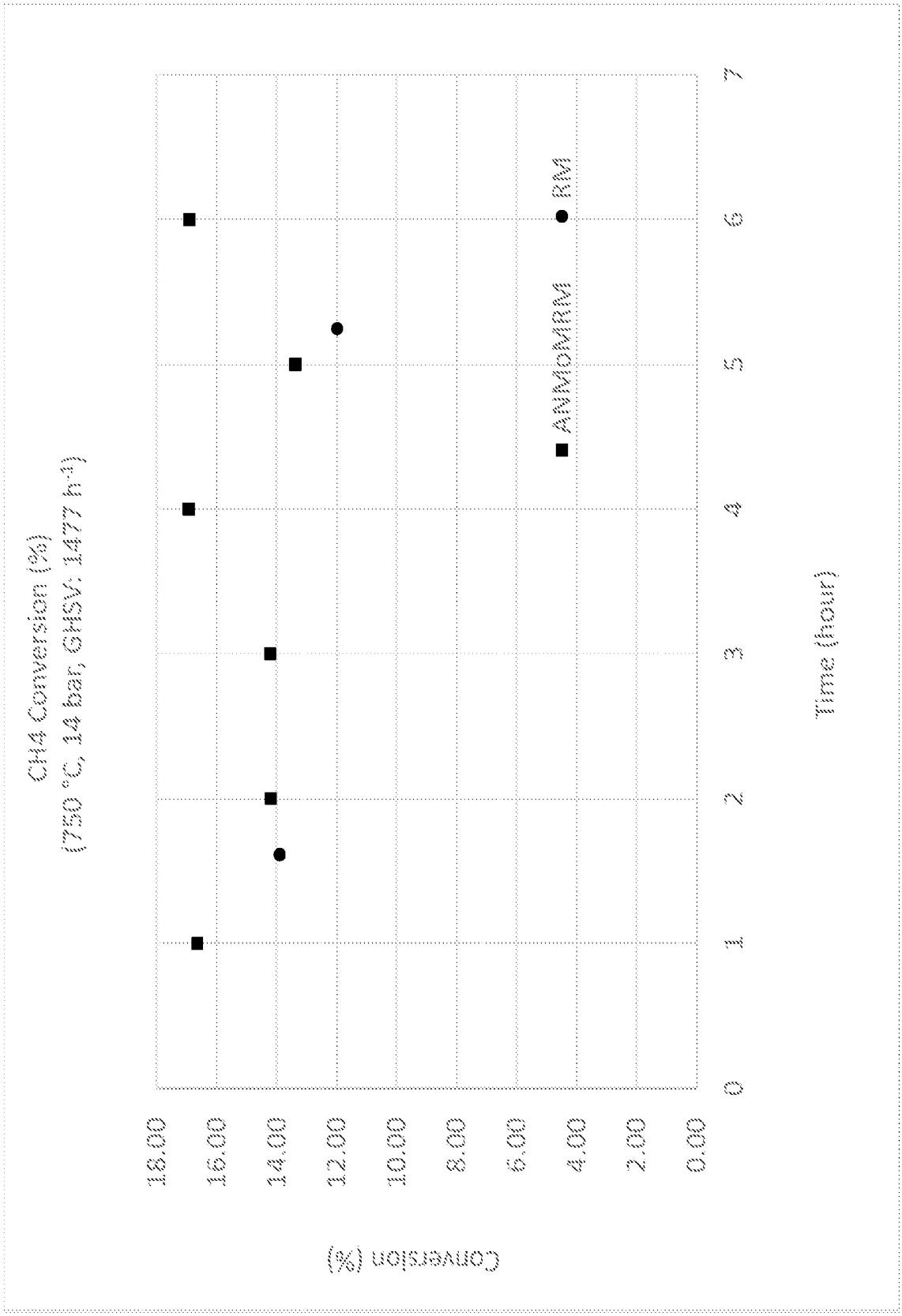

CH4 Conversion (%)
(750 °C, 14 bar, GHSV: 1477 h-1)
Conversion (%)
18.00
16.00
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0
1
2
3
4
5
6
7
Time (hour)
ANMOMRM
RM

FIG. 1

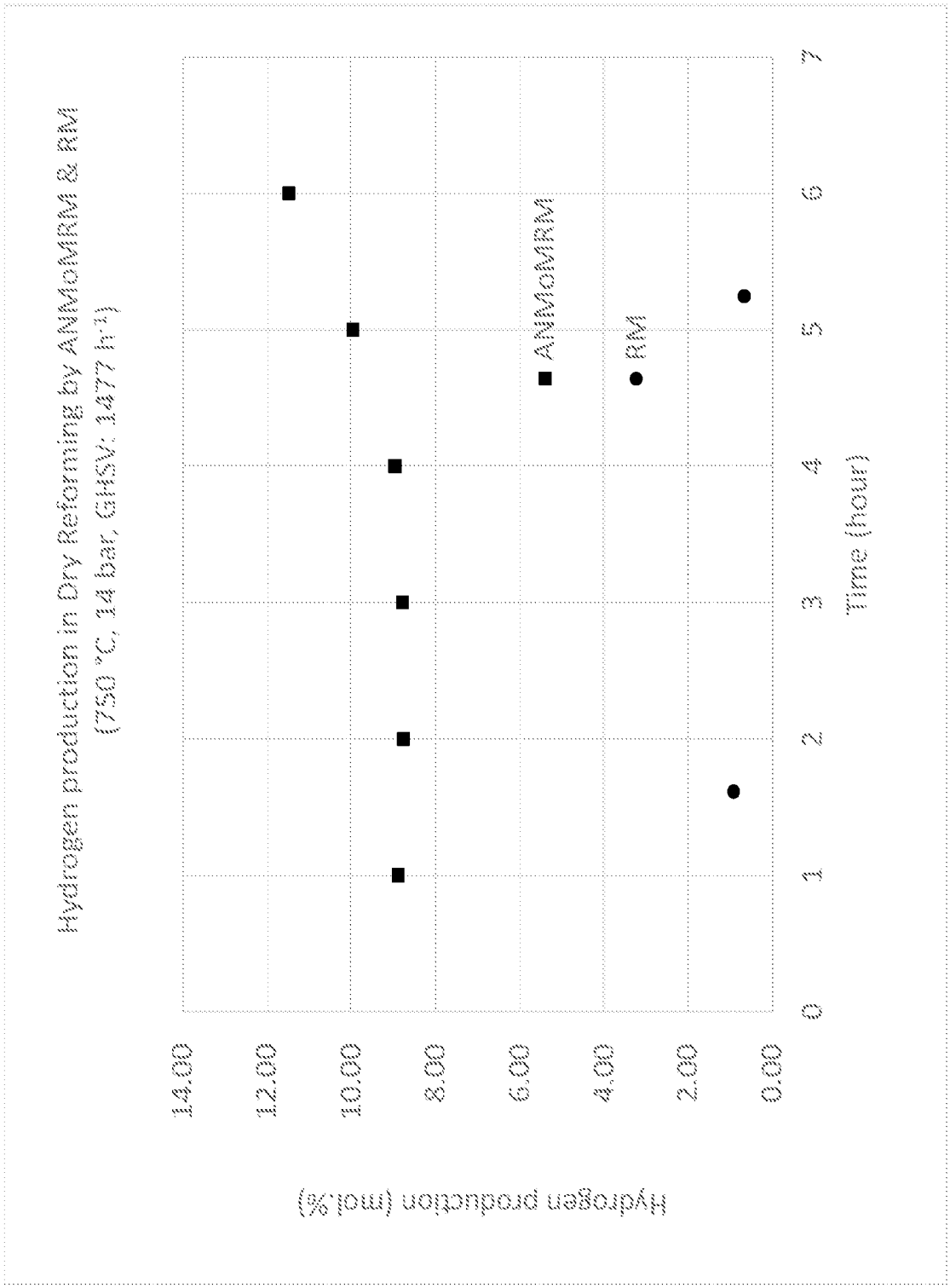

Hydrogen production in Dry Reforming by ANMoMRM & RM
(750 °C, 14 bar, GHSV: 1477 h-1)
Hydrogen production (mol.%)
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0
1
2
3
4
5
6
7
Time (hour)
ANMoMRM
RM

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2021/015303

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/38 B01J23/84 C01B3/40
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)
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)
EPO-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	EBRAHIMINEJAD MITRA ET AL: "Hydrocracking and hydrodesulfurization of diesel over zeolite beta-containing NiMo supported on activated red mud", ADVANCED POWDER TECHNOLOGY, vol. 30, no. 8, 17 May 2019 (2019-05-17), pages 1450-1461, XP085713767, ISSN: 0921-8831, DOI: 10.1016/J.APT.2019.04.021	1-25
A	paragraph [02.2]; figures 1a,1b,4,5,7	26-47
X	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; examples 1,3	1-12

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"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	Date of mailing of the international search report
22 March 2021	30/03/2021

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Cristescu, Ioana

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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 8	1-47
A	US 2019/308183 A1 (AGBLEVOR FOSTER [US] ET AL) 10 October 2019 (2019-10-10) claims 1-7	1-47
A	JAHROMI HOSSEIN ET AL: "Hydrodeoxygenation of Aqueous-Phase Catalytic Pyrolysis Oil to Liquid Hydrocarbons Using Multifunctional Nickel Catalyst", INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, vol. 57, no. 39, 7 September 2018 (2018-09-07), pages 13257-13268, XP055787757, ISSN: 0888-5885, DOI: 10.1021/acs.iecr.8b02807 Retrieved from the Internet: URL:https://pubs.acs.org/doi/pdf/10.1021/acs.iecr.8b02807> paragraph [0003]; table 3	1-47
A	RU 2 542 177 C1 (FEDERAL NOE G BJUDZHETNOE UCHREZHDENIE NATSIONAL NYJ I SKIJ TS KURCHAT) 20 February 2015 (2015-02-20) paragraph [0017] - paragraphs [0018], [0022]; figure 1; table 3	1-47

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2021/015303

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0000285 A1	06-01-2000	NONE	
US 2019308183 A1	10-10-2019	NONE	
RU 2542177 C1	20-02-2015	----------	