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(54) **Title:** CERAMIC CATALYST, METHOD OF PRODUCTION AND USES THEREOF

(57) **Abstract:** The present disclosure provides a catalyst and method for obtaining the same. The catalyst comprises α1-Al_2O_3 associated with cobalt oxide including at least Co^{2+} and Co^{3+} oxidation states. The method comprises impregnating α-Al_2O_3 with an aqueous solution comprising Co^{2+} to form impregnated α-Al_2O_3; and subjecting said impregnated α-Al_2O_3 to thermal treatment causing formation of cobalt oxide. Also disclosed is a process for hydrogen generation, the process comprises contacting a catalyst comprising α-Al_2O_3 associated with cobalt oxide including at least Co^{2+} and Co^{3+} oxidation states with a solution comprising borohydride compound and proton donor solvent.

CERAMIC CATALYST, METHOD OF PRODUCTION AND USES THEREOF

TECHNOLOGICAL FIELD

The present disclosure relates to chemical catalysts.

BACKGROUND ART

References considered to be relevant as background to the presently disclosed subject matter are listed below:

- L. Wei, X. Dong, M. Ma, Y. Lu, D. Wang, S. Zhang, D. Zhao, Q. Wang. (2017). Co_3O_4 hollow fiber: an efficient catalyst precursor for hydrolysis of sodium borohydride to generate hydrogen. International Journal of Hydrogen Energy.
- T. Hung, H. Kuo, C. Tsai, H. Chen, R. Liu, B. Weng, J. Lee. (2011). An alternative cobalt oxide-supported platinum catalyst for efficient hydrolysis of sodium borohydride. Journal of Materials Chemistry(21), 11754-11759.
- Y. Huang, K. Wang, L. Cui, W. Zhu, A. M. Asiri, X. Sun. (2016). Effective hydrolysis of sodium borohydride driven by self-supported cobalt oxide nanorod array for on-demand hydrogen generation. Catalysis Communications, 87, 94-97.
- Korean Patent Application publication No. 101336975
- US patent application publication No. 20070004582

Acknowledgement of the above references herein is not to be inferred as meaning that these are in any way relevant to the patentability of the presently disclosed subject matter.

BACKGROUND

Although hydrogen has great potential as a clean and renewable energy source, its practical use as a fuel for transportation and power generation hinges on the development

of safe and efficient methods for storage, distribution, and controlled release. One way to store hydrogen is by using borohydride compounds (e.g., KBH_4, $NaBH_4$), which can release hydrogen upon demand through a chemical reaction.

For example, the dehydrogenation reaction of potassium borohydride dissolved in water is illustrated by the equation below:

$$KBH_4 + 2H_2O \rightarrow 4H_2 + KBO_2$$

Borohydride compounds are stable and can store a high density of hydrogen, making these compounds attractive candidates for hydrogen storage.

Catalysts can improve the kinetics of borohydride dehydrogenation. Several types of catalysts have been explored for borohydride dehydrogenation, including noble metals (e.g., platinum (Pt) and palladium (Pd)) and non-noble metals (e.g., nickel (Ni) and cobalt (Co)).

L. Wei et al. describe the development of a catalyst for sodium borohydride hydrolysis to generate hydrogen. The catalyst precursor was a Co_3O_4 hollow fiber composed of a nanoparticles array, prepared by combustion method with a template of cotton absorbent. Cobalt oxide is reduced by $NaBH_4$, and the resulting active Co_xB compounds further catalyze the hydrolysis of $NaBH_4$ to generate hydrogen.

T. Hung et al, describe a Pt/Co_3O_4 catalyst for hydrogen generation in a sodium borohydride system.

Y. Huang et al, describe self-supported cobalt oxide nanorod arrays on a Ti sheet (Co_3O_4 NA/Ti) that can drive the dehydrogenation of $NaBH_4$ in alkaline solutions.

KR101336975 describes a catalyst for manufacturing alkylamine from reductive amination.

US20070004582 describes metal oxide catalyst for hydrogen generation and method of producing the same.

GENERAL DESCRIPTION

The present disclosure provides, in accordance with its first aspect, a catalyst comprising α-Al_2O_3 associated with cobalt oxide, including at least Co^{2+} and Co^{3+} oxidation states.

In accordance with a second aspect of the presently disclosed subject matter, there is provided a method of preparing a catalyst, the method comprises

impregnating α-Al_2O_3 with an aqueous solution comprising Co^{2+} to form impregnated α-Al_2O_3; and

subjecting said impregnated α-Al_2O_3 to thermal treatment causing formation of cobalt oxide.

In accordance with a third aspect of the presently disclosed subject matter, there is provided a catalyst, obtained or obtainable by the method of the presently disclosed second aspect.

Yet, in accordance with a fourth aspect of the presently disclosed subject matter, there is provided a process for hydrogen generation, the process comprises contacting a catalyst comprising α-Al_2O_3 associated with cobalt oxide including at least Co^{2+} and Co^{3+} oxidation states with a solution comprising borohydride compound and proton donor solvent.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to better understand the subject matter that is disclosed herein and to exemplify how it may be carried out in practice, embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

Figure 1 is a schematic illustration of possible phases of cobalt oxide as a function of oxygen content.

Figure 2 is a graph providing a time and temperature-dependent calcination profile during the formation of a catalyst in accordance with some examples of the presently disclosed subject matter.

Figure 3 is a graph showing the prediction of total hydrogen evolution after 100 hours of using a catalyst according to some examples of the presently disclosed subject matter, as determined using a HOD system with 5M KBH_4.

Figure 4 is an XRD analysis of α-Al_2O_3, impregnated with 2.4%wt $CoCl_2 \cdot 6H_2O$ and calcinated at 450°C according to a non-limiting example of the presently disclosed subject matter.

Figure 5 is an XRD analysis of α-Al_2O_3, impregnated with 24%wt $CoCl_2 \cdot 6H_2O$ and calcinated at 450°C according to another non-limiting example of the presently disclosed subject matter.

Figure 6 is an XRD analysis of α-Al_2O_3, impregnated with 54%wt $CoCl_2 \cdot 6H_2O$ and calcinated at 450°C according to yet another non-limiting example of the presently disclosed subject matter.

Figure 7 is an XRD analysis of α-Al_2O_3, impregnated with 64%wt $Co(NO_3)_2 \cdot 6H_2O$ and calcinated at 450°C according to a non-limiting example of the presently disclosed subject matter.

Figure 8 is an XRD analysis of α-Al_2O_3, impregnated with 54%wt $CoCl_2 \cdot 6H_2O$ using degassing methods and calcinated at 450°C, according to yet another non-limiting example of the presently disclosed subject matter.

Figure 9 is a graph showing catalytic activity as a function of cycles using two different catalysts of the presently disclosed subject matter.

Figure 10 is a cross-section SEM image (WD 6.13, Energy 15keV, magnification 10.00kx) of α-Al_2O_3, impregnated with 54%wt $CoCl_2 \cdot 6H_2O$ and calcinated at 450°C, without using degassing methods, showing that there is no visible cobalt oxide inside internal examined bead.

Figure 11 is a cross-section SEM image (WD 6.13, Energy 20keV, magnification 10.00kx) of α-Al_2O_3, impregnated with 54%wt $CoCl2 \cdot 6H_2O$ using degassing methods and calcinated at 450°C, showing tetrahedral particles of the Co_3O_4 (circled).

Figure 12 is an XRD analysis of α-Al_2O_3, impregnated with 54%wt $CoCl_2 \cdot 6H_2O$ and calcinated at 250°C according to another non-limiting example of the presently disclosed subject matter.

Figure 13 is an XRD analysis of α-Al_2O_3, impregnated with 54%wt $CoCl_2 \cdot 6H_2O$ and calcinated at 650°C according to yet another non-limiting example of the presently disclosed subject matter.

Figure 14 is an XRD analysis of α-Al_2O_3, impregnated with 54%wt $CoCl_2 \cdot 6H_2O$ and calcinated at 850°C according to yet another non-limiting example of the presently disclosed subject matter.

Figure 15 is a graph showing the activity of a ceramic catalyst in a 3KW system (HOD system) using 5M KBH_4; The ceramic catalyst is α-Al_2O_3, impregnated with 54%wt $CoCl_2 \cdot 6H2O$ and calcinated at 450°C.

DETAILED DESCRIPTION

Catalysts are employed in various applications both in laboratories and in industry to mediate chemical reactions. Catalysts operate by providing an alternative reaction route, wherein the activation energy is lower route is not mediated by the catalyst.

The present disclosure is based on the development of a catalyst using a ceramic porous material as a carrier for cobalt oxide.

It has been found that when selecting, as the ceramic carrier, α-Al_2O_3 over other phases of Al_2O_3 phases or over other possible ceramic carriers (e.g., TiO_2 and SiO_2), the resulting catalyst has hydrogen gas generating activity that is improved over the other ceramic carriers, *inter alia*, in mechanical stability and/or durability. For example, it has been found that the catalyst based on α-Al_2O_3 allows sufficient/effective hydrogen gas production even after numerous hydrogen gas production cycles (runs), while maintaining the catalyst's integrity and functionality (no mechanical degradation was observed or detected) and while not being affected by the mechanical stresses occurring during operation of a hydrogen-on-demand (HOD) system.

Thus, in accordance with a first aspect of the presently disclosed subject matter, there is provided a catalyst comprising α-Al_2O_3 associated with cobalt oxide including at least Co^{2+} and Co^{3+} oxidation states.

A unique property of the presently disclosed catalyst is its durability during multiple cycles of operation. In some examples, the catalyst disclosed herein exhibits less than 7% weight loss after 15 cycles in 5M KBH_4. At times, the catalyst disclosed herein exhibits less than 6% weight loss after 15 cycles in 5M KBH_4. Furhter, at times, the catalyst disclosed herein exhibits less than 5% weight loss after 15 cycles in 5M KBH_4. This is significant as

compared to the immediate dissolution exhibited with a reference catalyst based on γ-Al_2O_3 , under the same conditions.

In the context of presently disclosed subject matter, when referring to cobalt oxide, it is to be understood to refer to any chemical entity comprising at least cobalt and oxygen. In some examples of the presently disclosed subject matter, the cobalt oxide is selected from the group consisting of Co_3O_4, Co_2O_3, CoO, Co_2AlO_4, $CoAl_2O_4$.

In some examples of the first aspect of the presently disclosed subject matter, the cobalt oxide comprises at least Co_3O_4.

Without being bound by theory, **Figure 1** provides a schematic illustration of possible phases of cobalt oxide as a function of oxygen content.

The cobalt oxide is associated with the α-Al_2O_3. In some examples of the first aspect of the presently disclosed subject matter, the α-Al_2O_3 is porous and constitutes a porous carrier for the cobalt oxide.

In some examples of the first aspect of the presently disclosed subject matter, the cobalt oxide is encaged within at least some of the pores of the porous α-Al_2O_3. The encagment can be viewed, for example, by scanning electron microscope (SEM) as further exemplified hereinbelow.

In some examples of the first aspect of the presently disclosed subject matter, at least part of the cobalt oxide associated with the α-Al_2O_3 is in particulate form. Similarly, the particulate form can be viewed, e.g., by SEM.

In some examples of the first aspect of the presently disclosed subject matter, when the cobalt oxide is in particulate form, e.g., a crystalline form.

In some examples of the first aspect of the presently disclosed subject matter, when in crystalline form, the cobalt oxide may have a geometrical shape, such as a tetrahedron, pyramid, and octahedron.

In some examples of the presently disclosed subject matter, at least part of the cobalt oxide associated with the porous α-Al_2O_3 has a tetrahedral shape.

In some examples of the presently disclosed subject matter, at least part of the cobalt oxide associated with the porous α-Al_2O_3 has an octahedral shape.

In some examples of the presently disclosed subject matter, at least part of the cobalt oxide associated with the porous α-Al_2O_3 has a combination of a tetrahedral and an octahedral shape.

In some examples of the first aspect of the presently disclosed subject matter, the cobalt oxide in particulate form has a particle size of at least 1nm.

In some examples of the first aspect of the presently disclosed subject matter, the cobalt oxide in particulate form has a particle size of at most 1mm.

In some examples of the first aspect of the presently disclosed subject matter, the cobalt oxide in particulate form has a particle size of between about 1nm to about 900 μm .

In some examples of the first aspect of the presently disclosed subject matter, the cobalt oxide in particulate form has a particle size of between about 1nm and about 500μm, at times between about 50nm and about 400μm, at times between about 100nm and about 600 μm, at times between about 500nm and about 250μm, at times, between about 1 μm and 250 μm, or any other range within the range of 1nm to about 900 μm.

In some examples of the first aspect of the presently disclosed subject matter, the cobalt oxide is present in the catalyst in an amount that constitutes at least 0.1wt% out of the total weight of said catalyst. In some examples, the amount of the cobalt oxide present in the catalyst is at least about 0.5wt% out of the total weight of said catalyst; at times, at least about 5wt%; at times, at least about 10wt%; at times, at least about 15wt%; at times, at least about 20wt%; at times, at least about 25wt%; at times, at least about 30wt%; at times, at least about 35wt%.

In some examples of the first aspect of the presently disclosed subject matter, cobalt oxide is present in the catalyst in an amount that constitutes not more than 40wt% out of the total weight of the catalyst.

In some examples, the amount of the cobalt oxide present in the catalyst is at most about 38wt% out of the total weight of said catalyst; at times, at most about 36wt%; at times, at most about 34wt%; at times, at most about 32wt%; at times, at most about 30wt%; at times, at most about 28wt%; at times, at most about 26wt%; at times, at most about 24wt%; at times, at most about 22wt%; at times, at most about 20wt%; at times, at most about 18wt%, at times, at most about 16wt%, at times, at most about 14wt%, at times, at most about 12wt%; at times, at most about 10wt%, out of the total weight of the catalyst.

In some examples of the first aspect of the presently disclosed subject matter, the cobalt oxide is present in the catalyst in an amount that constitutes between about 0.1wt% and about 40wt% out of the total weight of the catalyst.

In some examples, the amount of the cobalt oxide present in the catalyst is between any range falling between 0.1wt% and 40wt%, out of the total weight of the catalyst.

In some examples, the amount of the cobalt oxide present in the catalyst is at least 1wt% out of the total weight of said catalyst; at times, at least about 2wt% out of the total weight of said catalyst; at times, at least about 3wt% out of the total weight of said catalyst; at times, at least about 4wt% out of the total weight of said catalyst; at times, at least about 5wt% out of the total weight of said catalyst; at times, at least about 6wt% out of the total weight of said catalyst; at times, at least about 7wt% out of the total weight of said catalyst; at times, at least about 8wt% out of the total weight of said catalyst; at times, at least about 9wt% out of the total weight of said catalyst; at times, at least about 10wt% out of the total weight of said catalyst; at times, at least about 15wt% out of the total weight of said catalyst; at times, at least about 20wt% out of the total weight of said catalyst.

In some examples, the amount of the cobalt oxide present in the catalyst is at most 40wt% out of the total weight of said catalyst; at times, at most about 35wt% out of the total weight of said catalyst; at times, at most about 30wt% out of the total weight of said catalyst; at times, at most about 25wt% out of the total weight of said catalyst.

In some examples, the amount of the cobalt oxide present in the catalyst is between about 0.5wt% and about 38% out of the total weight of said catalyst; at times, between about 0.5wt% and about 30wt%, at times, between about 2wt% and about 25wt%, at times, between about 4wt% and about 35wt%, at times between about 2wt% and about 25wt%.In some examples of the first aspect of the presently disclosed subject matter, the particulate form of porous α-Al_2O_3 has a particle size of between about 1mm and about 10mm.

In some examples of the first aspect of the presently disclosed subject matter, the porous α-Al_2O_3 is also in particulate form, having a shape of particles, sheets, tubes, pellets etc. it is appreciated that due to its size, the porous α-Al_2O_3 cannot be a free flowing powder.

In some examples of the first aspect of the presently disclosed subject matter, the α-Al_2O_3 has a surface area, in the absence of said cobalt oxide, of less than about 10 m^2/gr, between about 0.1 m^2/gr and about 10 m^2/g.

In some examples of the first aspect of the presently disclosed subject matter, the catalyst is essentially free of electrically conductive substances.

In the context of the present disclosure, when referring to "*electrically conductive substances*" it is to be understood to encompass any chemical substance that can participate in an electrochemical reaction and/or to conduct electrons. In some examples, the catalyst is essentially free of electrically conductive metals. In some examples, the catalyst is essentially free of noble metals.

In the context of the presently disclosed subject matter, the term "*essentially free*" is to be understood to mean that there is either no detectable amount of the substance being essentially absent from the catalyst or the amount is insufficient to participate in an electrochemical reaction or does not affect the performance of the catalyst. In some examples, the term "*essentially free*" can include the presence of trace amount of an electrically conductive substance, the amount being insignificant and/or insufficient to participate in an electrochemical reaction or to affect the performance of the catalyst.

In accordance with the presently disclosed first aspect, the catalyst exhibits catalytic activity, at least for the dehydrogenation of a target compound.

In some examples, the target compound is potassium borohydride.

In some examples, the target compound is lithium borohydride.

In some examples, the target compound is ammonium borohydride.

In some examples, the target compound is tetramethyl ammonium borohydride.

In some examples, the target compound is sodium borohydride.

In some examples, the target compound is a mixture of any of the above.

The catalyst disclosed herein demonstrated a beneficiary catalytic activity as determined using a Hydrogen-On-Demand (HOD) release system operated using 5M KBH_4 in H_2O.

When referring to a catalytic activity it is to be understood as the capability of the catalyst to catalyze the production of hydrogen gas in an HOD release system, as compared to the production rate, under the same conditions, in the absence of the catalyst.

"*Hydrogen-On-Demand*" (HOD) release systems are well-known in the art and readily available. In some examples of the presently disclosed subject matter, the HOD release system employed by the present disclosure is as described in International Patent Application Publication No. WO 2019/202391, the content of which is incorporated herein, in its entirety, by reference.

In some examples of the presently disclosed subject matter, the catalytic activity is determined when the system is operated at elevated temperatures, e.g., above 50°C; at times, above 60°C; at times above 70°C.

In some examples of the presently disclosed subject matter, the catalytic activity is determined when the system is operated at elevated pressure, e.g., above 1bar; at times, above 2 bars; at times above 3 bars; at times, above 4 bars, at times, above 5 bars, at times even at about 6 bars.

Thus, in the context of the presently disclosed subject matter, the catalyst can be defined as one having a statistically significant catalytic activity in generating hydrogen gas, as determined by a HOD release system in the presence of 5M KBH_4 in H_2O.

The presently disclosed catalyst exhibits beneficial mechanical stability and/or durability. Surprisingly, it has been found that even after numerous hydrogen gas production cycles (runs), the catalyst maintained its integrity and functionality (no mechanical degradation was observed or detected) and was not affected by the mechanical stresses occurring during the operation of a hydrogen-on-demand system.

Thus, in some examples of the presently disclosed subject matter, the catalyst is characterized by its ability to maintain its catalytic level, i.e. hydrogen activity (rate H_2 production per gram catalyst). In some examples, stability is characterized in that the catalyst does not substantially pulverize in time.

In some other examples of the presently disclosed subject matter, the catalyst is characterized by its ability to maintain less than 7%, at times, less than 6%, at times, less than 5% weight loss after 15 cycles in 5M KBH_4, under the fuel conditions including are high pH (above 12 or even above 13), temperature of approximately 120°C, high pressure ($\leq$10 bar, e.g. between 2 and 10 bar).

In accordance with a second aspect of the presently disclosed subject matter, there is provided a method of preparing a catalyst, the method comprising

impregnating α-Al_2O_3 with an aqueous solution comprising Co^{2+} to form impregnated α-Al_2O_3; and

subjecting the impregnated α-Al_2O_3 to thermal treatment causing formation of cobalt oxide.

In some examples of the presently disclosed method, the aqueous solution comprises cobalt salt.

In some examples of the presently disclosed method, the cobalt salt within the aqueous solution is selected from the group consisting of cobalt acetate ($Co(CH_3COO)_2$), cobalt bromide ($CoBr_2$), cobalt chloride ($CoCl_2$), cobalt formate ($Co(HCOO)_2$), cobalt nitrate ($Co(NO_3)_2$), cobalt sulfate ($CoSO_4$), cobalt tartrate ($CoC_4H_4O_6$), and combinations thereof.

In some preferred example of the presently disclosed subject matter, the cobalt salt comprises at least cobalt chloride ($CoCl_2$).

In some preferred example of the presently disclosed subject matter, the cobalt salt comprises at least cobalt nitrate ($Co(NO_3)_2$).

In some preferred example of the presently disclosed subject matter, the cobalt salt comprises at least cobalt sulfate ($CoSO_4$).

In some preferred example of the presently disclosed subject matter, the cobalt salt comprises a combination of cobalt chloride, cobalt nitrate, and cobalt sulfate.

In some examples of the presently disclosed method, the cobalt salt(s) are at a total concentration of at least 2wt%, irrespective of whether there is a single type of salt or a combination of salts.

In some examples of the presently disclosed method, the cobalt salt(s) are at a concentration within a range of between about 2wt% and about 60wt% when determined at a temperature of 20°C. In some examples of the presently disclosed method, the cobalt salt(s) are at a concentration close to their solubility limit, and in some examples it is around about 80gr/100ml as determined at 20°C.

In some examples of the presently disclosed method, the α-Al_2O_3 is subjected to negative pressure at least prior to its impregnation.

In some examples of the presently disclosed method, the α-Al_2O_3 is subjected to negative pressure at least during said impregnation.

In the context of the presently disclosed subject matter, when referring to "*negative pressure*" it is to be understood as exposing the α-Al_2O_3 to a pressure below 1 Atmosphere. It has been found that exposing the α-Al_2O_3 to negative pressure improves the capacity of α-Al_2O_3 to capture the cobalt to form the cobalt oxide particles inside the α-Al_2O_3 pores and thus provides a higher yield in the presently disclosed method.

Without being bound by theory, it is believed that the exposure of the α-Al_2O_3 to negative pressure results in removal of at least some impurities or otherwise undesired substances occupying the pores of α-Al_2O_3 particles.

In some examples of the presently disclosed subject matter, the method comprises drying the impregnated α-Al_2O_3 prior to applying the thermal treatment.

Drying of the impregnated α-Al_2O_3 can be by any technique known in the art to allow water removal from the impregnated α-Al_2O_3. For example, drying can be within an oven, or by applying hot air onto the impregnated α-Al_2O_3, centrifugation of the impregnated α-Al_2O_3, applying negative pressure on the impregnated α-Al_2O_3, and any combination thereof.

In some examples, the drying of the impregnated α-Al_2O_3 is by subjecting the impregnated α-Al_2O_3 to temperatures between about 100ºC and about 250ºC; at times, between about 100ºC and about 200 ºC; at times, between about 100ºC and about 150 ºC.

In some examples of the presently disclosed subject matter, the drying of the impregnated α-Al_2O_3 is by heating the same to a temperature of up to 200°C.

In some examples of the presently disclosed subject matter, the drying of the impregnated α-Al_2O_3 comprises step-wise drying.

In the context of the presently disclosed subject matter, when referring to a "*step-wise*" process, e.g., step-wise heating, it is to be understood to mean the gradual increase of the temperature in a series of controlled, discrete increments or steps.

The impregnated α-Al_2O_3 (either with or without the drying thereof after impregnation) is then subjected to thermal treatment.

In some examples of the presently disclosed subject matter, the thermal treatment comprises heating the impregnated α-Al_2O_3 to a temperature between about 150°C and about 1000°C.

In some examples, the thermal treatment comprises heating the impregnated α-Al_2O_3 to a temperature range of between about 200°C and about 900°C; at times, between about 250°C and about 1000°C; at times, between about 250°C and about 900°C.

In some examples of the presently disclosed subject matter, the thermal treatment is conducted under any one of oxygen environment, nitrogen environment, argon environment, hydrogen environment.

In some examples of the presently disclosed subject matter, the thermal treatment should take place for a time duration sufficient to effectively produce cobalt oxide particles associated with the α-Al_2O_3. In the context of the presently disclosed subject matter, an effective association between the α-Al_2O_3 and the cobalt oxide is one exhibiting a wt% of cobalt oxide out of a total weight of the catalyst of at least 0.2wt%; at times, at least 1wt%; at times, at least 2wt%; at times, at least 3wt%; at times, at least 4wt%; at times, at least 5wt%; at times, at least 6wt%; at times, at least 7wt%; at times, at least 8wt%.

In some examples of the presently disclosed subject matter, the thermal treatment is applied for at least about 1hour; at times, for at least 1.5 hours; at times, for at least 2 hours; at times, for at least 2.5 hours; at times, for at least 3 hours; at times, for at least 3.5 hours; at times, for at least 4 hours.

In some examples of the presently disclosed subject matter, the thermal treatment is applied for about 4±1 hours.

In some examples of the presently disclosed subject matter, the thermal treatment comprises step-wise heating of said impregnated α-Al_2O_3.

The presently disclosed subject matter also provides, in accordance with a further aspect thereof, a catalyst obtained or obtainable by the presently disclosed method.

The presently disclosed subject matter further provides, in accordance with a fourth of its aspects, a process for hydrogen generation making use of the presently disclosed catalyst. It is to be understood that all definitions of the catalyst provided with respect to the

presently disclosed first, second and third aspects also apply to the process according to the presently disclosed fourth aspect.

In accordance with the presently disclosed fourth aspect, the presently disclosed process comprises contacting the presently disclosed catalyst (comprising α-Al_2O_3 associated with cobalt oxide including at least Co^{2+} and Co^{3+} oxidation states) with a solution comprising borohydride compound and proton donor solvent.

In the context of the presently disclosed subject matter, when referring to a "*proton donor solvent*" it is to be understood to mean any solvent capable of, in addition to dissolving borohydride salt, to release or donate protons (H^+) in a chemical reaction. The proton donor solvent is also known by the term "protic solvent".

In some examples of the presently disclosed process for generating hydrogen, the proton donor solvent is selected from the group consisting of: water, ethanol, methanol, propanol, isopropanol, butanol, isobutanol, propanediol, ethylene glycol, glycerol, and mixtures thereof.

In some preferred examples, the proton donor solvent is water.

In accordance with the presently disclosed fourth aspect, the borohydride compound is selected from the group consisting of: potassium borohydride, sodium borohydride, lithium borohydride, ammonium borohydride, tetramethyl ammonium borohydride, and mixtures thereof.

In some preferred examples of the presently disclosed process for generating hydrogen, the borohydride compound comprises or is potassium borohydride.

Without being bound by theory, it is believed that in the presence of the presently disclosed catalyst, hydrogen generation occurs such that one proton (H^+) is donated by water and the borohydride donates a hydride (hydrogen anion, H^-), together forming H_2.

It has been found that the use of the presently disclosed catalyst allows its use in more than one hydrogen generation cycle, i.e., in two or more runs on the HOD system, without the need to replace the catalyst. In some examples, the catalyst can be used in more than 10 cycles, at times, in more than 20 cycles; at times, in more than 30 cycles; at times, in more than 40 cycles; at times, in more than even 45 cycles or even more than 50 cycles,

while essentially maintaining the mechanical integrity and/or catalytic activity of the catalyst.

Thus, in accordance with the presently disclosed subject matter, the catalyst is one that maintains its mechanical integrity and/or catalytic activity for at least 40 hydrogen generation cycles.

All definitions, as defined and used herein, should be understood to control over dictionary definitions, definitions in documents incorporated by reference, and/or ordinary meanings of the defined terms.

As used herein, the indefinite articles "*a*", "*an*" and "*the*" include singular as well as plural references unless the context clearly dictates otherwise. In other words, unless clearly indicated to the contrary, these should be understood to mean “at least one.”.

The term "*about*" as used herein indicates values that may deviate up to 1%, more specifically 5%, more specifically 10%, more specifically 15%, and in some cases up to 20% higher or lower than the value referred to, the deviation range including integer values, and, if applicable, non-integer values as well, constituting a continuous range. In some examples of the presently disclosed subject matter, the term "*about*" refers to ± 10 %.

The phrase “*and/or*,” as used herein in the specification and in the claims, should be understood to mean “either or both” of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Multiple elements listed with “and/or” should be construed in the same fashion, i.e., “one or more” of the elements so conjoined. As used herein in the specification and in the claims, “or” should be understood to have the same meaning as “and/or” as defined above. For example, when separating items in a list, “or” or “and/or” shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as “only one of” or “exactly one of,” or, when used in the claims, “consisting of,” will refer to the inclusion of exactly one element of a number or list of elements.

Further, as used herein, the term "*comprising*" is intended to mean that a described product and/or process includes the recited element, but not excluding other elements. The term "*consisting essentially of*" is used to define a described product and/or process which

includes the recited elements but exclude other elements that may have an essential significance on the described product and/or process. "*Consisting of*" shall thus mean excluding more than trace elements of other elements. Embodiments defined by each of these transition terms are within the scope of this invention.

The invention will now be exemplified in the following description of experiments that were carried out in accordance with the invention. It is to be understood that these examples are intended to be in the nature of illustration rather than of limitation. Obviously, many modifications and variations of these examples are possible in light of the above teaching. It is therefore, to be understood that within the scope of the present disclosure, the invention may be practiced otherwise, in a myriad of possible ways, than as specifically described hereinbelow.

DESCRIPTION OF NON-LIMITING EXAMPLES

Materials And Methods

Al_2O_3 (alpha and theta), TiO_2 and SiO_2 were purchased from Saint Gobain. $CoCl_2 \cdot H_2O$ was purchased from Alfa Aesar. NaH_2PO_2 was purchased from Alfa Aesar. NaOH was purchased from SDFCL. KBH_4 was purchased from Goldman.

Substrate Impregnation

5-15gr of the substrate in the form of beads were immersed in 100ml of cobalt solution and incubated for 12-24 hr. Following the incubation, the beads were filtered from the solution and washed 3 times. The beads were laid in a ceramic crucible and placed in an oven.

Calcination

The time-temperature profile of the calcination process is described in **Figure 2**.

The calcination was performed by controlled heating of the sample in an ambient atmosphere using the following heating program:

- 3°C/min until reaching 150°C (~35min).
- 10.5 hours at 150°C.
- 3°C /min until reaching the target calcination temperature.
- 4 hours at target calcination temperature.
- Non-controlled cooling to room temperature.

X-ray Diffraction (XRD)

The phase amount of Co_3O_4 was calculated using Rietveld analysis.

Scanning Electron Microscopy (SEM)

SEM imaging was performed at the acceleration voltage 10-20 KeV and Magnification range 1K-50K;

Activity of ceramic catalyst in 3KW system

The catalytic activity was determined using "Hydrogen-On-Demand" (HOD) release system as described in International Patent Application Publication No. WO 2019/202391, the content of which is incorporated herein, in its entirety, by reference.

Generally, activity (H_2 ml/sec/gr) was calculated in the following method: 50g of 2.3M KBH_4 and ceramics were placed in a 100ml flask. An upside-down measuring tube filled with water and placed in a bath was connected, using a hose, to the flask. The hydrogen generated flowed through the tube, pushing the water down the measuring tube. The amount of time it took to push a water volume (equivalent to the hydrogen volume generated) is the activity calculation.

Example 1 – Substrate selection

The substrate must be stable under the fuel conditions, which are high pH, temperature of approximately 120°C, high pressure (≤10 bar) and have minimal erosion from the hydrogen evolution.

The following substrates were examined: rutile-TiO_2, SiO_2, γ-Al_2O_3, Θ-Al_2O_3, α-Al_2O_3.

Table 1: Substrate weight loss (after 15 cycles in 5M KBH_4)

Substrate type	**Weight loss**
γ-Al_2O_3	Immediate dissolution
Θ-Al_2O_3	91.5%
α-Al_2O_3	**4.2%**
TiO_2	7.6%*
SiO_2	Immediate dissolution

* based on 5 cycles and extrapolated to 15 cycles.

Figure 3 illustrates that the Co_3O_4 catalyst deposited on θ-alumina substrate exhibited a parabolic behavior, whereby the hydrogen production increased initially but then decreased over the cycles in fuel (5M KBH_4 solution). This behavior was due to the high substrate dissolution rate during the process. Therefore, based on the catalytic behavior and the substrate's high dissolution rate, it was concluded that the θ-alumina substrate was not suitable as ceramic support for this application.

α-Al_2O_3 had the lowest weight loss rate while providing the maximum hydrogen production (**Table 1** and **Figure 3**).

Example 2 – Optimizing Co deposition solution

Two types of cobalt solution were examined:

- **Solution A**: 0.1M $CoCl_2 \cdot 6H_2O$, 0.4M $NaH_2PO_2 \cdot H_2O$ and pH=9.3.
- **Solution B:** $CoCl_2$ dissolved in water: 2.4%wt [$CoCl_2 \cdot 6H_2O$].

Table 2: Co deposition on a θ-Al_2O_3 substrate and resulting catalytic activity

Solution	Weight increase	Activity [H_2ml/sec/gr]
Solution A	4%	0.8
Solution B	1%	0.3

Table 2 demonstrates that the inclusion of sodium hypophosphite additive (Solution A) has a significant positive impact on both cobalt deposition (a 4% weight increase with Solution A) and catalytic activity (0.8 ml/sec/g). However, Solution B was preferable due to the solubility limit of $CoCl_2$ in the presence of hypophosphite and the fact that hypophosphite provides no significant advantage over Solution B at the solubility limit.

The next step was to find the cobalt concentration that would yield the highest weight increase and activity. Due to the dissolution of θ-Al_2O_3, the work was continued with α-Al_2O_3.

Another way to increase the final amounts of cobalt oxide is by changing the concentration in the impregnation solution.

Three concentrations levels were used: 2.4wt%, 24wt% and 54wt% of $CoCl_2 \cdot 6H_2O$ (**Table 3**). The samples were calcinated at 450 °C.

Based on the XRD analysis, as the percentage of $CoCl_2 \cdot 6H_2O$ increases from 2.4wt% to 24wt% and then to 54wt%, the resulting weight percentage of Co_3O_4 also increases from 0.2wt% (**Figure 4**; See **Table 6** for 2Θ° values) to 2.6wt% (**Figure 5;** See **Table 6** for 2Θ° values) and further to 5.1wt% (**Figure 6;** See **Table 6** for 2Θ° values).

Table 3: Effect of $CoCl_2$ concentration on the amount of Co_3O_4 and catalytic performance

$CoCl_2$ Concentration	Weight increase	Activity [H_2ml/sec/gr]	%Co_3O_4 (XRD)
2.4%wt $CoCl_2$	0%	0.2	0.2
24%wt $CoCl_2$	3%	0.2	2.6
54%wt $CoCl_2$	6%	1.1	5.1

Table 3 reveals a clear correlation between the concentration of cobalt salt and the resulting yield of cobalt oxide, with the latter increasing proportionally to the former. Notably, the solubility limit for cobalt chloride salt is 54%wt. By utilizing this concentration, cobalt oxide reached approximately 5.1%, a finding that was validated by XRD analysis (**Figure 6;** See **Table 6** for 2Θ° values).

Utilizing a cobalt salt with higher solubility in water made it feasible to achieve a more significant final load of Co_3O_4. Specifically, XRD analysis (**Figure 7;** See **Table 6** for 2Θ° values) shows that when a 64wt% solution of $Co(NO_3)_2 \cdot 6H_2O$ was employed, a weight increase of about 8% Co_3O_4 was obtained.

Example 3 – Degassing

Degassing is a process that evacuates air or other substances (e.g., volatiles, humidity, etc.) trapped inside the pores of the porous ceramic support. To increase the cobalt oxide load inside the pores, a degassing procedure was employed on α-Al_2O_3 beads that were placed in a flask under vacuum conditions for three hours. Then 54wt% $CoCl_2$ solution was injected into the flask and kept under vacuum for two more hours. The

volume of the solution injected was equivalent of the volume of the pores according to the manufacturer's specification. Finally, the beads were calcinated at 450°C. Based on the XRD analysis, this procedure resulted in Co_3O_4 percentage reaching 9wt% (**Figure 8;** See **Table 6** for the 2Θ° values).

As further detailed in **Table 4**, the degassing increased Co_3O_4 load from 5wt% to 9wt%.

Table 4: Effect of degassing on the amount of Co_3O_4 and catalytic performance

Impregnation method	Weight increase	Activity [H_2ml/sec/gr]	%Co_3O_4 (XRD)
12-28 hours	5.8%	1.1	5
Degassing	11.5%	0.4	9

It should be noted that while the initial activity was lower for higher Co_3O_4 loads, it is assumed that the short test duration prevented all the fuel from penetrating the internal pores, thus limiting the observation of the true impact of the degassing method on the initial activity.

As demonstrated in **Figure 9**, the degassing procedure resulted in a higher Co_3O_4 load, which in turn yielded a ~20% increase in the total H_2 produced in each cycle.

Furthermore, SEM examination clearly indicates that the degassing procedure facilitates the incorporation of cobalt oxide particles inside the porous support:

Figure 10 shows a cross-sectional SEM image of α-Al2O_3, impregnated for 18 hours with 54wt% $CoCl_2 \cdot 6H_2O$ (without the degassing step) and calcinated at 450°C. There is no detectable cobalt oxide inside the examined ceramic bead (See **Table 6** for the 2Θ° values).

Figure 11 shows a cross-sectional SEM image of α-Al_2O_3, impregnated with 54%wt $CoCl_2 \cdot 6H_2O$ using degassing method and calcinated at 450°C. The octahedral Co_3O_4 particles (circled) are abundantly present inside the examined ceramic bead (See **Table 6** for the 2Θ° values).

Example 4 – Optimizing calcination temperature

The desired catalytic phase is controlled by the calcination temperature. Four different calcination temperatures were examined (i.e., 250°C, 450°C, 650°C and 850°C) using α-Al_2O_3, impregnated with 54%wt $CoCl_2 \cdot 6H_2O$.

At 250°C, the ceramic substrate retained purple color indicating that not all $CoCl_2$ was converted into cobalt oxide. XRD revealed that there's only a small fraction (0.1%) is cobalt oxide and most of the cobalt is in $CoCl_2$ form (**Figure 12;** See **Table 6** for the 2Θ° values). Therefore, while calcination at 250°c shows high weight increase and high activity it will not persist over time because the active $CoCl_2$ will be quickly washed out from the ceramics.

As summarized in **Table 5** below, at higher temperatures, (450°C, 650°C and 850°C) similar amounts of Co_3O_4, of ca. 5wt% were produced (as determined using XRD analysis (See **Figure 6**, **Figure 13** and **Figure 14** for calcination temperatures of 450°C, 650°C and 850°C respectively; See **Table 6** for the 2Θ° values).

Table 5: Effect of calcination temperature on the amount of Co_3O_4 and catalytic performance

Calcination temp.	Weight increase	Activity [H_2ml/sec/gr]	%Co_3O_4 (XRD)
250°C	25%	3.3	0.1
450°C	5.8%	1.1	5
650°C	6%	0.7	5
850°C	6.3%	0.1	5.4

Table 6: 2Θ° **values of XRD pattern**

Figure	XRD pattern
Figure 4	Al_2O_3 (2Θ°= 25.5, 35, 37.7, 41.6, 43.2, 46.1, 52.4, 57.4, 59.6, 61, 61.2, 66.4, 68.1, 70.3, 74.2, 76.8, 77.1) Co_3O_4 (2Θ°= 31.2, 36.7, 59.3, 59.3, 65.1, 68.5, 69.6, 77.3)

Figure 5	Al_2O_3 (2Θ°= 25.5, 35.1, 37.7, 41.6, 43.3, 46.1, 52.5, 57.4, 59.7, 61, 61.2, 66.4, 68.1, 70.3, 74.2, 76.8, 77.2) Co_3O_4 (2Θ°= 31.2, 36.8, 38.5, 44.7, 49, 55.6, 59.3, 65.2, 68.5, 74, 77.3, 78.3)
Figure 6	Al_2O_3 (2Θ°= 25.5, 35.1, 37.7, 41.6, 43.3, 46.1, 52.5, 57.4, 59.7, 61.1, 61.2, 66.5, 68.1, 70.4, 74.2, 76.8, 77.2) Co_3O_4 (2Θ°= 31.2, 36.8, 38.5, 44.7, 55.6, 59.3, 59.3, 65.2, 68.6, 77.3)
Figure 7	Al_2O_3 (2Θ°= 25.4, 35, 37.6, 43.2, 46, 52.4, 57.3, 59.6, 61, 61.2, 66.4, 68.1, 74.2, 76.7, 77.1) Co_3O_4 (2Θ°= 31.1, 36.7, 38.4, 44.7, 55.5, 59.2, 59.2, 65.1, 68.5, 77.2, 78.3)
Figure 8	Al_2O_3 (2Θ°= 25.4, 35, 37.6, 43.2, 46, 52.4, 57.3, 59.6, 61, 61.1, 66.4, 68, 74.1, 76.7, 77.1) Co_3O_4 (2Θ°= 31.1, 36.7, 38.4, 44.6, 55.5, 59.2, 59.2, 65.1, 68.5, 74, 77.2, 78.2)
Figure 12	Al_2O_3 (2Θ°= 25.5, 35.1, 37.7, 43.3, 46.1, 52.5, 57.4, 59.7, 61.1, 61.2, 66.5, 68.2, 70.4, 74.2, 76.8, 77.2) $CoCl_2 \cdot 6H_2O$ (2Θ°= 25.1, 28.6, 29.8, 30.4, 31.7, 32.4, 32.7, 32.9, 34.9, 37.2, 40.6, 40.8, 40.8, 40.9, 41, 43.4, 43.5, 44.4, 45.5, 45.6, 46.5, 46.8, 47.7, 48.6, 48.7, 49.5, 50.3, 51.7, 53.6, 54.3, 55.2, 57, 57.1, 57.4, 57.6, 58.5, 59.4, 61.6, 62.6, 63.3, 63.9, 67.9, 68.5, 69, 69.6, 74.4, 74.8, 76.7) CoO (2Θ°= 34.0)
Figure 13	Al_2O_3 (2Θ°= 25.5, 35, 37.7, 43.2, 46.1, 52.4, 57.4, 59.6, 61, 61.2, 66.4, 68.1, 70.3, 74.2, 76.8, 77.1) Co_3O_4 (2Θ°= 31.2, 36.7, 38.4, 44.7, 55.6, 59.3, 59.3, 65.1)
Figure 14	Al_2O_3 (2Θ°= 25.4, 35, 37.6, 41.5, 43.2, 46, 52.4, 57.4, 59.6, 61, 61.2, 66.4, 68.1, 70.3, 74.2, 76.8, 77.1)

	Co_3O_4 (2Θ°= 31.1, 36.7, 38.4, 44.7, 55.5, 59.2, 59.2, 65.1, 74, 77.2, 78.3)

Example 5 – Ceramic catalyst performance

The performance of the ceramic catalyst (α-Al_2O_3, impregnated with 54wt% $CoCl_2 \cdot 6H_2O$ and calcinated at 450°C) was tested in the 3KW system using 5M KBH_4. The catalyst weight was adjusted to give the proper hydrogen flow. The results show stable performance after 40 cycles (**Figure 15**).

Furthermore, throughout the process, no residues indicating the dissolution of the ceramic support were detected, suggesting a high level of durability for the ceramic catalyst.

CLAIMS:

1. A catalyst comprising α-Al_2O_3 associated with cobalt oxide including at least Co^{2+} and Co^{3+} oxidation states.

2. The catalyst of claim 1, wherein at least part of said cobalt oxide is in particulate form.

3. The catalyst of claim 1 or 2, wherein said cobalt oxide is selected from the group consisting of Co_3O_4, Co_2O_3, CoO, Co_2AlO_4, $CoAl_2O_4$.

4. The catalyst of any one of claims 1 to 3, wherein said cobalt oxide comprises Co_3O_4.

5. The catalyst of any one of claims 1 to 4, wherein said α-Al_2O_3 is porous and said cobalt oxide is at least within said pores of said α-Al_2O_3.

6. The catalyst of any one of claims 1 to 5, comprising said cobalt oxide in an amount of between about 0.1wt% and about 40wt% out of the total weight of said catalyst.

7. The catalyst of any one of claims 2 to 6, wherein said particulate form of said cobalt oxide has a particle size of between about 10nm to about 10 micron.

8. The catalyst of any one of claims 1 to 7, being essentially free of detectable amount of noble metals.

9. The catalyst of any one of claims 1 to 8, being essentially free of detectable amount of electrically conductive substances.

10. The catalyst of any one of claims 1 to 9, exhibiting catalytic activity for dehydrogenation of a target compound selected from the group consisting of potassium borohydride, sodium borohydride, lithium borohydride, ammonium borohydride, tetramethyl ammonium borohydride, and mixtures thereof.

11. The catalyst of claim 10, wherein said target compound is potassium borohydride.

12. The catalyst according to claim 10 or 11, having catalytic activity when determined in a Hydrogen On Demand release system operated at 5M KBH_4 in H_2O.

13. A method of preparing a catalyst, the method comprises

impregnating α-Al_2O_3 with an aqueous solution comprising Co^{2+} to form impregnated α-Al_2O_3; and

subjecting said impregnated α-Al_2O_3 to thermal treatment causing formation of cobalt oxide.

14. The method of claim 13, wherein said aqueous solution comprises cobalt salt.

15. The method of claims 14, wherein said cobalt salt is selected from the group consisting of cobalt acetate ($Co(CH_3COO)_2$), cobalt bromide ($CoBr_2$), cobalt chloride ($CoCl_2$), cobalt formate ($Co(HCOO)_2$), cobalt nitrate ($Co(NO_3)_2$), cobalt sulfate ($CoSO_4$), cobalt tartrate ($CoC_4H_4O_6$), and combinations thereof.

16. The method of claim 14 or 15, wherein said cobalt salt comprises cobalt chloride ($CoCl_2$).

17. The method of claim 14 or 15, wherein said cobalt salt comprises cobalt nitrate ($Co(NO_3)_2$).

18. The method of any one of claims 13 to 17, wherein said cobalt salt is at a concentration of at least 2wt%.

19. The method of any one of claims 14 to 18, wherein said cobalt salt is at a concentration within a range of between about 2wt% and about 60wt% when determined at a temperature of 20°C.

20. The method of any one of claims 13 to 19, comprising subjecting said α-Al_2O_3 to negative pressure at least prior to said impregnation.

21. The method of any one of claims 13 to 20, comprising subjecting said α-Al_2O_3 to negative pressure at least during said impregnation.

22. The method of any one of claims 13 to 21, wherein said thermal treatment comprises heating said impregnated α-Al_2O_3 to a temperature between about 150°C and about 1000°C.

23. The method of any one of claims 13 to 22, wherein said thermal treatment is conducted under a gas selected from the group consisting of oxygen, hydrogen, nitrogen, argon and mixtures thereof.

24. The method of any one of claims 13 to 23, wherein said thermal treatment is applied for a time period of at least about 1 hour.

25. The method of any one of claims 13 to 24, wherein said thermal treatment comprises step-wise heating of said impregnated α-Al_2O_3.

26. The method of any one of claims 13 to 25, comprising drying the impregnated α-Al_2O_3 prior to said thermal treatment.

27. The method of claim 26, comprises heating said impregnated α-Al_2O_3 to a temperature of up to about 250°C.

28. The method of claim 26 or 27, wherein said drying comprises step-wise drying.

29. A catalyst obtained or obtainable by the method of any one of claims 13 to 28.

30. A process for hydrogen generation, the process comprises contacting a catalyst comprising α-Al_2O_3 associated with cobalt oxide including at least Co^{2+} and Co^{3+} oxidation states with a solution comprising borohydride compound and proton donor solvent.

31. The process of claim 30, wherein said catalyst is as defined in any one of claims 1 to 12.

32. The process of claim 30 or 31, wherein said borohydride compound is selected from the group consisting of: potassium borohydride, sodium borohydride, lithium borohydride, ammonium borohydride, tetramethyl ammonium borohydride, and mixtures thereof.

33. The process of any one of claims 30 to 32, wherein said borohydride compound comprises potassium borohydride.

34. The process of any one of claims 30 to 33, wherein the proton donor solvent is selected from the group consisting of: water, ethanol, methanol, propanol, isopropanol, butanol, isobutanol, propanediol, ethylene glycol, glycerol, and mixtures thereof.

35. The process of any one of claims 30 to 34, wherein the proton donor solvent comprises water.

36. The process of any one of claims 30 to 35, comprising two or more hydrogen generation cycles.

37. The process of claim 36, wherein said catalyst maintains its mechanical integrity and/or catalytic activity for at least 40 hydrogen generation cycles.

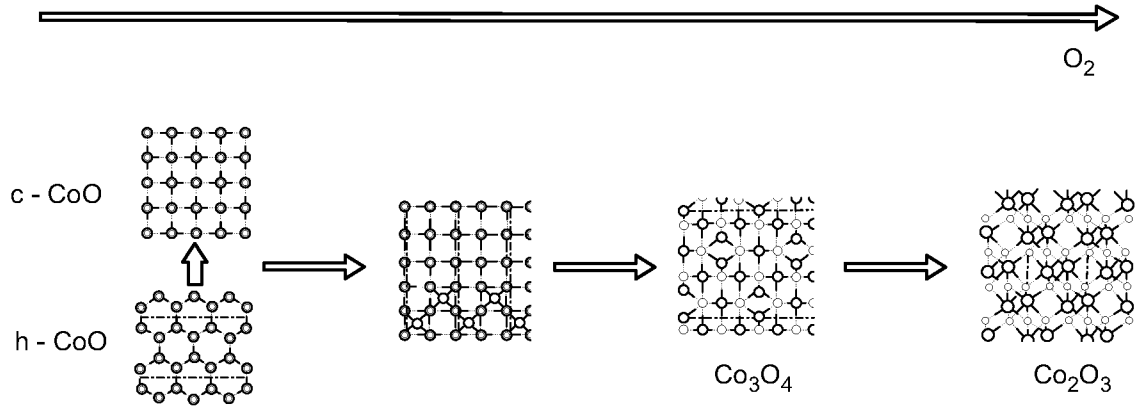

FIG. 1

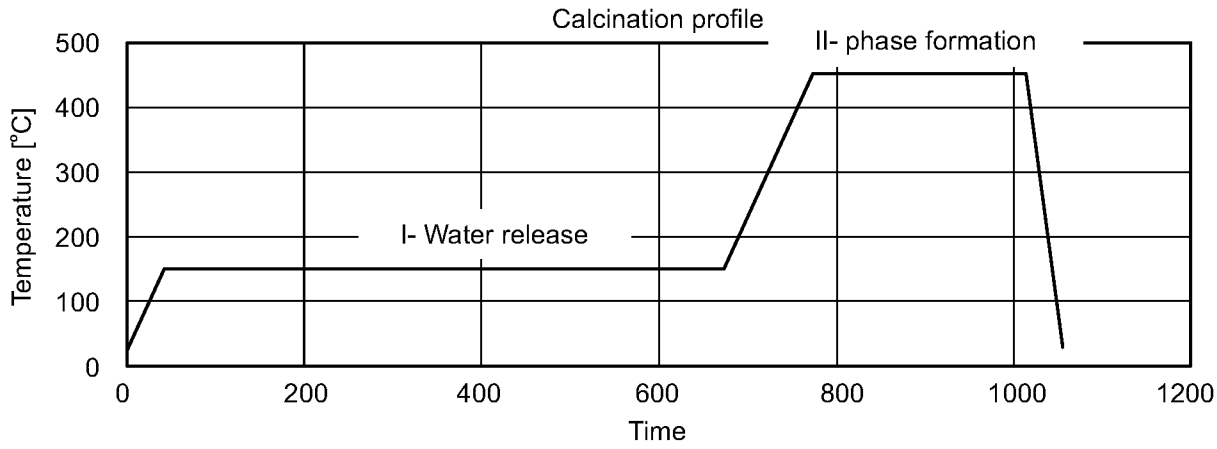

FIG. 2

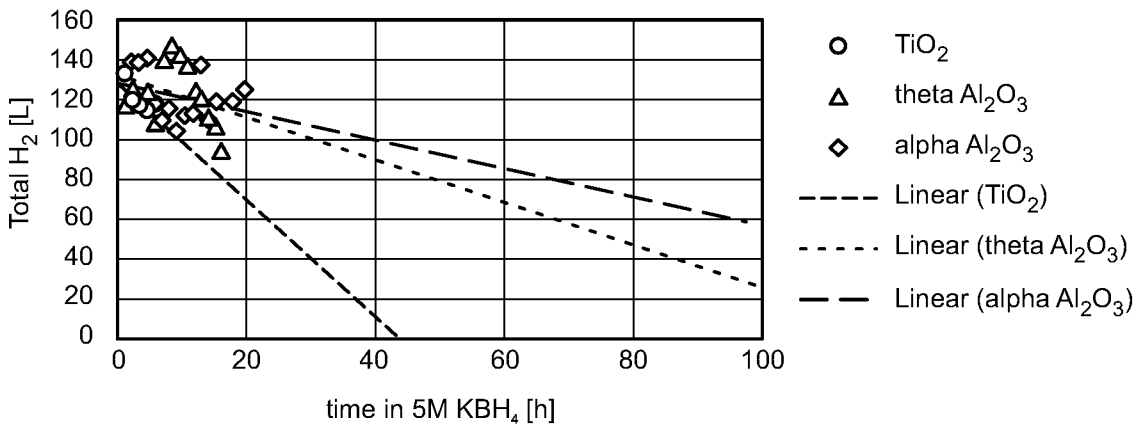

FIG. 3

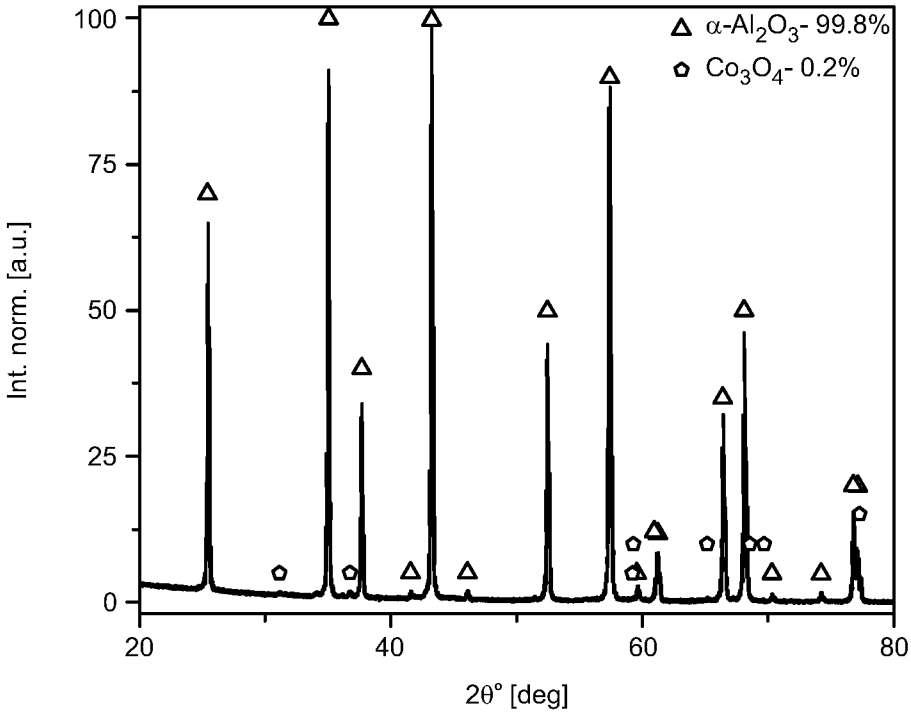
α-Al2O3- 99.8%
Co3O4- 0.2%
Int. norm. [a.u.]
2θ° [deg]
0
25
50
75
100
20
40
60
80

FIG. 4

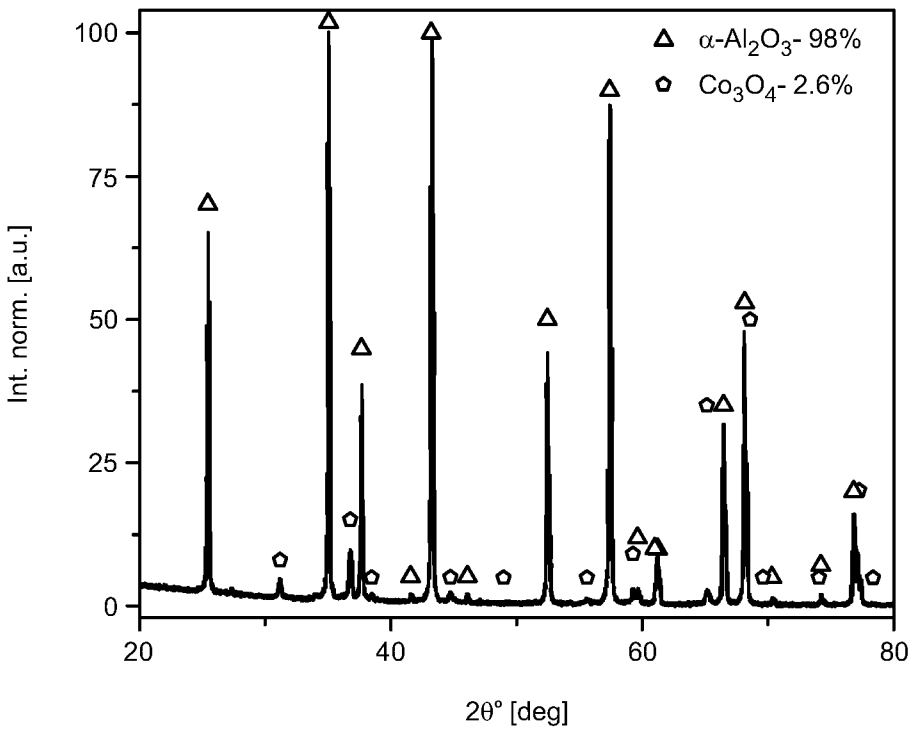
α-Al2O3- 98%
Co3O4- 2.6%
Int. norm. [a.u.]
2θ° [deg]
0
25
50
75
100
20
40
60
80

FIG. 5

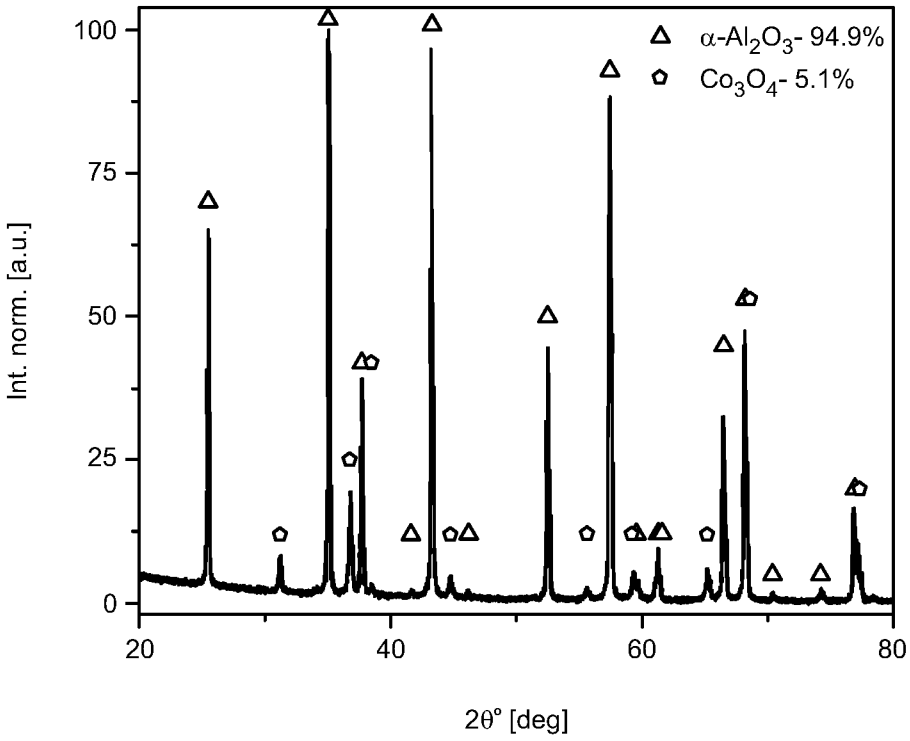
α-Al2O3- 94.9%
Co3O4- 5.1%
Int. norm. [a.u.]
2θ° [deg]
0
25
50
75
100
20
40
60
80

FIG. 6

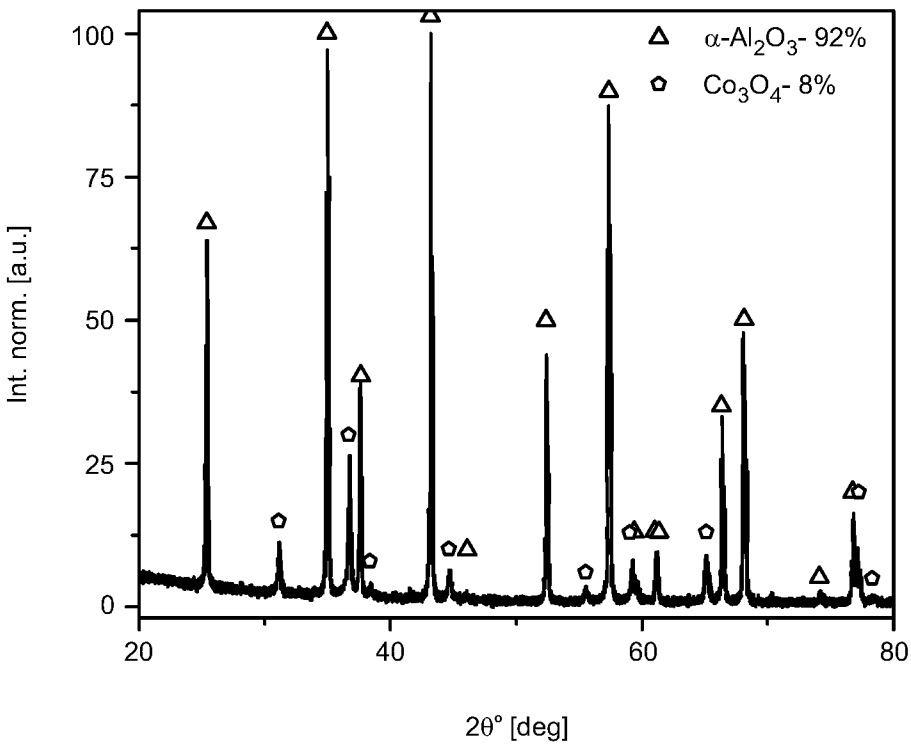
α-Al2O3- 92%
Co3O4- 8%
Int. norm. [a.u.]
2θ° [deg]
0
25
50
75
100
20
40
60
80

FIG. 7

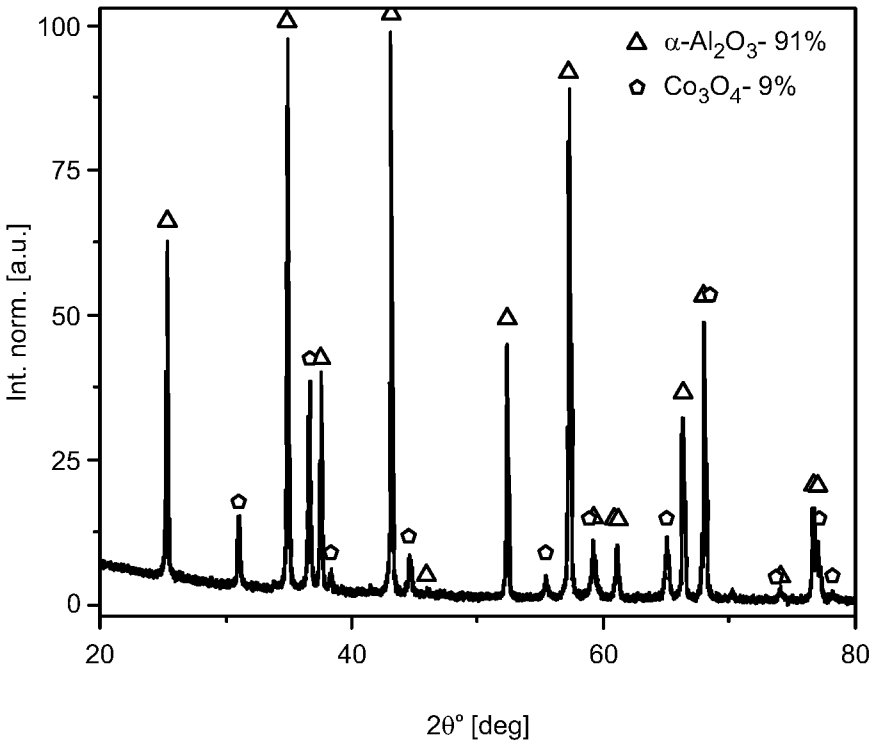
α-Al2O3- 91%
Co3O4- 9%
Int. norm. [a.u.]
2θ° [deg]
0
25
50
75
100
20
40
60
80

FIG. 8

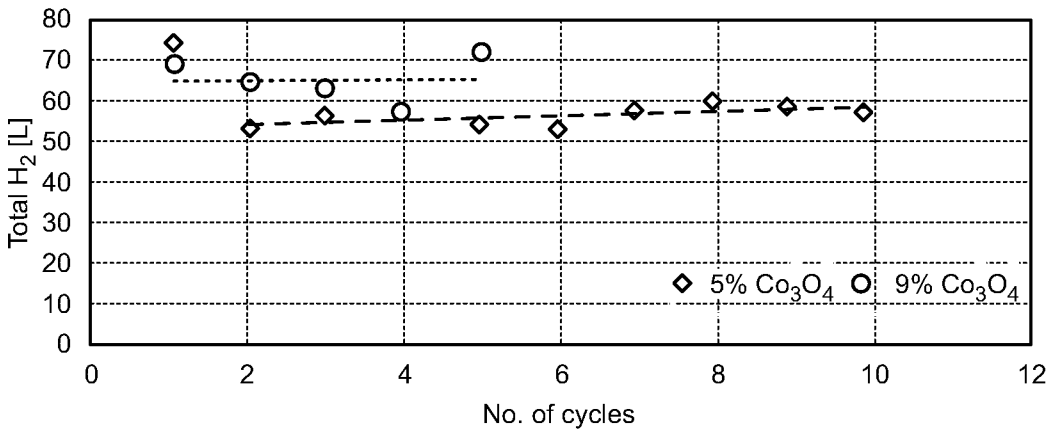
Total H2 [L]
No. of cycles
5% Co3O4
9% Co3O4
0
10
20
30
40
50
60
70
80
0
2
4
6
8
10
12

FIG. 9

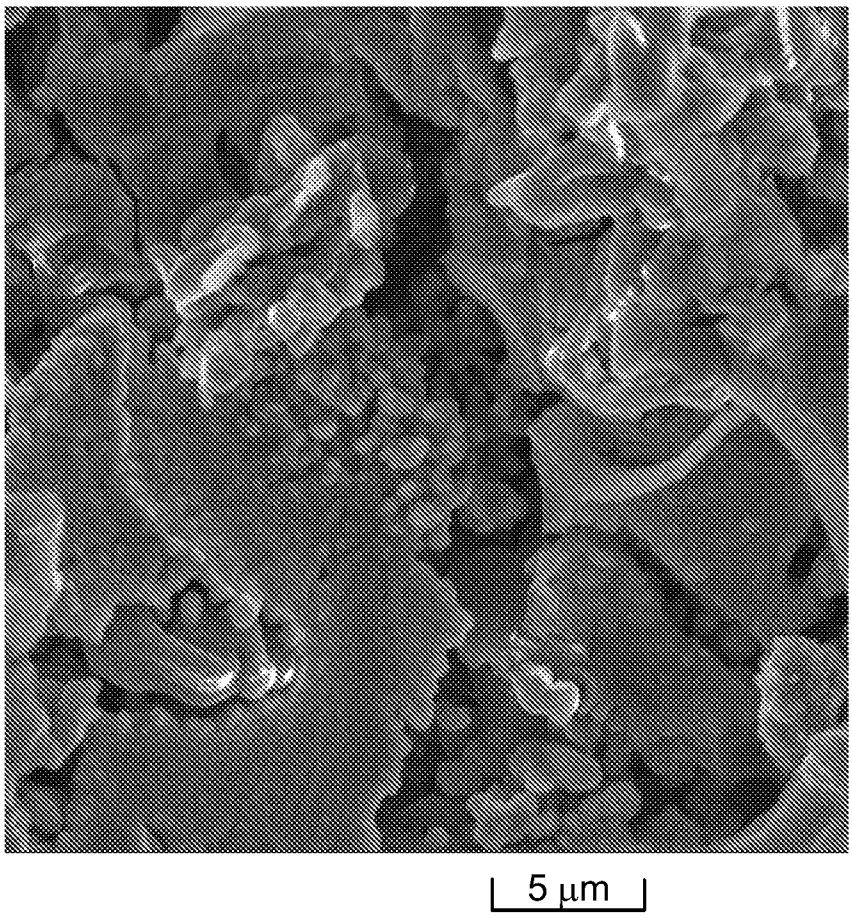

FIG. 10

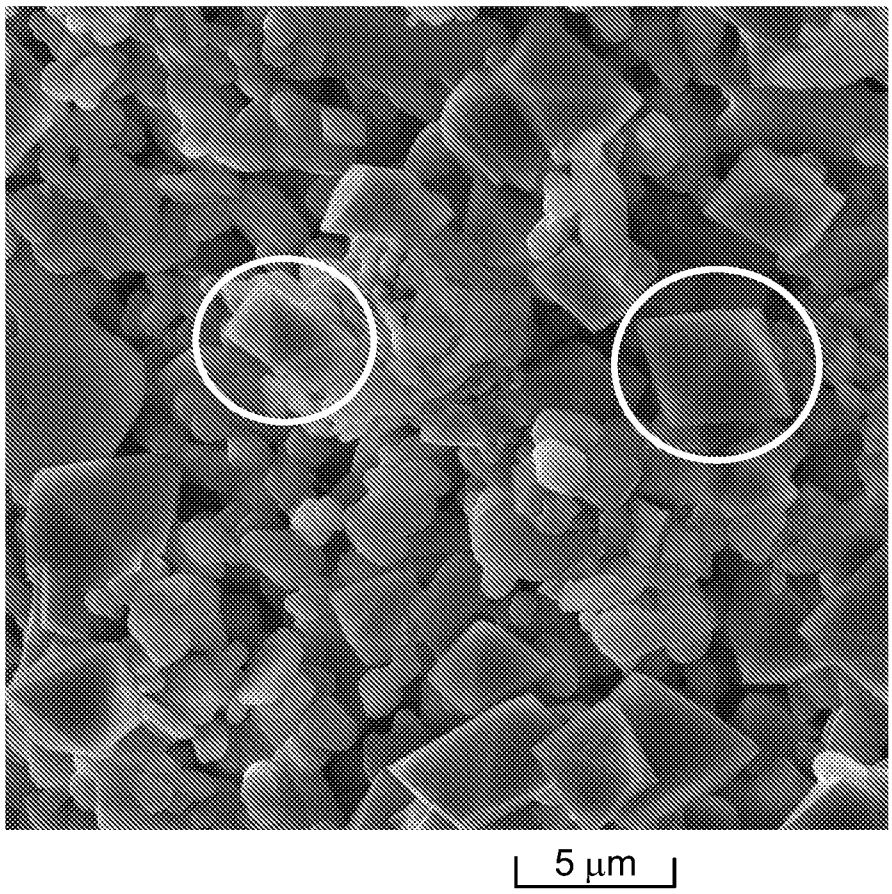

FIG. 11

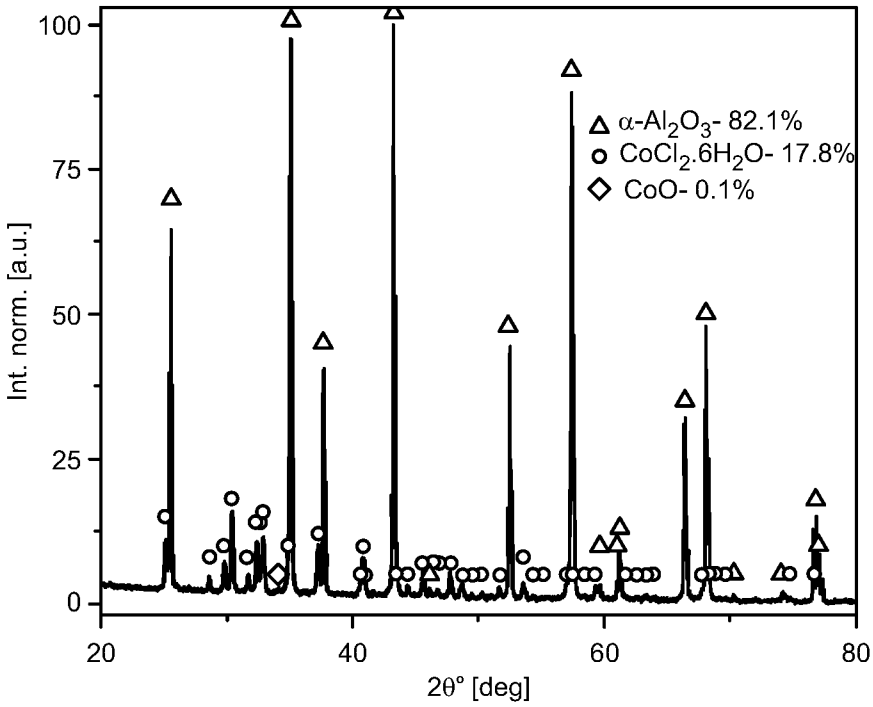
100
75
50
25
0
Int. norm. [a.u.]
20
40
60
80
2θ° [deg]
α-Al2O3- 82.1%
CoCl2.6H2O- 17.8%
CoO- 0.1%

FIG. 12

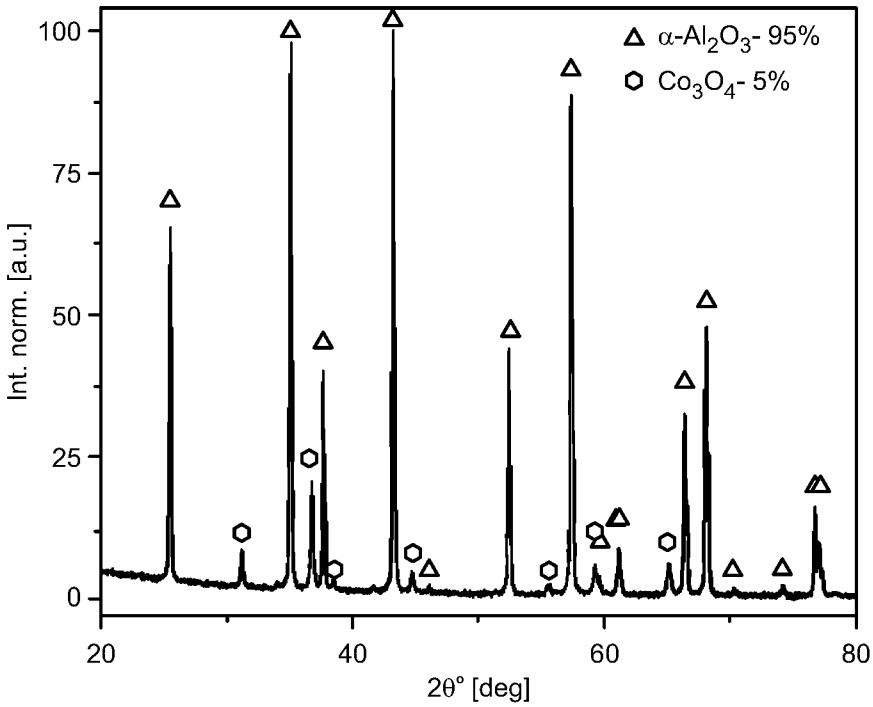
100
75
50
25
0
Int. norm. [a.u.]
20
40
60
80
2θ° [deg]
α-Al2O3- 95%
Co3O4- 5%

FIG. 13

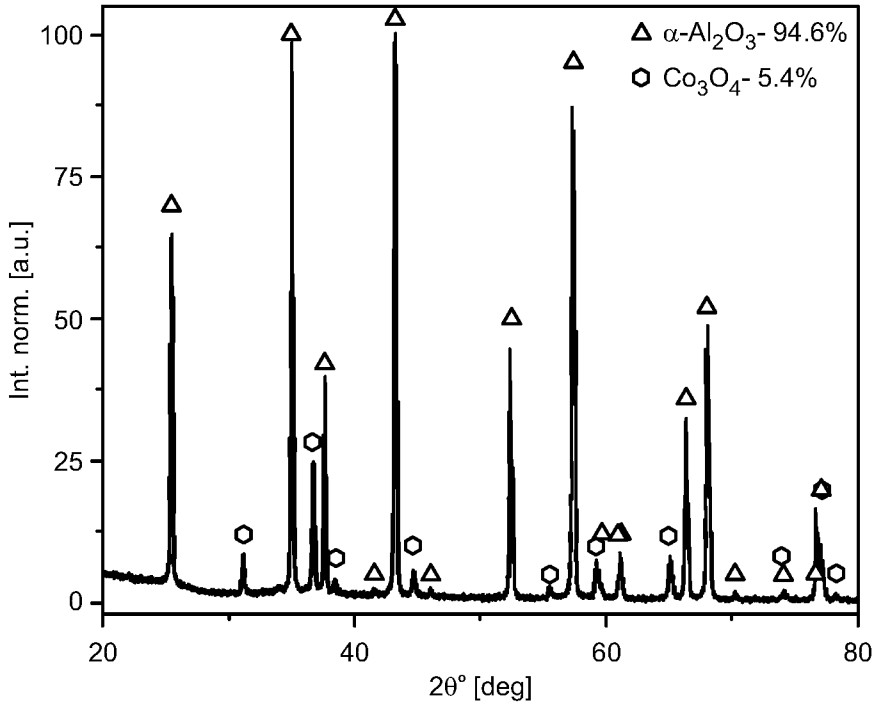
α-Al2O3- 94.6%
Co3O4- 5.4%
Int. norm. [a.u.]
2θ° [deg]
0
25
50
75
100
20
40
60
80

FIG. 14

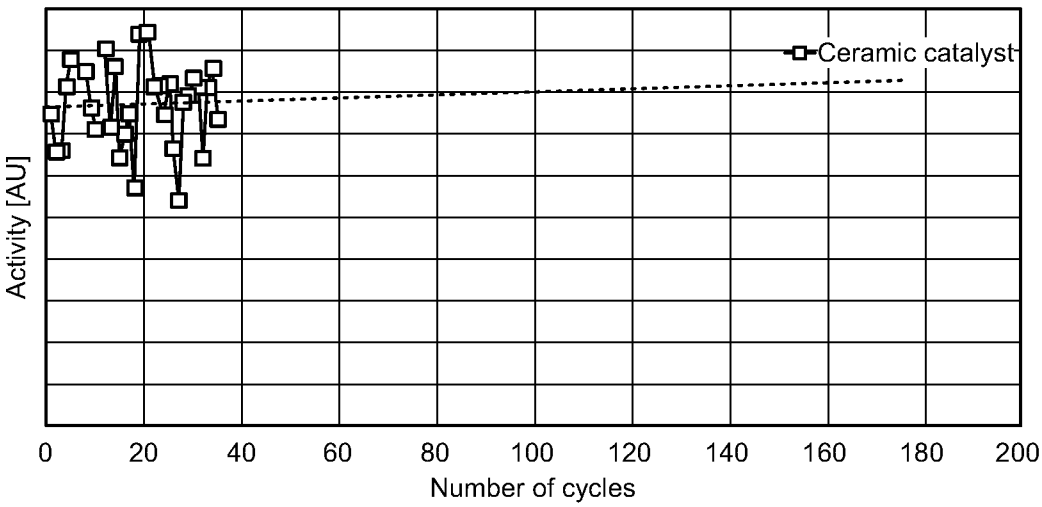
Ceramic catalyst
Activity [AU]
Number of cycles
0
20
40
60
80
100
120
140
160
180
200

FIG. 15

INTERNATIONAL SEARCH REPORT

International application No
PCT/IL2024/050562

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J21/04 B01J23/75 B01J37/02 B01J37/08 B01J37/28
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)
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	CN 108 862 191 A (SHENZHEN YAHUA WEIYI TECH CO LTD) 23 November 2018 (2018-11-23) claims; examples; tables; compounds ----- -/--	1-37

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

[x] 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
30 August 2024	20/09/2024

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	de Cauwer, Robby

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IL2024/050562

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GUDYKA SYLWIA ET AL: "Enhancing the deN2O activity of the supported Co3O4¦[alpha]-Al2O3catalyst by glycerol-assisted shape engineering of the active phase at the nanoscale", APPLIED CATALYSIS B. ENVIRONMENTAL, ELSEVIER, AMSTERDAM, NL, vol. 201, 17 August 2016 (2016-08-17), pages 339-347, XP029750829, ISSN: 0926-3373, DOI: 10.1016/J.APCATB.2016.08.034 2 Experimental part 2.1 Catalysts preparation 3 Results and discussion; figures; tables; compounds	1-15, 17-19, 22-29
A	KR 2012 0103323 A (KOREA RES INST CHEM TECH [KR]; NAT UNIV CHUNGBUK IND ACAD [KR]) 19 September 2012 (2012-09-19) the whole document	1-37
A	US 2004/242941 A1 (GREEN MALCOLM LESLIE HODDER [GB] ET AL) 2 December 2004 (2004-12-02) the whole document	1-37
A	US 2007/004582 A1 (LIM MYONG HOON [KR] ET AL) 4 January 2007 (2007-01-04) the whole document	1-37

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IL2024/050562

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