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(71) Applicant: **SABIC GLOBAL TECHNOLOGIES B.V.** [NL/NL]; Plasticslaan 1, 4612 PX Bergen op Zoom (NL).

(72) Inventors; and

(71) Applicants *(for US only)*: **MAMEDOV, Edouard** [US/US]; SABIC T&I, 1600 Industrial Blvd., Sugar Land, Texas 77478 (US). **ARAUJO, Armando** [US/US]; SABIC T&I, 1600 Industrial Blvd., Sugar Land, Texas 77478 (US). **CASPER, Michelle** [US/US]; SABIC T&I, 1600 Industrial Blvd., Sugar Land, Texas 77478 (US). **LIANG, Wugeng** [US/US]; SABIC T&I, 1600 Industrial Blvd., Sugar Land, Texas 77478 (US).

(74) Agent: **COLAPRET, Kay Ann**; Norton Rose Fulbright US LLP, 98 San Jacinto Blvd., Suite 1100, Austin, Texas 78701 (US).

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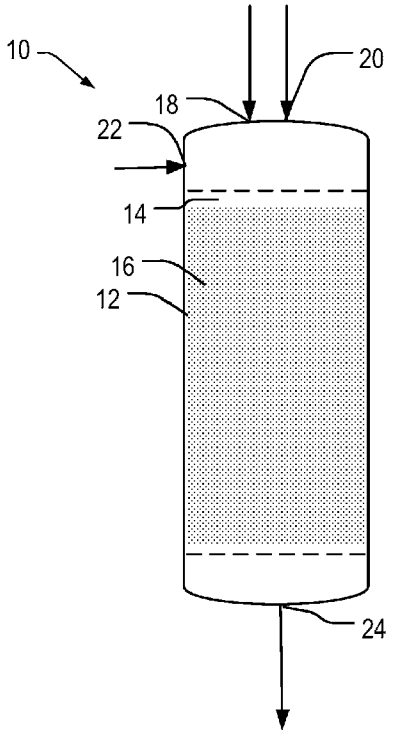

FIG. 1

(57) Abstract: Catalysts and uses thereof in the oxyhalogenation of methane reaction are described. The cerium-lanthanum oxide catalyst has a formula of $Ce_aLa_bO_x$ where $0 < a \leq 100$, $0.5 < b \leq 50$, and x is determined by valence requirements of the cerium and lanthanum. The catalyst has a surface area of at least 30 m^2/g to 100 m^2/g.

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MIXED CERIUM-LANTHANUM OXIDE CATALYSTS AND SYSTEMS FOR OXIDATIVE HALOGENATION OF AN ALKANE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Patent Application No. 62/351,624 filed June 17, 2016, which is hereby incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION

A. Field of the Invention

[0002] The invention generally concerns mixed cerium-lanthanum oxide catalysts and methods to prepare and use the catalysts in the oxidative halogenation of an alkane reaction. The mixed cerium-lanthanum oxide catalysts include $Ce_aLa_bO_x$ where $0 < a \leq 100$, $0.5 < b \leq 50$, and x is determined by valence requirements of the cerium and lanthanum. The $Ce_aLa_bO_x$ catalysts have a surface area of 30 m^2/g to 100 m^2/g.

B. Description of Related Art

[0003] Alkanes can be converted to light olefins via a two-step process, first by oxidative chlorination (oxychlorination) of an alkane, *e.g.*, methane, to an alkyl chloride, *e.g.*, monochloromethane (CH_3Cl). In the second step, the alkyl halide can be converted to light olefins (for example, ethylene, propylene, and/or butylene).

[0004] Monochloromethane can be made through a process termed "oxychlorination." By way of example, an oxychlorination of methane reaction can include feeding methane, natural gas or light hydrocarbon alkanes (*e.g.*, C_1-C_4 alkanes), an oxygen source, and a chlorine source such as hydrogen chloride or chlorine gas to a reactor containing a catalyst. The product stream can include monochloromethane, heavy chlorinated hydrocarbons, and light components (*e.g.*, methane, carbon oxides, and inert gases) as shown in the general reaction scheme below;

$$CH_4 + HCl + O_2 \xrightarrow[\text{inert gas}]{\text{catalyst}} CH_{4-x}Cl_x + H_2O + \text{inert gas, where } x \text{ is 1 to 4.}$$

[0005] Another process to make monochloromethane uses elemental chlorine (Cl_2) as the feed gas. In this process, chlorine, oxygen containing gas, and the hydrocarbon to be chlorinated are contacted with a metal halide catalyst. The chlorine reacts with the hydrocarbon to produce hydrogen chloride and a chlorinated product of the hydrocarbon. Hydrogen chloride produced in this manner is then converted to elemental chlorine by a well-known series of reactions, thereby providing additional chlorine for the chlorination of more hydrocarbon feed.

[0006] Challenges associated with the commercialization of an alkyl halogenation process, especially a methane oxychlorination process, include the development of selective and stable catalysts for the particular alkane. Conventional catalysts for oxidative chlorination of methane to methyl chloride contain copper as a primary catalytic metal. These catalysts suffer from volatilization of the copper salts, which renders the catalysts inactive over time.

[0007] Other conventional catalysts for the oxychlorination of methane include lanthanum and/or cerium based compounds. By way of example, Podkolzin *et al.*, *J. Am. Chem. Soc.* 2007, 129, 2569, describes irreducible lanthanum compounds, such as LaOCl and $LaCl_3$ These catalyst suffer from low methane conversion. He *et al.*, *Angew, Chem. Int. Ed.* 2012, 51, 2438, describes mixed Ce-Fe and Ce-Ni oxides for the catalysis of the methane oxychlorination reaction. These catalysts suffer in that high reaction temperatures are required to give sufficient conversion of methane. Peringer *et al.*, *Topics in Catalysis*, 2009, 52(9), 1220-1231, describes a supported Ce/LaOCl catalyst for oxidative chlorination of methane to methyl chloride doped with nickel to reduce adsorption of methyl chloride on the surface of the catalyst.

[0008] Cerium-lanthanum catalysts are typically prepared by sol-gel or hydrothermal processes. By way of example, Colon *et al.*, *Physical Chemistry Chemical Physics*, 2000, 2(19), 4453-4459, describes a sol-gel preparation of a CeO_2-La_2O_3 catalyst having a relatively low surface area, thereby making the catalyst inefficient for large scale use. Chinese Patent Publication CN 102120183 describes hydrothermally preparing a cerium-lanthanum based catalyst using NaOH as a precipitator. This results in a tri-component catalyst of Ce-La-Na oxide.

[0009] Despite the foregoing, the above-mentioned catalysts suffer from low alkane (*e.g.*, methane) conversion, production of di-, tri-, etc. halide species and/or carbon oxides during the oxyhalogenation reaction, and/or deactivation due to leaching of the catalytic metal.

SUMMARY OF THE INVENTION

[00010] A discovery has been made that provides a solution to the problems associated with producing halogenated alkanes from an alkane containing feed. The solution resides in the production of mixed cerium-lanthanum oxide catalysts having a general formula of $Ce_aLa_bO_x$ and a surface area of 30 m^2/g to 100 m^2/g. In particular instances, the catalysts do not include an active LaOCl phase as described in the literature. Rather, the catalysts have an active CeO_2 phase, an active La solid solution in CeO_2 phase, and/or an active La_2O_3 phase, or any combination thereof. In some preferred aspects, the catalysts can have an active La solid solution in CeO_2 phase (*i.e.*, CeO_2 phase doped with La). Without wishing to be bound by theory, it is believed that catalysts having these structural features can have higher catalytic activity (*e.g.*, higher selectivity for halogenated alkanes) at lower reaction temperatures when compared to currently known catalysts such as those discussed above.

[00011] In one particular aspect of the present invention, there is disclosed a Ce-La oxide catalyst capable of catalyzing an oxidative halogenation of an alkane reaction. The catalyst can have a formula of $Ce_aLa_bO_x$, where $0 < a \leq 100$, $0.5 < b \leq 50$, and x is determined by valence requirements of the cerium and lanthanum. In a particular aspect, a is 1 to 100, b is 1 to 15, and x is 3 to 205. The surface area of the catalyst can be at least 10 m^2/g to 100 m^2/g, preferably from 30 m^2/g to 80 m^2/g, and more preferably from 40 m^2/g to 70 m^2/g. The catalyst can include an active CeO_2 phase and a selective active La_2O_3 phase. In other aspects, the catalyst can have an active and selective La solid solution in CeO_2 phase. In still other aspects, the catalyst can have an active CeO_2 phase, an active and selective La solid solution in CeO_2 phase, and a selective La_2O_3 phase. In even other aspects, the catalyst can have an active and selective La solid solution in CeO_2 phase and a selective La_2O_3 phase. Without wishing to be bound by theory, it is believed that the presence of these phases in the catalyst structure can provide greater catalytic activity performance when compared with a physical mixture of CeO_2 and La_2O_3. In some aspects of the invention, the metal oxide catalyst is a bulk metal oxide catalyst. The molar ratio of La_2O_3 to CeO_2 (La:Ce) in the catalyst can be from $0.005 < \text{La:Ce} \leq 30$, $0.01 < \text{La:Ce} \leq 15$, or $0.02 < \text{La:Ce} \leq 7.5$. The molar ratio of CeO_2 to La_2O_3 (Ce:La) may range from 100:1 to 1:15, 75:1 to 1:10, or 50:1 to

1:7. The catalysts of the present invention can catalyze the production of halogenated alkanes (*e.g.*, monohalogenated alkanes) from alkanes and hydrogen halide at a reaction temperature of less than 500 °C, more preferably 400 °C to 500 °C, and most preferably 400 °C to less than 450 °C. The catalysts can have a monohalogenated alkane selectivity of at least 60%, at least 70%, at least 80%, at least 90%, 60% to 90%, 60% to 80%, or 60 % to 70%.

[00012] Also disclosed is a method of making the mixed cerium-lanthanum oxide catalysts of the present invention. The method can include the steps of precipitating a mixed cerium-lanthanum catalyst precursor from an aqueous solution having a cerium salt and a lanthanum salt (*e.g.*, lanthanum chloride and lanthanum nitrate). In contrast to conventional co-precipitation or hydrothermal procedures, the cerium and lanthanum salts are dissolved, or substantially dissolved, in water and precipitated from the solution as a hydroxide gel. Dissolution of the individual components followed by precipitation as a hydroxide gel allows for the metals to recombine in the same crystal lattice instead of being admixed together. The precipitated material can then be dried at a temperature of 30 °C to 150 °C, 50 °C to 140 °C, 80 °C to 130 °C, or 100 °C to 125 °C. The dried material can then be calcined at a temperature of 550 °C to 800 °C, preferably 550 °C to 750 °C, more preferably from 550 °C to 650 °C, for a sufficient period of time to obtain a catalyst of the present invention.

[00013] In another aspect of the invention, a method for converting an alkane (*e.g.* methane) to an alkyl halide (*e.g.*, monochloromethane) is described. The method can include contacting a catalyst of the present invention with a gaseous feed stream or feed streams that include(s) an alkane or a mixture of alkanes, a hydrogen halide gas (*e.g.*, HCl, HBr, HI or HF), and oxygen gas under conditions sufficient to produce an alkyl halide. The alkane can include C_1 to C_{20} alkanes, more preferably C_1 to C_5 alkanes, and most preferably C_1 to C_3 alkanes. C_1 (*i.e.*, methane) is particularly preferred. Reaction conditions can include a reaction temperature of 300 °C to 550 °C, preferably from 350 °C to 450 °C, and more preferably from 400 °C to 450 °C. The reaction can be operated at atmospheric or elevated pressure. The reaction pressure can be 0.1 MPa to 5 MPa or 0.1 MPa to 1 MPa. The contact time of the reactants with the catalyst may range from 0.1 second to 10 seconds, more preferably from 0.5 to 2 seconds, most preferably from 0.8 to 1.2 seconds. Under reaction conditions of 400 °C to 450 °C, the catalysts of the invention can have a selectivity to monohalogenated species (*e.g.*, monochloromethane) of 20 to 25%, preferably from 50 to

92%, more preferably from 60 to 91%, and most preferably from 70 to 90%. In some embodiments, the reactant feed can be heated to a temperature less than 700 °C, preferably 275 °C to less than 700 °C, more preferably 300 °C to 550 °C, and most preferably 300 °C to 450 °C. When the catalysts of the present invention are contacted with a reactant feed that includes methane gas, oxygen gas, and HCl gas, the monochloromethane selectivity can be at least 80%.

[00014] In another aspect of the invention, a system for performing the oxidative halogenation method is described. The system can include: a first inlet or first set of inlets for providing an alkane feed, an alkyl halide feed, or a feed having a mixture of alkane and alkyl halide; a second inlet for providing hydrogen halide; a third inlet for providing oxygen; a reaction zone that is configured to be in fluid communication with the first, second and third inlets; and an outlet configured to be in fluid communication with the reaction zone to remove the produced alkyl halide from the reaction zone.

[00015] The term "catalyst" means a substance, which alters the rate of a chemical reaction. "Catalytic" means having the properties of a catalyst.

[00016] The term "bulk metal oxide catalyst" as that term is used in the specification and/or claims, means that the catalyst includes at least one metal, and does not require a carrier or a support.

[00017] The phrase "chlorinated hydrocarbons" refers to chlorinated hydrocarbons having a general formula of $CH_{4-x}X_x$, where x is 1 to 4. Non-limiting examples of halogenated hydrocarbons include monochloromethane, dichloromethane, chloroform, and carbon tetrachloride. "di, tri, etc., halogenated hydrocarbons" are defined as $CH_{4-x}X_x$, where x is 2 to 4.

[00018] The term "hydrogen chloride" or "hydrogen halide" refers to the compound made up of hydrogen chloride (HCL) or hydrogen and a halogen anion, and may not be indicative of the phase (*e.g.*, gas or liquid) of the compound. "Hydrochloric acid" refers to aqueous hydrogen chloride.

[00019] The phrase "light components" or "light hydrocarbons" refer to compounds or hydrocarbons that are not condensable at standard temperature and pressure (25 °C and 1

atm). By way of example, hydrocarbons having from 1 to 4 carbon atoms (C_1 to C_4) are considered light hydrocarbons.

[00020] The term "inert" is defined as chemically inactive or substantially inactive under the reaction conditions. Non-limiting examples of inert chemical compounds in the context of this invention include helium, nitrogen, and argon.

[00021] The term "conversion" means the mole fraction (i.e., percent) of a reactant converted to a product or products.

[00022] The term "selectivity" refers to the percent of converted reactant that went to a specified product, for example, monochloromethane selectivity is the % of methane that forms monochloromethane.

[00023] The terms "inhibiting" or "reducing" or "preventing" or "avoiding" or any variation of these terms, when used in the claims and/or the specification includes any measurable decrease or complete inhibition to achieve a desired result.

[00024] The term "substantially" and its variations are defined as being largely but not necessarily wholly what is specified as understood by one of ordinary skill in the art. In one non-limiting embodiment, substantially refers to ranges within 10%, within 5%, within 1%, or within 0.5%.

[00025] The term "effective," as that term is used in the specification and/or claims, means adequate to accomplish a desired, expected, or intended result.

[00026] The use of the words "a" or "an" when used in conjunction with the term "comprising" in the claims or the specification may mean "one," but it is also consistent with the meaning of "one or more," "at least one," and "one or more than one."

[00027] The term "about" or "approximately" are defined as being close to as understood by one of ordinary skill in the art, and in one non-limiting embodiment the terms are defined to be within 10%, preferably within 5%, more preferably within 1%, and most preferably within 0.5%.

[00028] The terms "wt.%" or "vol.%" refers to a weight or volume percentage of a component, respectively, based on the total weight or the total volume of material that

includes the component. In a non-limiting example, 10 grams of component in 100 grams of the material that includes the component is 10 wt.% of component.

[00029] The words "comprising" (and any form of comprising, such as "comprise" and "comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and any form of including, such as "includes" and "include") or "containing" (and any form of containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

[00030] The catalysts of the present invention can "comprise," "consist essentially of," or "consist of" particular ingredients, components, compositions, *etc.* disclosed throughout the specification. With respect to the transitional phase "consisting essentially of," in one non-limiting aspect, a basic and novel characteristic of the catalysts of the present invention are their abilities to catalyze the oxyhalogenation of alkane reaction at temperatures of less than 550 °C.

[00031] Other objects, features and advantages of the present invention will become apparent from the following figures, detailed description, and examples. It should be understood, however, that the figures, detailed description, and examples, while indicating specific embodiments of the invention, are given by way of illustration only and are not meant to be limiting. Additionally, it is contemplated that changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[00032] **FIG. 1** is a schematic of a system for producing halogenated alkanes using the catalysts of the present invention.

[00033] **FIGS. 2A** shows X-ray diffraction (XRD) patterns for catalysts of the present invention and comparative catalysts.

[00034] **FIG. 3** is a graph showing conversion and selectivity data for catalysts of the present invention.

[00035] While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of example in the drawings and may herein be described in detail. The drawings may not be to scale.

DETAILED DESCRIPTION OF THE INVENTION

[00036] The currently available catalysts used in the oxidative halogenation of alkanes reaction require high reaction temperatures (*e.g.*, greater than 550 °C) and have poor yields. Thus, these catalysts require increased energy input and longer reaction runs to yield more product.

[00037] The catalysts of the present invention, by comparison, can be operated at lower reaction temperatures (*e.g.*, less than 550 °C) while maintaining acceptable conversion and selectivity parameters for the oxidative halogenation of alkanes reaction. Without wishing to be bound by theory, it is believed that these lower reaction temperatures and increased conversion and selectivity parameters are obtained by the presence of an active CeO_2 phase, an active and selective La solid solution in CeO_2, and/or a selective La_2O_3 phase in the catalysts of the present invention. Notably, these achievements can be realized without the presence of an active LaOCl phase, which is found in conventional La- or Ce- based catalysts.

[00038] These and other non-limiting aspects of the present invention are described in further detail in the following sections.

A. Catalysts

[00039] The catalysts of the present invention can have a general formula of $Ce_aLa_bO_x$ where $0 < a \leq 100$, $0.5 < b \leq 50$, and x is determined by valence requirements of the cerium and lanthanum. In a preferred embodiment, a is 20 to 100, 20 to 90, 30 to 80, or about 44, b is 0.5 to 2, and x is 30 to 205. In another embodiment, a is 15 to 25, b is 1 to 15, and x is 30 to 55. In yet another embodiment, a is 1 to 100, b is 1 to 15, and x is 3 to 205. In some embodiments, a is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 100, or any range or value there between. In some embodiments, b can be 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1., 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10,

15, 20, 25, 30, 35, 40, 45, 50 or any value or range there between. In certain embodiments, *x* can be 30 to 55, 35 to 50, or 30, 30.5, 31, 31.5, 32, 32.5, 33, 33.5, 34, 34.5, 35, 35.5, 36, 36.5, 37, 37.5, 38, 38.5, 39, 39.5, 40, 40.5, 41, 41.5, 42, 42.5, 43, 43.5, 44, 44.5, 45, 45.5, 46, 46.5, 47, 47.5, 48, 48.5, 49, 49.5, 50, 50.5, 51, 51.5, 52, 52.5, 53, 53.5, 54, 54.5, 55, or any range or value there between. In certain embodiments, the catalysts preferably include an active CeO_2 phase, a selective La_2O_3 phase, and/or an active and selective La solid solution in CeO_2. The phrase "active and selective La solid solution in CeO_2" includes the situation where an La atom(s) has (have) incorporated into a CeO_2 crystal lattice. In a particular embodiment, the catalyst does not include a LaOCl phase. The catalysts of the invention can be characterized by X-ray Diffraction spectra, *e.g.*, such as is shown in FIG. 2A of the Examples. The catalysts can have a surface area of at least 30 m^2/g to 100 m^2/g, 35 m^2/g to 95 m^2/g, 40 m^2/g to 90 m^2/g, 45 m^2/g to 85 m^2/g, 40 m^2/g to 75 m^2/g, or 30 m^2/g, 31 m^2/g, 32 m^2/g, 33 m^2/g, 34 m^2/g, 35 m^2/g, 36 m^2/g, 37 m^2/g, 38 m^2/g, 39 m^2/g, 40 m^2/g, 41 m^2/g, 42 m^2/g, 43 m^2/g, 44 m^2/g, 45 m^2/g, 46 m^2/g, 47 m^2/g, 48 m^2/g, 49 m^2/g, 50 m^2/g, 55 m^2/g, 56 m^2/g, 57 m^2/g, 58 m^2/g, 59 m^2/g, 60 m^2/g, 61 m^2/g, 62 m^2/g, 63 m^2/g, 64 m^2/g, 65 m^2/g, 66 m^2/g, 67 m^2/g, 68 m^2/g, 69 m^2/g, 70 m^2/g, 71 m^2/g, 72 m^2/g, 73 m^2/g, 74 m^2/g, 75 m^2/g, 76 m^2/g, 77 m^2/g, 78 m^2/g, 79 m^2/g, 80 m^2/g, 81 m^2/g, 82 m^2/g, 83 m^2/g, 84 m^2/g, 85 m^2/g, 86 m^2/g, 87 m^2/g, 88 m^2/g, 89 m^2/g, 90 m^2/g, or any range or value there between as determined by Brunauer-Emmett-Teller (BET) nitrogen adsorption technique.

B. Method of Making the Catalysts

[00040] The catalysts of the present invention can be made by processes such as those exemplified in a non-limiting manner in the Examples section. Salts of lanthanum and cerium (*e.g.*, $La(NO_3)_3$ or $LaCl_3$ and $Ce(NO_3)_3$ or $CeCl_3$) can be combined with water (*e.g.*, de-ionized water) to obtain clear solutions. The cerium salt solution can be added to the lanthanum salt solution or *vice versa* to obtain a clear solution containing lanthanum and cerium ions completely, or substantially completely dissolved in the solution. The molar ratio of the salts (for example, $Ce(NO_3)_3$ and $La(NO_3)_3$ can be 2:1 to 30:1, 5:1 to 30:1, 5:1 to 15:1, or 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, 11:1, 12:1, 13:1, 14:1, 15:1, 16:1, 17:1, 18:1, 19:1, 20:1, 21:1, 22:1, 23:1, 24:1, 25:1, 26:1, 27:1, 28:1, 29:1, 30:1, or any range or value there between. The molar ratio of M^1 to M^2 (*e.g.*, Ce:La) can be greater than 1, or 1.5, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, or any value there between. In a particular instance, the Ce:La molar ratio can be 5 to

30, 5 to 15, or 7 to 12. Aqueous base (*e.g.*, ammonium hydroxide) can be added to the solution in an amount effective to precipitate a cerium/lanthanum hydroxide gel from the solution. The pH of the solution can be 9 to 11, 9.5 to 10.5, or 10 to 10.5 after addition of the base. The gel can contain cerium and lanthanum hydroxides. The cerium/lanthanum gel solution can be heated from 30 °C to 90 °C, 35 °C to 85 °C, 40 °C to 80 °C , 45 °C to 75 °C, or 30 °C, 35 °C, 40 °C, 45 °C, 50 °C, 55 °C, 60 °C, 65 °C, 70 °C, 75 °C, 80 °C, 85 °C, 90 °C or any value or range there between with agitation to further the formation of the cerium/lanthanum gel material. In some embodiments, the gel can be separated from the solution using known separation techniques (*e.g.*, centrifugation, filtration, *etc.*). The separated gel can be washed with water (*e.g.*, deionized water) to remove any excess base. Washing and filtering the gel can be repeated as necessary to remove all, or substantially all, of the base from the gel. Residual water can be removed from the gel by heating the solution (*e.g.*, drying the solution) at a temperature from 50 °C to 150 °C, or 75 °C to 120 °C, or 50 °C, 60 °C, 65 °C, 70 °C, 75 °C, 80 °C, 85 °C, 90 °C, 95 °C, 100 °C, 110 °C, 115 °C, 120 °C, 125 °C, 130 °C, 135 °C, 140 °C, 145 °C, 150 °C or any range or value there between for a time period sufficient (*e.g.*, 3 to 24 hours, 8 to 20 hours, or 9 hours) to remove all or a majority of the water to produce a dried powdered material. In some instances, the preferred range is 110 °C to 130 °C. The dried Ce/La material can be calcined by heating the dried material to an average temperature between 400 °C and 800 °C, 500 °C to 700 °C, with 550 °C and 650 °C being preferred, at a rate of about 1 °C per minute and holding at between 550 °C and 650 °C for 3 to 12 hours or 4 to 8 hours in the presence of an oxygen source (*e.g.*, air). In some embodiments, the dried material can be calcined in a step-wise manner. By way of example, the dried material can be calcined in air at 110 °C to 130 °C, or 120 °C for 1 to 8 hours, or 3 hours and at 500 °C to 800 °C, or 550 °C for 8 hours. After calcination, the catalyst may be cooled at a rate of about 1 °C per minute to ambient temperature (about 22 to 27 °C). In a preferred aspect of the invention, the calcining temperature is about 550 °C at 4 to 8 hours.

C. Reactants

[00041] The reactant mixture in the context of the present invention can be a gaseous mixture that includes, but is not limited to, alkane hydrocarbons or mixtures of alkanes and alkyl halides. The alkanes or mixtures of alkanes and alkyl halides can include natural gas, liquefied petroleum gas containing C_1-C_5 hydrocarbons, or C_6 + heavy hydrocarbons (*e.g.*, C_6

to C_{24} hydrocarbons such as diesel fuel, jet fuel, gasoline, tars, kerosene, etc.). In a preferred aspect, the hydrocarbon is a mixture of hydrocarbons that is predominately methane (*e.g.*, natural gas). The hydrogen halide can be in gaseous form, non-limiting examples of which include HCl, HBr, HI, HF, or HAt. The oxygen containing gas used in the present invention can be air, oxygen enriched air, oxygen gas, and can be obtained from various sources. The mole ratio of the alkane to the hydrogen halide can be 0.5:1 to 10:1 or 1:1 to 6:1. The mole ratio of the alkane to oxygen can be 0.5:1 to 30:1, preferably 1:1 to 20:1. The reactant mixture can further contain other gases (*e.g.*, nitrogen, carbon dioxide, *etc.*), provided that these gases do not negatively affect the reaction. Carbon dioxide may be from natural gas, or a waste or recycle gas stream (*e.g.*, from a plant on the same site, like for example from ammonia synthesis) or after recovering the carbon dioxide from a gas stream. In a preferred embodiment, the feed stream further comprises a gaseous diluent such as nitrogen, helium, argon, carbon dioxide, or water, or any combination thereof.

D. Oxidative Halogenation of Alkane Process

[00042] In one particular aspect of the invention, a method of producing a haloalkane such as chloromethane is provided. The method can include converting an alkane, *e.g.*, methane, to an alkyl halide, *e.g.*, monochloromethane, by contacting a catalyst of the present invention with an alkane (gas), a hydrogen halide (gas), and oxygen (gas) under conditions sufficient to produce the alkyl halide. The method conditions can include a temperature of 300 °C to 550 °C, preferably 350 °C to 450 °C, a pressure of 0.1 MPa to 5 MPa or preferably 0.2 MPa to 3 MPa, and/or a contact time of 0.1 to 10 seconds, or 0.5 to 5 seconds. The mole ratio of the alkane to the hydrogen halide can be 0.5 to 10, preferably 1 to 6. The mole ratio of the alkane to oxygen can be 0.5 to 30, preferably 1 to 20. In a preferred embodiment, the mole ratio of gaseous diluent to methane is 0 to 20, preferably from 0 to 10, more preferably from 5 to 7, or from 10 to 15.

[00043] Referring to FIG. 1, a schematic of system 10 for the production of a halogenated alkane such as monochloromethane is depicted. System 10 can include a continuous flow reactor 12 and a reaction zone 14 that includes the catalytic mixed cerium-lanthanum material 16. A reactant stream that includes an alkane (*e.g.*, methane, ethane, butane, propane, *etc.*, preferably methane) can enter the continuous flow reactor 12 *via* the feed inlet 18. A stream containing the hydrogen halide may enter the continuous flow reactor *via* feed inlet 20. An oxygen containing gas (oxidant) can enter the reactor 12 *via* inlet 22. In some aspects of the

invention, methane, oxygen, and/or halogen halide containing gas are fed to the reactor *via* one inlet or a combination of inlets. For example, the hydrogen halide, oxygen, and alkane can be combined into one stream, two streams (e.g., alkane + hydrogen halide as stream 1 and oxygen as stream 2) or can be separated into three individual streams. The reactants can be provided to the continuous flow reactor 12 such that the reactants mix in the reactor to form a reactant mixture prior to contacting the catalytic material 16 in the reaction zone 14. In some instances, the catalytic material can be layered or in beds in the continuous flow reactor 12. The catalytic material can include one or more of the catalytic mixed cerium-lanthanum materials of the present invention. The continuous flow reactor can be a fixed bed reactor or fluidized circulating bed reactor (*e.g.*, an ebullating bed reactor). In some embodiments, any one of the feeds may include a gaseous diluent. The gaseous diluent may be, for example, nitrogen, helium, argon, carbon dioxide, or water, or any combination thereof. When present, the mole ratio of gaseous diluent to alkane (*e.g.*, methane) can be 0:20 0:10, 0:20, 0:19, 0:18, 0:17, 0:16, 0:15, 0:14, 0:13, 0:12, 0:11, 0:10 or any value or range there between.

[00044] Reaction zone 14 and one or more of the reactant feeds can be heated to a temperature of 300 °C to 550 °C, 350 °C to 450 °C, 400 °C to 425 °C, or 300 °C, 310 °C, 320 °C, 330 °C, 340 °C, 350 °C, 360 °C, 370 °C, 380 °C, 390 °C, 400 °C, 410 °C, 420 °C, 430 °C, 440 °C, 450 °C, 460 °C, 470 °C 480 °C, 490 °C, 500 °C, 510 °C, 520 °C, 530 °C, 540 °C, 550 °C or any value or range there between using known heating sources (*e.g.*, heaters, heat exchangers, steam, oil, high temperature circulating fluid, or combinations thereof). Reactor 12 can be operated at atmospheric or elevated pressure. The reaction pressure can be from 0.1 MPa to 1 MPa, 0.2 to 0.8 MPa, 0.15 to 0.75 MPa, or 0.1 MPa, 0.2 MPa, 0.3 MPa, 04 MPa, 0.5 MPa, 0.6 MPa, 0.7 MPa, 0.8 MPa, 0.9 MPa, or 1 MPa or any range or value there between. The gas hourly space velocity (GHSV) of reactor 12 can be 0.5 hr^{-1} to 5 hr^{-1}, preferably 1 hr^{-1} to 4 hr^{-1}, or 2 hr^{-1} to 3 hr^{-1}. Contact of the alkane, oxygen, and the hydrogen halide with the catalytic mixed cerium-lanthanum material 16 of the present invention under these conditions can produce a product stream that includes the monohalogenated alkane. The selectivity of this reaction for monohalogenated alkane can be at least 70%, preferably at least 80%, more preferably at least 85%, or most preferably 90% to 95%. The production of di-, tri- or higher substituted halogenated alkanes and/or carbon oxides can be less than 30%, 10% to 20%, 1 to 10%, or 1% to 5%.

[00045] The product stream can exit the continuous flow reactor 12 *via* product outlet 24 and be transported to a collection zone. In the collection zone, the reaction mixture can be quenched and the monohalogenated alkane can be separated from the heavy halogenated alkanes and acidic water. In the collection zone, the halogenated alkane or halogenated alkane fractions can be separated from the quench stream (*e.g.*, aqueous acid stream) using known separation techniques, for example, distillation, absorption, membrane technology, *etc.*, to produce a monohalogenated alkane product.

[00046] The separated or mixture of products can be used in additional downstream reaction schemes to create additional products such as ethylene and propylene. Examples of other products include chemical products such as methanol production, olefin synthesis (*e.g.*, *via* Fischer-Tropsch reaction), aromatics production, carbonylation of methanol, carbonylation of olefins, the reduction of iron oxide in steel production, *etc.* The method can further include isolating and/or storing the produced gaseous mixture or the separated products.

EXAMPLES

[00047] The present invention will be described in greater detail by way of specific examples. The following examples are offered for illustrative purposes only, and are not intended to limit the invention in any manner. Those of skill in the art will readily recognize a variety of noncritical parameters, which can be changed or modified to yield essentially the same results.

EXAMPLE 1
(Preparation of $Ce_{100}La_1O_{201.5}$)

[00048] A catalyst according to the invention was made by preparing separate solutions of cerium chloride and lanthanum chloride by dissolving $CeCl_3 \cdot 7H_2O$ (44.98 g) and $LaCl_3 \cdot 7H_2O$ (0.46 g), respectively, in de-ionized water (100 mL) at room temperature under stirring. The lanthanum chloride solution was added drop-wise to the cerium chloride solution, and the resulting clear solution was stirred for 20 minutes. Then aqueous ammonium hydroxide solution (45.73 g, 28.0-38.0% NH_3 basis) was added drop-wise to the mixed solution to precipitate lanthanum and cerium hydroxides. The suspension was stirred for 1 hour to ensure complete precipitation, followed by centrifugal separation of gel from supernatant. The gel was washed with water and centrifuged two times to remove residual base. After that, it was dried in air overnight at 75 °C, and step-wise calcined in air at 120 °C

for 3 hours and at 550 °C for 8 hours. The powder material obtained had a nominal elemental composition of $Ce_{100}La_1O_{201.5}$. For testing in catalytic oxychlorination of methane, this material was sized to 18-35 mesh.

EXAMPLE 2
(Preparation of $Ce_{45}La_1O_{91.5}$)

[00049] A catalyst according to the invention was made by preparing separate solutions of cerium chloride and lanthanum chloride by dissolving $CeCl_3 \cdot 7H_2O$ (44.98 g) and $LaCl_3 \cdot 7H_2O$ (0.91 g), respectively, in de-ionized water (100 mL) at room temperature under stirring. The lanthanum chloride solution was added drop-wise to the cerium chloride solution, and the resulting clear solution was stirred for 20 minutes. Then aqueous ammonium hydroxide solution (45.8 g, 28.0-38.0% NH_3 basis) was added drop-wise to the mixed solution to precipitate lanthanum and cerium hydroxides. The suspension was stirred for 1 hour to ensure complete precipitation, followed by centrifugal separation of gel from supernatant. The gel was washed with water and centrifuged two times to remove residual base. After that, it was dried in air overnight at 75 °C, and step-wise calcined in air at 120 °C for 3 hours and at 550 °C for 8 hours. The pale yellow powder material obtained had a nominal elemental composition of $Ce_{45}La_1O_{91.5}$. For testing in catalytic oxychlorination of methane, this material was sized to 18-35 mesh.

EXAMPLE 3A
(Preparation of $Ce_{15}La_1O_{31.5}$)

[00050] A catalyst according to the invention was prepared by adding $La(NO_3)_3 \cdot 6H_2O$ (0.82 g) to 5 ml of de-ionized water to obtain a clear solution of lanthanum nitrate. $Ce(NO_3)_3 \cdot 6H_2O$ (12.4 g) was added to deionized water (15 mL) to obtain a clear solution of cerium nitrate. Cerium nitrate solution was added into the lanthanum nitrate solution, and a clear mixture was obtained. The mixed solution was heated at 80 °C for 2 hours under agitation and then dried overnight in air at 120 °C. The dried material was then calcined in air at 650 °C for 6 hours to give a solid with nominal composition $Ce_{15}La_1O_{31.5}$. The powder obtained was pelletized, crushed and sieved to 18-35 mesh for catalytic testing.

EXAMPLE 3B
(Preparation of $Ce_{15}La_1O_{31.5}$)

[00051] A catalyst according to the invention was made by preparing separate solutions of cerium chloride and lanthanum chloride by dissolving $CeCl_3 \cdot 7H_2O$ (43.9 g) and $LaCl_3 \cdot 7H_2O$

(1.51 g), respectively, in de-ionized water (100 mL) at room temperature under stirring. The lanthanum chloride solution was added drop-wise to the cerium chloride solution, and the resulting clear solution was stirred for 20 minutes. Then aqueous ammonium hydroxide solution (45.8 g, 28.0-38.0% NH_3 basis) was added drop-wise to the mixed solution to precipitate lanthanum and cerium hydroxides. The suspension was stirred for 1 hour to ensure complete precipitation, followed by centrifugal separation of gel from supernatant. The gel was washed with water and centrifuged two times to remove residual base. After that, it was dried in air overnight at 75 °C, and step-wise calcined in air at 120 °C for 3 hours and at 550 °C for 8 hours. The powder material obtained had a nominal elemental composition of $Ce_{15}La_1O_{31.5}$. For testing in catalytic oxychlorination of methane, this material was sized to 18-35 mesh.

EXAMPLE 4
(Preparation of $Ce_{28}La_1O_{57.5}$)

[00052] Separate solutions of cerium chloride and lanthanum chloride were prepared by dissolving respectively $CeCl_3 \cdot 7H_2O$ (43.9 g) and $LaCl_3 \cdot 7H_2O$ (1.51 g) in de-ionized water (100 ml) at room temperature under stirring. The lanthanum chloride solution was added drop-wise to the cerium chloride solution, and the resulting clear solution was stirred for 20 minutes. Then aqueous ammonium hydroxide solution (45.8 g 28.0-38.0% NH_3 basis) was added drop-wise to the mixed solution to precipitate lanthanum and cerium hydroxides. The suspension was stirred for 1 hour to ensure complete precipitation, followed by centrifugal separation of gel from supernatant. The gel was washed with water and centrifuged two times to remove residual base. After that, it was dried in air overnight at 75 °C and step-wise calcined in air at 120 °C for 3 hours and at 550 °C for 8 hours. The powder material obtained had a nominal elemental composition of $Ce_{28}La_1O_{57.5}$. For testing in catalytic oxychlorination of methane, this material was sized to 18-35 mesh in a standard way.

EXAMPLE 5
(Preparation of $Ce_7La_1O_{15.5}$)

[00053] A catalyst according to the invention was made by adding $La(NO_3)_3 \cdot 6H_2O$ (3.3 g) to deionized water (5 mL) to obtain a clear solution lanthanum nitrate. $Ce(NO_3)_3 \cdot 6H_2O$ (23.1 g) was added to deionized water (25 mL) to obtain a clear solution of cerium nitrate. The cerium nitrate solution was added into the lanthanum nitrate solution, and a clear mixture was obtained. The mixture was heated at 80 °C for 2 hours under agitation, dried at 120 °C for overnight, and then calcined in air at 650 °C for 6 hours. The solid material prepared in this

way had a nominal composition $Ce_7La_1O_{15.5}$. For evaluating catalytic behavior, it was ground to powder, pelletized, crushed and sieved to 18-35 mesh.

EXAMPLE 6
(Preparation of $Ce_1La_1O_{3.5}$)

[00054] A catalyst according to the invention was prepared by adding $La(NO_3)_3 \cdot 6H_2O$ (13.0 g) to deionized water (30 mL) to obtain a clear solution of lanthanum nitrate. $Ce(NO_3)_3 \cdot 6H_2O$ (12.9 g) was added to deionized water (30 mL) to obtain a clear solution of cerium nitrate. The cerium nitrate solution was added into lanthanum nitrate solution, and a clear mixed solution was obtained. This mixture was heated at 80 °C for 2 hours under agitation, and then was dried overnight in air at 120 °C. The dried material was calcined in air at 650 °C for 6 hours to give a powder solid of the nominal composition $Ce_1La_1O_{3.5}$. For testing in methane oxychlorination reaction, it was sized to 18-35 mesh.

EXAMPLE 7
(Preparation of $Ce_1La_{15}O_{24.5}$)

[00055] A catalyst of the invention was prepared by adding $La(NO_3)_3 \cdot 6H_2O$ (24.8 g) to deionized water (40 mL) to obtain a clear solution of lanthanum nitrate. $Ce(NO_3)_3 \cdot 6H_2O$ (1.65 g) was added to deionized water (10 mL) to obtain a clear solution of cerium nitrate. The cerium nitrate solution was added into lanthanum nitrate solution to obtain a clear mixed solution. This mixture was heated at 80 °C for 2 hours under agitation, and then was dried overnight in air at 120 °C. The dried material was calcined in air at 650 °C for 6 hours. The powder obtained had the nominal composition $Ce_1La_{15}O_{24.5}$. It was pelletized, crushed and sieved to 18-35 mesh for testing in methane oxychlorination reaction.

EXAMPLE 8
(Comparative Catalyst 1- Preparation of CeO_2)

[00056] A cerium oxide catalyst was prepared by adding $Ce(NO_3)_3 \cdot 6H_2O$ (12.5 g) to deionized water (10 mL) to obtain a clear solution, which was heated at 80 °C for 2 hours under agitation. After that, the solution was dried in air at 120 °C for overnight and then calcined at 650 °C for 6 hours. The product, thus prepared, had nominal composition CeO_2. For testing in methane oxychlorination, it was ground to fine powder, pressed, crushed and sieved to 16-35 mesh.

EXAMPLE 9
(Comparative Catalyst 2- Preparation of $Ce_3Fe_1O_{7.5}$)

[00057] Following the procedure is described in *Angew. Chem. Int. Ed. 2012, 51, 2438.* $Fe(NO_3)_3 \cdot 9H_2O$ (0.52 g) and $Ce(NO_3)_3 \cdot 6H_2O$ (1.73 g) were dissolved in deionized water (10 mL) at room temperature to obtain a clear yellow solution, which was stirred for 2 hours. A NaOH solution (9 M) was added dropwise to the mixed solution of iron and cerium nitrates with continuous stirring to give a brown slurry. This slurry was transferred to a Teflon™-lined stainless steel autoclave and treated hydrothermally at 100 °C for 24 hours without stirring. The product of hydrothermal treatment was recovered by means of centrifugation and washed several times with deionized water and ethanol. Then it was dried overnight at 60 °C and calcined in air at 600 °C for 6 hours. Powdered catalyst prepared in this way had the nominal elemental composition of $Ce_3Fe_1O_{7.5}$ and non-uniform morphology with elements of nanorod structure. For evaluating catalytic behavior, it was pelletized, crushed and sieved to 18-35 mesh.

EXAMPLE 10
(Comparative Catalyst 3-Preparation of La_2O_3)

[00058] Lanthanum nitrate $La(NO_3)_3 \cdot 6H_2O$ (53.1 g) was dissolved at room temperature in deionized water (100 mL) to obtain a clear solution. After stirring for 50 minutes, aqueous ammonium hydroxide solution (39.7 g, 28.0-38.0% NH_3 basis) was added drop-wise to the lanthanum nitrate solution. The resultant suspension was stirred for 1 hour to ensure complete precipitation. The resulting gel was separated from the supernatant by centrifugation for 15 minutes, washed and centrifuged two times with water to remove the residual base. After that, the gel was dried overnight at 75 °C, and calcined in air step-wise at 120 °C for 3 hours and at 550 °C for 8 hours. The white powder obtained was individual lanthanum oxide La_2O_3 according to the XRD analysis. It was pelletized, crushed and sieved to 18-35 mesh for testing in methane oxychlorination reaction.

EXAMPLE 11
(Characterization of Catalysts of the Present Invention)

[00059] **X-ray Diffraction (XRD) Analysis.** XRD analysis of the Ce-La oxide catalysts of the present invention from Examples 1-4, and comparative catalysts CeO_2 and La_2O_3 was performed using a X'Pert Pro MPD Diffractometer manufactured by PANalytic B.V. (The Netherlands). FIG. 2A shows XRD patterns of CeO_2, (top pattern), Catalyst Examples 1, 2, 3A and 4 of the present invention, and La_2O_3 (2nd from bottom pattern), and LaOCl (bottom

pattern) respectively. From the XRD, it was determined that catalyst Example 1 ($Ce_{100}La_1O_{201.5}$), Example 2 ($Ce_{45}La_1O_{91.5}$), Examples 3A and 3B ($Ce_{15}La_1O_{31.5}$), and Example 4 ($Ce_{28}La_1O_{57.5}$) had similar phase compositions, which were different than the phase patterns of LaOCl and La_2O_3. The presence of only CeO_2 lines in catalyst Examples 1, 2, 3A, 3B, 4 and 8 along with their small shift (about 0.1 Θ) to lower 2Θ in La-Ce oxides implied the formation of La solid solution in CeO_2. Thus, $Ce_{100}La_1O_{201.5}$, $Ce_{45}La_1O_{91.5}$, $Ce_{15}La_1O_{31.5}$, and $Ce_{28}La_1O_{57.5}$ catalysts can be considered cerium dioxide doped with lanthanum.

[00060] **Surface Area.** Surface area of some catalysts by using BET nitrogen adsorption technique, which were in m^2/g as follows: Example 2 Catalyst– 40.7; Example 3A Catalyst – 68.3; Example 3B Catalyst– 47.6; Comparative Catalyst 1 – 83.9; Comparative Catalyst 2 – 68.0; Comparative Catalyst 3 – 13.2.

EXAMPLE 12
(Oxychlorination of Methane Reaction)

[00061] Catalysts of the present invention (Examples 1-7) as well as in the Comparative Catalysts 1-3 (Examples 9-11) were tested for methane oxychlorination to methyl chloride in a ½ inch O.D. fixed bed tubular reactor. The tube was made of Hastelloy and coated inside with Dursan® compatible with hydrogen chloride. Catalytic experiments were conducted at atmospheric pressure, temperatures 400 and 450 °C, and feed flow rate 100 ml/min. The feed consisted of 65% CH_4, 10% HCl, 3.1% O_2 and 21.9% N_2. The reactor was loaded with catalyst (1 g) mixed with inert material (2 g, quartz chips). Contact time of the feed with catalyst varied from 0.8 to 1.3 seconds depending on catalyst density. All reactants and reaction products were analyzed on line by gas chromatography. Major reaction products were methyl chloride CH_3Cl, methylene chloride CH_2Cl_2 and carbon oxides, mostly CO. In some experiments, the production of trace amounts of chloroform $CHCl_3$ and carbon tetrachloride was observed. Carbon balance ranged from 98.3 to 99.9%. The results of testing catalysts under the specified conditions are presented in Table 1. Comparative Catalysts 1 and 3 are individual oxides CeO_2 and La_2O_3. Upon comparison of the results, La_2O_3 and CeO_2 were less effective in terms of production of target methyl chloride CH_3Cl than the catalysts of the present invention. Examples 2-8 are mixed Ce-La oxides of different composition prepared from metal nitrates as well as from metal chlorides. Catalytic behavior of mixed Ce-La oxides was dependent on their elemental composition. Cerium-enriched

oxides $Ce_{100}La_1O_{201.5}$ (Example 1), $Ce_{45}La_1O_{91.5}$ (Example 2), $Ce_{15}La_1O_{31.5}$ (Example 3A), and $Ce_{28}La_1O_{57.5}$ (Example 4) were determined to be the most effective Ce-La oxide compositions in terms of catalyzing methane oxyclorination to methyl chloride. The selectivity to methyl chloride over these catalysts at 450 °C ranged from 80 to 88% at methane conversion around 7%. The $Ce_{15}La_1O_{31.5}$, $Ce_{28}La_1O_{57.5}$, $Ce_{45}La_1O_{91.5}$ and $Ce_{100}La_1O_{201.5}$ catalysts provided also considerably higher selectivity to methyl chloride than the $Ce_3Fe_1O_{7.5}$ catalyst of Comparative Catalyst 2 reported in the literature to be the best combination of cerium dioxide with oxide of transition metal. Methane conversion on the catalysts under comparison were close.

TABLE 1

Example number	Catalyst composition	Precursor Salt	Contact time (s)	Temp. (°C)	CH_4 Conv. (%)	Selectivity (%) CH_3Cl, CH_2Cl_2, CO_x
1	$Ce_{100}La_1O_{201.5}$	Chloride	0.8	400 450	2.6 7.0	91.0, 3.2, 5.6 85.5, 5.8, 9.0
2	$Ce_{45}La_1O_{91.5}$	Chloride	0.8	400 450	2.9 6.8	90.9, 3.0, 5.8 88.4, 5.8, 5.6
3A	$Ce_{15}La_1O_{31.5}$	Nitrate	1.2	400 450	3.3 7.2	72.8, 3.1, 20.3 80.4, 7.2, 10.6
3B	$Ce_{15}La_1O_{31.5}$	Chloride	1.2	400 450	3.2 6.5	72.9, 3.7, 20.7 80.4, 8.8, 9.9
4	$Ce_{28}La_1O_{57.}$	Chloride	1.3	400 450	3.2 6.7	72.9, 3.1, 20.5 82.4, 8.0, 9.0
5	$Ce_7La_1O_{15.5}$	Chloride	1.1	400 450	2.2 4.7	58.9, 1.4, 35.8 74.3, 4.7, 19.2
6	$Ce_1La_1O_{3.5}$	Nitrate	1.3	400 450	1.5 2.5	27.5, 0.3, 69.1 62.8, 2.1, 32.6
7	$Ce_1La_{15}O_{24.5}$	Nitrate	1.3	400 450	0.7 1.3	22.5, 0.1, 75.0 56.5, 1.0, 40.7
8	CeO_2 (Comparative)	Nitrate	0.9	400 450	4.5 8.2	79.4, 5.3, 14.4 68.1, 6.6, 23.3
9	$Ce_3Fe_1O_{7.5}$ (Comparative)	Nitrate	0.9	400 450	3.7 7.8	69.8, 3.5, 25.0 72.3, 7.5, 20.5
10	La_2O_3 (Comparative)	Nitrate	1.0	400 450	0.5 2.6	76.3, 0.7, 19.9 88.8, 3.3, 6.8

EXAMPLE 13
(Oxychlorination of Methane Reaction With Increased Oxygen Concentration)

[00062] $Ce_{15}La_1O_{31.5}$ catalyst was evaluated at a higher oxygen concentration in the feed. The reactor from Example 12 was charged with Example 3 catalyst ($Ce_{15}La_1O_{31.5}$, 1 g) mixed with inert material (2 g, quartz chips). The stoichiometric feed included 20% CH_4, 20% HCl,

8.4% O_2 and 51.6% N_2. This feed was provided at a continuous flow rate of 50 ml/min to the reactor, which was heated to 420 °C. The results of the continuous reaction are shown in FIG. 3. In FIG. 3, the methane conversion is shown by circular moniker data points denoted as circles (bottom line), and the monochloromethane selectivity is shown by the triangular moniker data points denoted as (top line). As shown in FIG. 3, with increasing time on stream from 2 to 10 hours, methane conversion slightly increased from 12.5 to 13% and then stayed unchanged at times on stream of up to 30 hours. Selectivity to methyl chloride decreased by 5% in the beginning of run to level off at 70% yielding 9.1% of methyl chloride. Major by-products were methylene chloride and carbon monoxide produced with selectivities 13% and 15%, respectively.

CLAIMS

1. A catalyst capable of catalyzing an oxidative halogenation of an alkane reaction, the catalyst having a formula of:

$$Ce_aLa_bO_x$$

where $0 < a \leq 100$, $0.5 < b \leq 50$, and x is determined by valence requirements of the cerium and lanthanum,

wherein the catalyst has a surface area of at least 30 m^2/g to 100 m^2/g, and

wherein the catalyst is capable of catalyzing an oxidative halogenation of an alkane reaction.

2. The catalyst of claim 1, wherein *a* is 1 to 100, *b* is 1 to 15, and *x* is 3 to 205.

3. The catalyst of any one of claims 1 to 2, wherein the catalyst comprises an active CeO_2 phase, an active and selective La solid solution in CeO_2 phase, a selective La_2O_3 phase, or any combination thereof.

4. The catalyst of any one of claims 1 to 3, wherein the catalyst does not include a LaOCl phase.

5. The catalyst of any one of claims 1 to 4, characterized by the X-ray Diffraction patterns of FIG. 2.

6. A method for converting an alkane to an alkyl halide, the method comprising contacting a gaseous feed stream comprising the alkane with a hydrogen halide and oxygen in the presence of a mixed cerium-lanthanum oxide catalytic material of any one of claims 1 to 5 under conditions sufficient to produce the alkyl halide.

7. The method of claim 6, wherein the alkane is methane and the hydrogen halide is hydrogen chloride, and wherein methyl chloride is produced.

8. The method according to any one of claims 6 to 7, wherein the conditions comprise a temperature of 300 °C to 550 °C, preferably 350 °C to 450 °C, a pressure of 0.1 MPa to 5 MPa or preferably 0.1 MPa to 1 MPa, and/or a contact time of 0.1 to 10 seconds, or 0.5 to 5 seconds.

9. The method of any one of claims 6 to 8, wherein the mole ratio of the alkane to the hydrogen halide is 0.5 to 10, preferably 1 to 6, and/or the mole ratio of the alkane to oxygen is 0.5 to 30, preferably 1 to 20.

10. The method of any one of claims 6 to 9, wherein the feed stream further comprises a gaseous diluent.

11. The method of claim 10, wherein the gaseous diluent is nitrogen, helium, argon, carbon dioxide, or water, or any combination thereof.

12. The method of any one of claims 10 to 11, wherein the mole ratio of gaseous diluent to methane is 0 to 20, preferably from 0 to 10.

13. A system for performing the method of any one of claims 6 to 12, comprising:

a first inlet or first set of inlets for providing an alkane feed and an alkyl halide feed or a feed having a mixture of alkane and alkyl halide;

a second inlet for providing hydrogen halide;

a third inlet for providing oxygen;

a reaction zone that is configured to be in fluid communication with the first, second and third inlets; and

an outlet configured to be in fluid communication with the reaction zone to remove produced alkyl halide from the reaction zone.

14. The system of claim 13, further comprising an aqueous quench zone in fluid communication with the outlet, the collection zone configured to quench the reaction mixture and separate the alkyl halide product stream from the hydrogen halide.

15. A method of making a mixed cerium-lanthanum oxide catalyst of any of claims 1 to 5, the method comprising:

(a) precipitating a mixed cerium-lanthanum catalyst precursor from an aqueous solution comprising a cerium salt, a lanthanum salt;

(b) separating the mixed cerium-lanthanum catalyst precursor from the solution; and

(c) forming the cerium-lanthanum oxide catalyst by:

(i) drying the mixed cerium-lanthanum oxide catalyst precursor at a temperature of 30 °C to 150 °C, preferably 110 °C to 130 °C; and

(ii) calcining the dried mixed cerium-lanthanum oxide catalyst precursor at a temperature of 500 °C to 800 °C, preferably 550 °C to 650 °C, to form the mixed cerium-lanthanum oxide catalyst.

16. The method of claim 15, wherein step (a) further comprises heating the solution comprising the cerium salt and the lanthanum salt at 30 °C to 80 °C to facilitate their interaction.

17. The method of any one of claims 15 or 16, further comprising adding hydroxide source to the solution comprising the cerium salt and the lanthanum salt, preferably ammonium hydroxide.

18. The method of any one of claims 15 to 17, wherein the mixed cerium-lanthanum oxide catalyst comprises an active CeO_2 phase, an active and selective La solid solution in CeO_2 phase, and/or a selective La_2O_3 phase.

19. The method of any one of claims 15 to 18, wherein the cerium salt is cerium chloride or cerium nitrate, or a combination thereof.

20. The method of any one of claims 15 to 19, wherein the lanthanum salt is lanthanum chloride or lanthanum nitrate, or a combination thereof.

AMENDED CLAIMS
received by the International Bureau on 07 September 2017 (07.09.2017)

1. A catalyst capable of catalyzing an oxidative halogenation of an alkane reaction, the catalyst having a formula of:

$$Ce_aLa_bO_x$$

where $0 < a \leq 100$, $0.5 < b \leq 50$, and x is determined by valence requirements of the cerium and lanthanum,

wherein the catalyst has a surface area of at least 30 m^2/g to 100 m^2/g, and

wherein the catalyst is capable of catalyzing an oxidative halogenation of an alkane reaction.

2. The catalyst of claim 1, wherein a is 1 to 100, b is 1 to 15, and x is 3 to 205.

3. The catalyst of claim 1, wherein the catalyst comprises an active CeO_2 phase, an active and selective La solid solution in CeO_2 phase, a selective La_2O_3 phase, or any combination thereof.

4. The catalyst of claim 1, wherein the catalyst does not include a LaOCl phase.

5. The catalyst of claim 1, characterized by the X-ray Diffraction patterns of FIG. 2.

6. A method for converting an alkane to an alkyl halide, the method comprising contacting a gaseous feed stream comprising the alkane with a hydrogen halide and oxygen in the presence of a mixed cerium-lanthanum oxide catalytic material of claim 1, under conditions sufficient to produce the alkyl halide.

7. The method of claim 6, wherein the alkane is methane and the hydrogen halide is hydrogen chloride, and wherein methyl chloride is produced.

8. The method of claim 6, wherein the conditions comprise a temperature of 300 °C to 550 °C, a pressure of 0.1 MPa to 5 MPa, a contact time of 0.1 to 10 seconds, or combinations thereof.

9. The method of claim 6, wherein the mole ratio of the alkane to the hydrogen halide is 0.5 to 10, the mole ratio of the alkane to oxygen is 0.5 to 30, or combinations thereof.

10. The method of claim 6, wherein the feed stream further comprises a gaseous diluent.

11. The method of claim 10, wherein the gaseous diluent is nitrogen, helium, argon, carbon dioxide, or water, or any combination thereof.

12. The method of claim 10, wherein the mole ratio of gaseous diluent to methane is 0 to 20.

13. A system for performing the method of claim 6, comprising:

a first inlet or first set of inlets for providing an alkane feed and an alkyl halide feed or a feed having a mixture of alkane and alkyl halide;

a second inlet for providing hydrogen halide;

a third inlet for providing oxygen;

a reaction zone that is configured to be in fluid communication with the first, second and third inlets; and

an outlet configured to be in fluid communication with the reaction zone to remove produced alkyl halide from the reaction zone.

14. The system of claim 13, further comprising an aqueous quench zone in fluid communication with the outlet, the collection zone configured to quench the reaction mixture and separate the alkyl halide product stream from the hydrogen halide.

15. A method of making a mixed cerium-lanthanum oxide catalyst claim 1, the method comprising:

(a) precipitating a mixed cerium-lanthanum catalyst precursor from an aqueous solution comprising a cerium salt and a lanthanum salt;

(b) separating the mixed cerium-lanthanum catalyst precursor from the solution; and

(c) forming the cerium-lanthanum oxide catalyst by:

(i) drying the mixed cerium-lanthanum oxide catalyst precursor at a temperature of 30 °C to 150 °C; and

(ii) calcining the dried mixed cerium-lanthanum oxide catalyst precursor at a temperature of 500 °C to 800 °C, to form the mixed cerium-lanthanum oxide catalyst.

16. The method of claim 15, wherein step (a) further comprises heating the solution comprising the cerium salt and the lanthanum salt at 30 °C to 80 °C to facilitate their interaction.

17. The method of claim 15, further comprising adding hydroxide source to the solution comprising the cerium salt and the lanthanum salt.

18. The method of claim 15, wherein the mixed cerium-lanthanum oxide catalyst comprises an active CeO_2 phase, an active and selective La solid solution in CeO_2 phase, and/or a selective La_2O_3 phase.

19. The method of claim 15, wherein the cerium salt is cerium chloride or cerium nitrate, or a combination thereof.

20. The method of claim 15, wherein the lanthanum salt is lanthanum chloride or lanthanum nitrate, or a combination thereof.

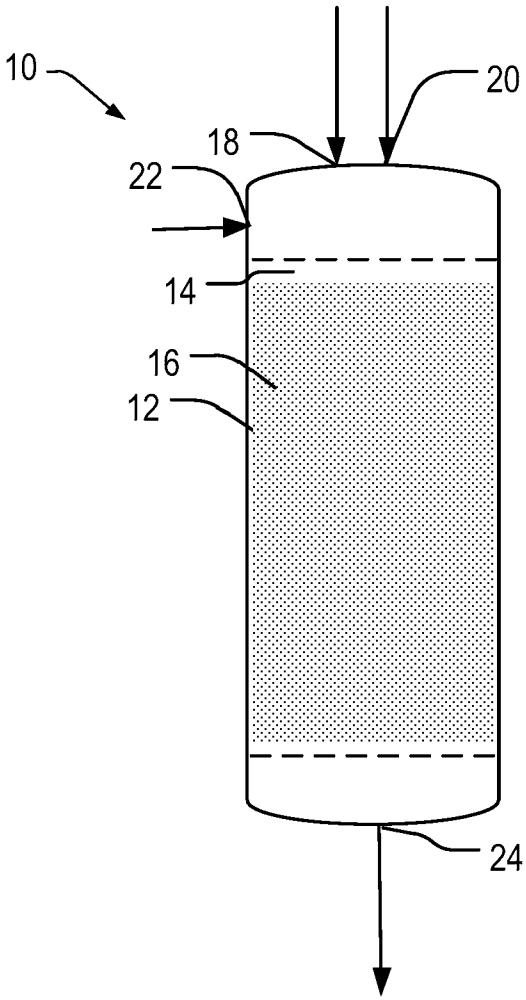

FIG. 1

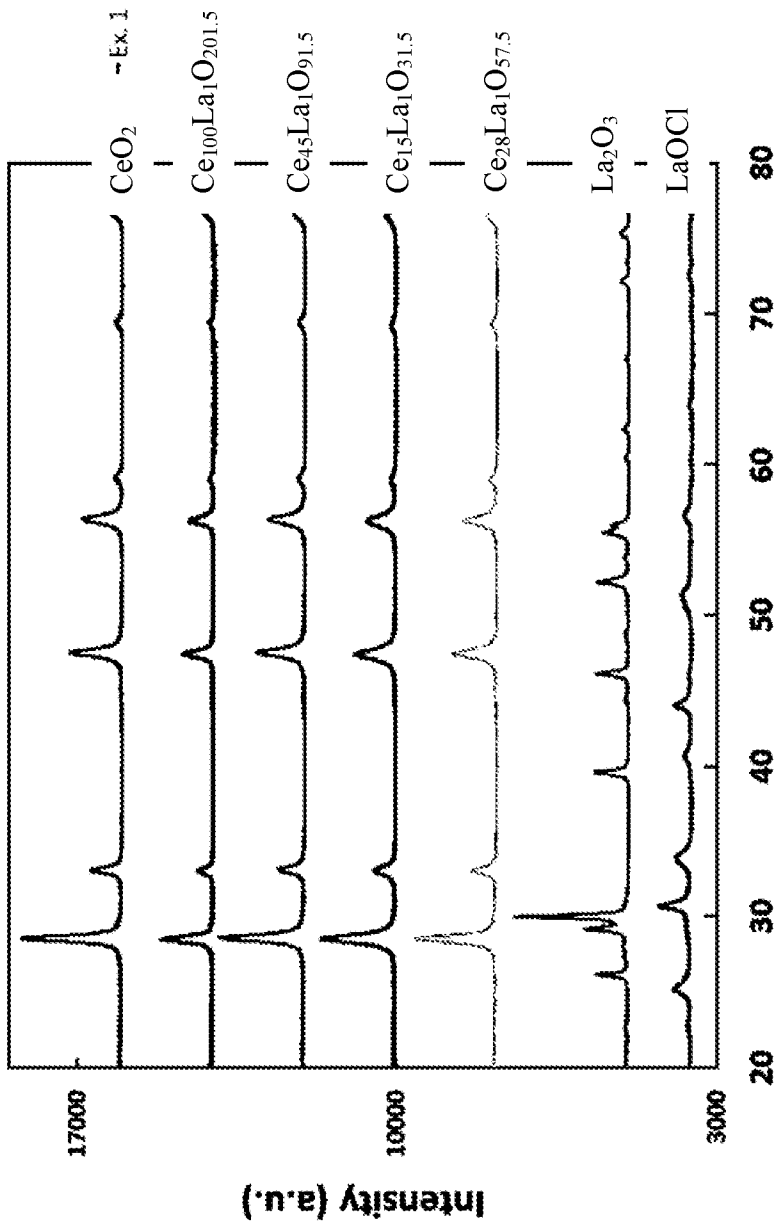
Intensity (a.u.)
17000
10000
3000
20
30
40
50
60
70
80
2θ(°)
Ex. 1
CeO2
Ce100La1O201.5
Ce45La1O91.5
Ce15La1O31.5
Ce28La1O57.5
La2O3
LaOCl

FIG. 2

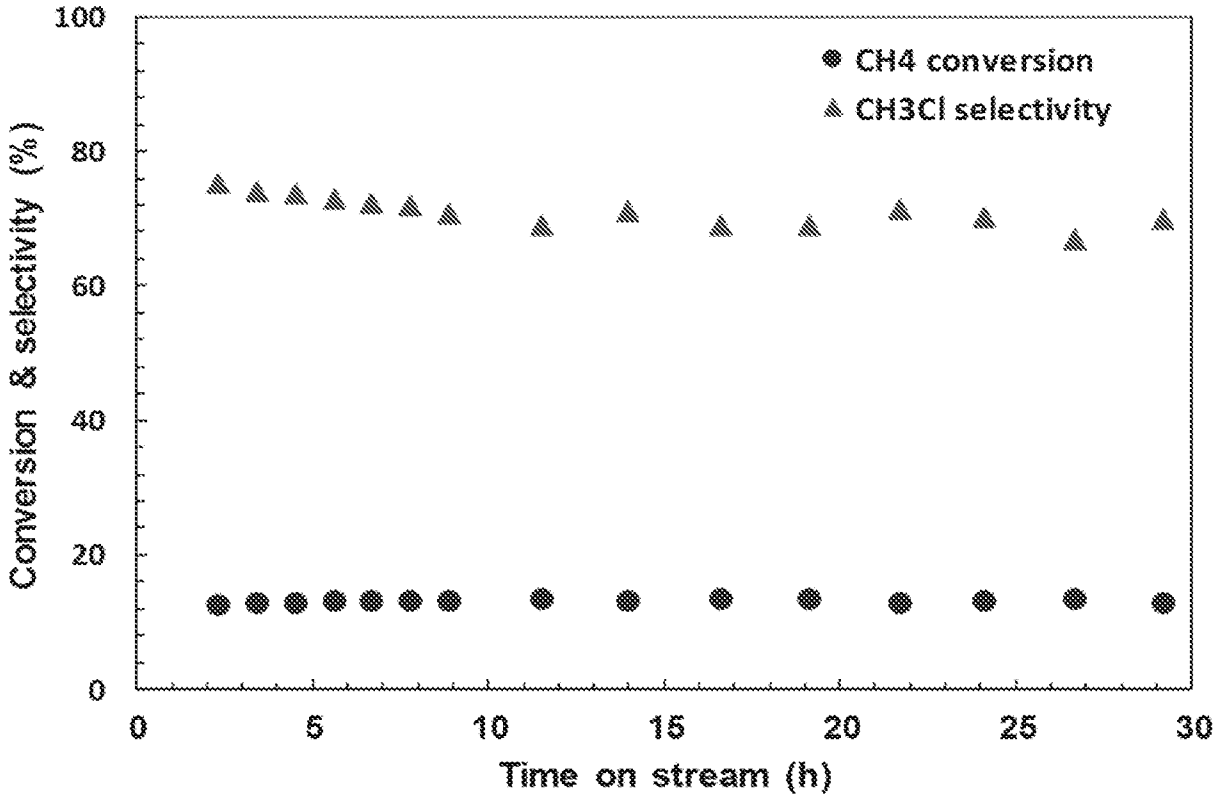
100
80
60
40
20
0
Conversion & selectivity (%)
0
5
10
15
20
25
30
Time on stream (h)
CH4 conversion
CH3Cl selectivity

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2017/052524

A. CLASSIFICATION OF SUBJECT MATTER

B01J 23/10(2006.01)i, B01J 35/00(2006.01)i, B01J 35/10(2006.01)i, C07C 17/07(2006.01)i, B01J 37/00(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)
B01J 23/10; C07C 17/15; B01J 35/00; B01J 35/10; C07C 17/07; B01J 37/00

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: catalyst, oxidative halogenation of alkane, CeaLabOx, ceria, lanthana, cerium, lanthanum, cerium lanthanum oxide, surface area, active CeO2 phase, La solid solution, La2O3 phase

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004-0158110 A1 (SCHWEIZER, ALBERT E. et al.) 12 August 2004 See claims 1-32.	1-3
A	FERREIRA, VICTOR J. et al., "Ce-Doped La2O3 based catalyst for the oxidative coupling of methane," Catalysis Communications, 2013, vol. 42, pages 50-53 See abstract; and pages 50, 51.	1-3
A	CN 102120183 A (GRADUATE SCHOOL OF THE CHINESE ACADEMY OF SCIENCES) 13 July 2011 See claims 1-4.	1-3
A	COLON, G. et al., "CeO2 catalytic system La2O3. Part I. Preparation and characterisation of catalysts," Physical Chemistry Chemical Physics, 2000, vol. 2, no. 19, pages 4453-4459 See abstract; and pages 4453, 4454.	1-3
A	FARRA, RAMZI et al., "Promoted ceria: A structural, catalytic, and computational study," ACS Catalysis, 2013, vol. 3, no. 10, pages 2256-2268 See abstract; and pages 2256-2258.	1-3

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

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 July 2017 (24.07.2017)	**01 August 2017 (01.08.2017)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea
Facsimile No. +82-42-481-8578

Authorized officer
KIM, Seung Beom
Telephone No. +82-42-481-3371

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2017/052524

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 7,11,14,16
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 7, 11, 14 and 16 refer to one of unsearchable claims which do not comply with PCT Rule 6.4(a).

3. ☒ Claims Nos.: 4-6,8-10,12,13,15,17-20
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/IB2017/052524

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004-0158110 A1	12/08/2004	AR 033909 A1	07/01/2004
		BR 0210049 A	17/08/2004
		CA 2448500 A1	28/11/2002
		CA 2448500 C	17/11/2009
		CN 100424056 C	08/10/2008
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		EP 1397330 A1	17/03/2004
		JP 2004-528386 A	16/09/2004
		JP 4275952 B2	10/06/2009
		KR 10-0886284 B1	04/03/2009
		KR 10-2004-0002987 A	07/01/2004
		RU 2003136824 A	10/04/2005
		RU 2284984 C2	10/10/2006
		US 6984763 B2	10/01/2006
		WO 02-094750 A1	28/11/2002
CN 102120183 A	13/07/2011	None	