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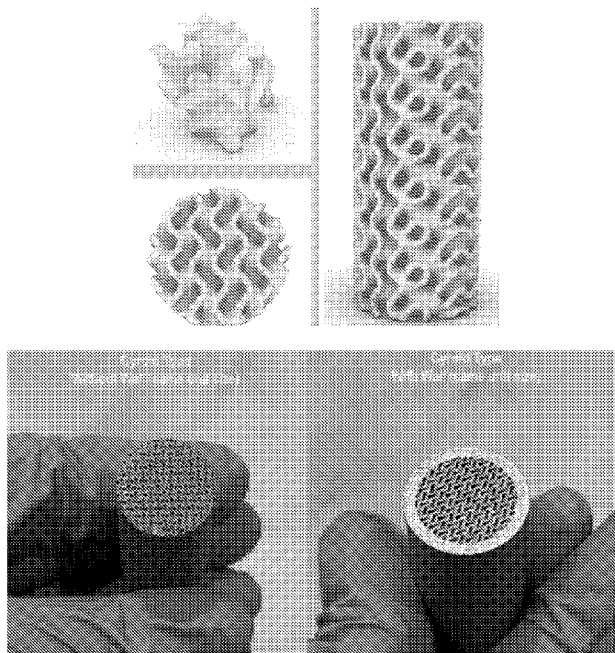


Figure 1

(57) Abstract: Provided herein is a catalyst-coated structured reactor, and a method of making such a reactor. Also provided herein is the use of such reactors in processes for producing chemical products, such as in the dry reforming of methane (DRM) process.

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CATALYST-COATED REACTOR

Field

The present disclosure relates to a catalyst-coated structured reactor, and a method of making such a reactor. It also relates to the use of such reactors in processes for producing chemical products, such as in the dry reforming of methane (DRM) process.

Background

The development of industrial processes for producing valuable chemicals is an important enterprise. In particular, processes for converting low value feedstocks into higher value materials (e.g. more complex or difficult to access chemicals) is of considerable value.

One example of such a process is dry reforming of methane (DRM), also known as carbon dioxide reforming of methane. DRM is a chemical reaction that involves the reaction between methane (CH₄) and carbon dioxide (CO₂) to produce syngas, which is a mixture of hydrogen (H₂) and carbon monoxide (CO). Dry reforming of methane is important for several reasons. It offers a potential pathway for converting two greenhouse gases, methane, and carbon dioxide, into valuable syngas, which can be used as a feedstock for the production of a variety of chemicals, including methanol, ammonia, and synthetic fuels. This can help reduce the carbon footprint of these industries by using carbon dioxide as a feedstock rather than releasing it into the atmosphere. In addition, dry reforming of methane can also be used as a method for converting natural gas, primarily composed of methane, into syngas. This can be particularly important in regions where natural gas is abundant but access to other feedstocks is limited. Syngas produced from dry reforming of methane can be used for various industrial applications.

A clean energy-based process is required to produce syngas (CO+H₂) via dry reforming of methane that is essential for the production of valuable chemicals through Fischer Tropsch synthesis. By combining the two Greenhouse Gases i.e., CO₂ and CH₄, we can produce syngas via reaction 1,



Dry reforming of methane is an endothermic process that requires high reaction temperatures i.e., (>800 °C) to achieve the reaction equilibrium and optimal conversion of the reactants, also to minimize coke formation. In addition to this, many simultaneous side reactions such as reverse water gas shift reaction (Eq. 2) affect the H₂:CO ratio and maintains it around 1.



Dry methane reforming provides a low carbon footprint as compared to partial oxidation and conventional steam reforming [1].

Significant gaps remain in this area of technology affecting its commercial viability.

5 Firstly, DRM reaction is highly endothermic and thus requires high temperature for conversion. Traditionally, this heat is supplied by conducting the reaction in a firebox via methane combustion outside fixed bed catalytic reactors. Secondly, rapid catalyst deactivation due to coking and sintering remains a limiting factor. Coking happens at temperatures below 800°C due to Boudouard reaction (Eq. 3) and methane cracking (Eq. 4). Simultaneously, the catalyst
10 may experience sintering due to high temperature support pore collapse and metal nanoparticles agglomeration [2].



One type of catalyst used in such processes are powdered catalysts, which consist of
15 fine particles of catalyst material that are mixed with the reactants in a reactor. Powdered catalysts have a high surface area, however they suffer from poor mass transfer and high pressure drop due to the formation of aggregates and the tendency to pack [3]. This can result in relatively low reaction rates and selectivity.

There is a need for improved processes for producing chemical products, e.g. in respect
20 of processes such as the DRM process. For example, there is further a need for improved catalysts and/or reactors useful in such processes.

Summary

The inventors have discovered new methods for making catalytic reactors, and new
25 catalytic reactors, which provide high performance in chemical processes such as the dry reforming of methane. For example, by immersing a structured reactor substrate in a catalyst precursor solution and drying the coated material, high performing catalytic reactors can be produced. Further, utilising reactors which are capable of generating heat by magnetic induction allows for operation of high temperature chemical processes using power originating
30 from renewable resources, rather than e.g. methane combustion.

The coated structured reactors developed showed high stability and good catalytic activity. No signs of significant coking were discovered from SEM imaging and CHNS analysis. Catalyst particles were promoted to grow on the surface of the substrate using an immersion coating technique.

5 Accordingly, in a first aspect, there is provided a method of making a catalyst-coated structured reactor, comprising

 at least partially immersing a structured reactor substrate which is formed of an electrically conductive material that is capable of generating heat *via* magnetic induction, in a catalyst precursor solution, thereby coating at least part of the surface of the substrate with the
10 solution;

 withdrawing the coated substrate from the solution; and

 drying the coated substrate;

 thereby providing a catalyst-coated structured reactor.

 In some embodiments, the substrate is at least partially immersed in and withdrawn from
15 the solution a plurality of times.

 In some embodiments, the substrate is dip-coated in the solution.

 In some embodiments, the substrate is subjected to multiple coating cycles, each coating cycle comprising:

 1a) at least partially immersing a conductive structured reactor substrate in a catalyst
20 precursor solution, so as to coat at least part of the surface of the substrate with the solution; and 1b) withdrawing the coated substrate from the solution; wherein 1a) and 1b) are carried out a plurality of times; and

 2) drying the coated substrate.

 Advantageously, subjecting a substrate to multiple coating cycles can provide for
25 increased catalyst deposition.

 In some embodiments, each coating cycle is carried out for a period of time in the range of from 5 to 10 hours.

 In some embodiments, the dried coated substrate is subjected to a calcination step.

 In some embodiments, the dried coated substrate or calcined coated substrate is
30 subjected to a reduction step by treatment with hydrogen.

 In some embodiments, the substrate is made of a nickel-based alloy.

 In some embodiments, the substrate is made of Inconel 625 alloy or C22 alloy.

In some embodiments, prior to immersion, the substrate is subjected to pre-treatment to prepare the surface for catalyst coating.

In some embodiments, pre-treatment comprises:

contacting the substrate with aqueous nitric acid,

5 contacting the substrate with acetone,

washing the substrate with water, and

drying the substrate.

In some embodiments, the substrate is produced by 3D printing.

In some embodiments, the substrate comprises a gyroid structure.

10 In some embodiments, the substrate does not have a circumferential wall.

In some embodiments, the catalyst which is coated on the substrate is a catalyst for dry reforming of methane.

In some embodiments, the catalyst is a nickel-based catalyst.

15 In some embodiments, the catalyst is or comprises Ni/SBA-15, Ni/MgO and NiO/Ce_{0.8}Gd_{0.2}O_{2-δ}, optionally wherein the catalyst is of the formula NiO/Ce_{0.8}Gd_{0.2}O_{2-δ}.

In some embodiments, the catalyst is Ni/MgO, which is sandwiched between coatings of MCM-41.

In some embodiments, the catalyst precursor solution comprises an aqueous solution of metal salts.

20 In some embodiments, the catalyst precursor solution is formed from cerium nitrate hexahydrate, gadolinium nitrate hexahydrate and nickel nitrate hexahydrate.

In some embodiments, the catalyst precursor solution comprises a viscosity adjuster, optionally polyvinylpyrrolidone.

25 In another aspect, there is provided a catalyst-coated structured reactor produced or producible by a method as defined herein. Advantageously the structured reactor finds use in catalysing chemical processes such as the dry reforming of methane.

In another aspect, there is provided a catalyst-coated structured reactor comprising:

30 a structured reactor substrate which is formed of an electrically conductive material that is capable of generating heat *via* magnetic induction, and which is coated with a nickel-based catalyst,

wherein the catalyst coating comprises NiO nanoparticles having a mean particle diameter in the range of from 20 to 80 nm. Advantageously the structured reactor finds use in catalysing chemical processes such as the dry reforming of methane.

In some embodiments, the nanoparticles of NiO have mean particle diameter in the range of from 40 to 60 nm.

In some embodiments, the mean particle diameter is determined using scanning electron microscopy (SEM).

5 In some embodiments, NiO nanoparticles are substantially uniformly dispersed on the surface of the substrate.

In another aspect, there is provided use of a catalyst-coated structured reactor as defined herein, in a process for producing a chemical product.

10 In another aspect, there is provided a process for dry reforming of methane, comprising: reacting carbon dioxide and methane in a catalyst-coated structured reactor as defined herein, at elevated temperature, to produce hydrogen and carbon monoxide.

In some embodiments, the feed flow ratio of carbon dioxide to methane is about 5:4.

In some embodiments, the reaction is carried out at a temperature in the range of from 800 to 1000°C, optionally about 900°C.

15 In some embodiments, the weight hourly space velocity (WHSV) is in the range of from 4000 to 100000 L/h.kg_{Cat}, optionally in the range of from 4000 to 5000 L/h.kg_{Cat}, or optionally about 4500 L/h.kg_{Cat}, or optionally in the range of from 10,000 to 30,000 L/h.kg_{Cat}, or optionally about 20,000 L/h.kg_{Cat}, or optionally in the range of from 50,000 to 70,000 L/h.kg_{Cat}, or optionally about 60,000 L/h.kg_{Cat}.

20

Brief Description of the Drawings

Figure 1 shows representations of a gyroid lattice and a structured monolith.

Figure 2 shows a schematic of an embodiment of a process for dry reforming of methane reaction using a catalyst-coated structured reactor according to the present disclosure.

25 Figure 3 shows graphs showing (a) Catalyst deposition vs number of coatings and (b) Catalyst specific loading vs number of coatings, for Gyroid With Wall and Gyroid Without Wall structured reactors in accordance with the present disclosure.

30 Figure 4 shows photographs of catalyst-coated structured reactors in accordance with the present disclosure: (a) GW NiO/Ce_{0.8}Gd_{0.2}O_{2-δ} coated monolith and (b) GWW NiO/Ce_{0.8}Gd_{0.2}O_{2-δ} coated monolith.

Figure 5 shows graphs of (a) Time vs Conversion GWW (b) Time vs Molar concentration GWW (c) Time vs Conversion GW (d) Time vs Molar concentration GW at 900 °C with 5:4 CO₂:CH₄ feed ratio and 4500 L/h.kg_{Cat} WHSV for DRM reaction.

Figure 6 shows graphs of (a) Time vs H_2/CO ratio GWW (b) Time vs H_2/CO ratio GW (c) Time vs Yield GWW and (d) Time vs Yield GW at 900 °C with 5:4 $CO_2:CH_4$ feed ratio and 4500 L/h.kg_{cat} WHSV for DRM reaction.

Figure 7 shows graphs of (a) Time on stream activity (Time vs Conversion) GWW and (b) WHSV vs Conversion GWW at 900 °C with 5:4 $CO_2:CH_4$ feed ratio for DRM reaction.

Figure 8 shows X-ray diffractograms showing (a) X-Ray Diffraction of substrate (precursor) dip coated and slurry coated $NiO/Ce_{0.8}Gd_{0.2}O_{2-\delta}$ catalyst.

Figure 9 shows Scanning Electron Microscopy images of (a) Fresh $NiO/Ce_{0.8}Gd_{0.2}O_{2-\delta}$ catalyst, (b) Spent catalyst $NiO/Ce_{0.8}Gd_{0.2}O_{2-\delta}$, (c) Coated Gyroid GWW, (d) Coated Gyroid GWW, (e) Coated Gyroid GW and (f) Coated Gyroid GW.

Figure 10 shows charts showing (a) Heat profile and (b) Power profile for Gyroid With Wall and Gyroid Without Wall catalyst-coated structured reactors in accordance with the present disclosure.

Figure 11a and 11b show SAED from two areas of a catalyst precursor solution-treated sample. Differences between the patterns indicate the sample is not uniform. The inserts on each pattern show the particles in the electron beam when the pattern was taken. Figure 11a shows strong evidence of NiO. Figure 11b shows reflections indicative of the support structures CeO_2 and Gd_2O_3 .

Figure 12 shows a) low magnification (25kx) imaging of a group of nanoparticles from a catalyst precursor solution-treated sample, and b) high magnification (700kx) imaging of the lattice fringes of a single particle. The interplanar spacing of this particle is consistent with NiO.

Figures 13 shows a) an aggregate from a slurry-treated sample imaged at 25kx magnification and b) a cluster of particles from the slurry imaged at 50kx magnification. The diameter of particles in the cluster is much smaller than is seen from the precursor sample.

Figure 14a and 14b show SAED from two areas of a slurry-treated sample. The diffraction patterns only indicate the presence of support structures. No reflection from NiO crystal planes were found.

Figure 15 shows a) a cluster from a slurry-treated sample imaged at 240kx magnification with a region of likely NiO circled, and b) a FFT of the cluster taken at higher magnification which shows weak peaks that correspond to NiO. All other peaks in (b) correspond to support structures.

Figure 16 shows SEM images for a catalyst precursor solution-treated sample.

Figure 17 shows SEM images for a slurry-treated sample.

Figure 18 shows SEM images for fresh powdered catalyst sample.

Figures 19 to 21 show images of different structured reactor designs, before and after coating with catalyst precursor solution.

5 Figure 22 shows a graph showing catalyst deposition vs number of coating cycles for different structured reactor designs.

Figures 23 and 24 show images of gyroid structured reactors coated with different catalysts.

10 Figure 25 shows a graph showing catalyst deposition vs number of coating cycles for gyroid structured reactors coated with different catalysts.

Figure 26 shows graphs of Time on stream activity (Time vs Conversion) 900 °C with 5:4 CO₂:CH₄ feed ratio (6000 L/h.kg_{cat}) for DRM reaction using NiO/SBA-15 catalyst.

Figure 27 shows graphs of Time on stream activity (Time vs Conversion) 900 °C with 5:4 CO₂:CH₄ feed ratio (6000 L/h.kg_{cat}) for DRM reaction using NiO/MgO-15 catalyst.

15 Figure 28 shows graphs of Time on stream activity (Time vs Conversion) 900 °C with 5:4 CO₂:CH₄ feed ratio (6000 L/h.kg_{cat}) for DRM reaction using NiO/MgO-MCM-41 sandwiched catalyst.

20 Figure 29 shows graphs of (a) Time on stream activity using Ni/MgO@MCM-41 catalyst showing CO and CH₄ conversions and H₂/CO ratio at 100,000 L.h⁻¹.kg_{cat}⁻¹ with CO₂:CH₄ = 5:4 diluted in Ar (CO₂=9.5%, CH₄=7.5%, Ar=83%) at 900 °C, 850 °C and 800 °C for the DRM reaction; and (b) Experimental (bullet points) and model conversion (- - - curves) for optimised kinetic parameters at the same operating conditions.

Detailed Description

Definitions

Unless specifically defined otherwise, all technical and scientific terms used herein shall be taken to have the same meaning as commonly understood by one of ordinary skill in the art.

30 The present disclosure refers to the entire contents of certain documents being incorporated herein by reference. In the event of any inconsistent teaching between the teaching of the present disclosure and the contents of those documents, the teaching of the present disclosure takes precedence.

It is to be understood that if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art in Australia or any other country

As used herein, the term “and/or”, e.g., “X and/or Y” shall be understood to mean either
5 "X and Y" or "X or Y" and shall be taken to provide explicit support for both meanings or for either meaning.

As used herein, the term about, unless stated to the contrary, refers to +/- 10%, of the designated value.

As used herein, the terms “a”, “an” and “the” include both singular and plural aspects,
10 unless the context clearly indicates otherwise.

Unless otherwise indicated, terms such as "first," "second," etc. are used herein merely as labels, and are not intended to impose ordinal, positional, or hierarchical requirements on the items to which these terms refer. Moreover, reference to a “second” item does not require or preclude the existence of lower-numbered item (e.g., a “first” item) and/or a higher-numbered
15 item (e.g., a “third” item).

As used herein, the phrase “at least one of”, when used with a list of items, means different combinations of one or more of the listed items may be used and only one of the items in the list may be needed. The item may be a particular object, thing, or category. In other words, “at least one of” means any combination of items or number of items may be used from
20 the list, but not all of the items in the list may be required. For example, “at least one of item A, item B, and item C” may mean item A; item A and item B; item B; item A, item B, and item C; or item B and item C. In some cases, “at least one of item A, item B, and item C” may mean, for example and without limitation, two of item A, one of item B, and ten of item C; four of item B and seven of item C; or some other suitable combination.

As used herein, the word “comprise” and other forms of the word, such as “comprising”
25 and “comprises,” means including but not limited to, and is not intended to exclude, for example, other additives, components, integers, or steps.

Catalyst-Coated Structured Reactor

30 In a first aspect, there is provided a method of making a catalyst-coated structured reactor, comprising

at least partially immersing a structured reactor substrate which is formed of an electrically conductive material that is capable of generating heat *via* magnetic induction, in a

catalyst precursor solution, thereby coating at least part of the surface of the substrate with the solution;

withdrawing the coated substrate from the solution; and

drying the coated substrate;

5 thereby providing a catalyst-coated structured reactor.

The method produces a catalyst-coated structured reactor. The structured reactor is produced from the reactor substrate by coating.

A structured reactor (and reactor substrate) is generally composed of a solid support having a defined geometry defining a volume for passage of chemicals. Typically, the
10 structured reactor (and the reactor substrate) is configured such that it contains voids and/or channels, for example it may have a parallel channel, open cell foam or stacked wire mesh configuration.

The structured substrate can provide a high surface area-to-volume ratio, which allows for efficient mass transfer and improved reaction kinetics. Providing a layer of catalyst material
15 ensures good contact between the reactants and the catalyst, leading to high selectivity and conversion rates.

An advantage of utilising a structured reactor is that they can be easily configured into different shapes and sizes, depending on the specific requirements of the reaction. They also have a long lifespan and can be reused multiple times with minimal degradation.

20 Any suitable reactor design may be utilised. In some embodiments, the structured reactor (and reactor substrate) has a structure selected from a honeycomb structure, a gyroid structure, a Voronoi structure and an octet structure. In some embodiments, the structured reactor (and reactor substrate) has a gyroid structure. Gyroid structures have been found to provide particularly good performance.

25 Any suitable overall shape can be used for the structured reactor (and reactor substrate). In some embodiments, the overall shape of the structured reactor (and reactor substrate) is cylindrical.

In some embodiments, the structured reactor (and reactor substrate) contains an outer wall, e.g. a circumferential wall, extending around the outside of the length of the structured
30 reactor, which restricts access of materials. Such an arrangement leaves the ends of the reactor accessible for entry of reactants, and exit of products. For example, the reactor may have a tubular arrangement, with an outer circumferential wall along the length of the reactor, and a

structure such as a gyroid, octet or Voronoi structure disposed inwardly of the circumferential wall which provides channels and/or voids for passage of material.

In some other embodiments, the structured reactor (and reactor substrate) does not have an outer wall, e.g. a circumferential wall, extending around the outside of the length of the structured reactor. In such an arrangement, the structure of the reactor (e.g. gyroid) may continue throughout the whole of the structured reactor up to its outer surfaces.

The structured reactor substrate is formed of an electrically conductive material that is capable of generating heat *via* magnetic induction. The use of such materials facilitates the use of magnetic induction heating. Magnetic induction heating uses electricity to generate an alternating magnetic field that induces eddy currents in a conductive material, which leads to resistive heating [4]. This method of heating is much cleaner and more efficient than traditional heating methods, as it can avoid the need for fossil fuels and reduce greenhouse gas emissions. Furthermore, the use of magnetic induction heating in carbon processes facilitates improvements in efficiency and productivity. For example, magnetic induction heating can may facilitate provision of more precise and uniform heating compared to traditional heating methods, and may can result in better quality products and reduced production times. Additionally, magnetic induction heating can be easily automated and controlled, allowing for more consistent and reliable processing.

Any suitable material may be used for the structured reactor substrate. For example, it may be a metallic material, such as an alloy. In some embodiments, the substrate contains nickel. In some embodiments, the substrate is made of a nickel-based alloy, e.g. an alloy in which nickel is the component present in the greatest amount by weight. In some embodiments, the substrate is made of Inconel 625 alloy or C22 alloy. Inconel 625 alloy (UNS designation N06625) is a nickel-based superalloy that has high strength and resistance to elevated temperatures. It is also known by the names Haynes 625, Nickeltvac 625, Nicrofer 625, Altemp 625 and Chronic 625. It has the composition: Ni 58%, Cr 20-23%, Mo 8-10%, Fe 5%, Nb + Ta 3.15-4.15%, Co 1%, Mn 0.5%, Si 0.5%, Al 0.4%, Ti 0.4%, C 0.1%, P 0.015% and S 0.015%. C22 alloy (also known as Hastelloy C-22) has the UNS number 06022. It is a nickel-chromium-molybdenum-tungsten alloy. It has the composition: C 0.10% max, Cr 20-22.5%, Co 2.5% max, Fe 2.0-6.0%, Mn 0.50% max, Mo 12.5-14.5%, P 0.02% max, Si 0.08% max, S 0.02% max, W 2.5-3.5%, V 0.35% max, and balance Ni.

The structured reactor substrate may be produced by any suitable means known in the art. For example, it may be produced by 3D printing.

The structured reactor substrate is at least partially immersed in a catalyst precursor solution, thereby coating at least part of the surface of the substrate with the solution.

The catalyst precursor solution contains components suitable for allowing coating of a structured reactor substrate with the desired materials.

5 The catalyst precursor solution contains a solvent. Typically, the catalyst precursor solution is an aqueous solution. In some embodiments, the solvent used in the catalyst precursor solution is water.

10 The catalyst precursor solution contains a catalyst precursor component or components (e.g. it can contain one or more materials) which, following coating and drying (and other processing steps if required), form the catalyst coated on the surface of the substrate. Any suitable catalyst (e.g. which is useful for the desired chemical reaction), and any suitable catalyst precursor components, may be used.

15 Catalysts include those containing noble metals (Rh, Ru, Pd, Pt and Ir) or transition metals (Ni, Co, Mo and Fe), supported on materials such as crystalline oxides, zeolites, spinels, perovskites or mesoporous supports [5].

Typically, one or more metal salts is used in the catalyst precursor solution, e.g. one or more metal salts which are soluble in the solvent used at the concentration required to provide an effective coating of the reactor substrate. The metal salts are typically salts of the metals required for the catalyst of interest.

20 In some embodiments, the catalyst precursor solution comprises an aqueous solution of metal salts. Any suitable counterion(s) may be used in the metal salt(s).

In some embodiments, the catalyst comprises nickel. In some embodiments, the catalyst is a nickel-based catalyst. In some embodiments, the catalyst precursor solution comprises a nickel salt, e.g. nickel nitrate hexahydrate.

25 In some embodiments, the catalyst comprises cerium. In some embodiments, the catalyst precursor solution comprises a cerium salt, e.g. cerium nitrate hexahydrate.

In some embodiments, the catalyst comprises gadolinium. In some embodiments, the catalyst precursor solution comprises a gadolinium salt, e.g. gadolinium nitrate hexahydrate.

30 In some embodiments, the catalyst comprises nickel, cerium and gadolinium. In some embodiments, the catalyst precursor solution is formed from cerium nitrate hexahydrate, gadolinium nitrate hexahydrate and nickel nitrate hexahydrate.

In some embodiments, the catalyst is $\text{NiO/Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$.

In some embodiments, the catalyst comprises magnesium. In some embodiments, the catalyst precursor solution comprises a magnesium salt. In some embodiments, the catalyst is NiO/MgO.

In some embodiments, the catalyst is or comprises Ni/SBA-15, Ni/MgO and
5 NiO/Ce_{0.8}Gd_{0.2}O_{2-δ}, optionally wherein the catalyst is of the formula NiO/Ce_{0.8}Gd_{0.2}O_{2-δ}.

In some embodiments, the catalyst comprises a support material.

In some embodiments, the catalyst comprises silicon. In some embodiments, the catalyst precursor solution comprises silica, e.g. mesoporous silica. In some embodiments, the catalyst precursor solution comprises mesoporous silica SBA-15. Mesoporous silica SBA-15
10 can be obtained from, e.g., Sigma-Aldrich (product code 914614). In some embodiments, the catalyst precursor solution comprises silica MCM-41 (MCM-41).

In some embodiments, the reactor substrate is provided with one or more coatings of active catalyst, sandwiched between coatings of a support material, such as a silica (e.g. MCM-41),

15 In some embodiments, the catalyst is Ni/MgO, which is sandwiched between coatings of MCM-41. In such embodiments, the structured reactor substrate is coated with one or more coatings of MCM-41 (e.g. by immersing in a solution containing MCM-41), followed by coating with one or more coatings of the active catalyst using a catalyst precursor solution containing nickel and magnesium salts, followed by coating with one or more coatings of
20 MCM-41.

If desired, the catalyst precursor solution may contain additional components.

In some embodiments, the catalyst precursor solution comprises a pH adjusting agent, which is used to adjust the pH to the desired value. pH adjusting agents may be acidic or basic. In some embodiments an acidic pH adjusting agent is used. For example, an organic or
25 inorganic acid may be used, e.g. nitric or hydrochloric acid. In some embodiments a basic pH adjusting agent is used. For example, it may be a metal hydroxide, e.g. an alkali metal hydroxide or alkaline earth metal hydroxide. For example, it may be potassium hydroxide.

In some embodiments, the catalyst precursor solution comprises a binding agent.

In some embodiments, the catalyst precursor solution comprises a viscosity adjuster.

30 In some embodiments, the catalyst precursor solution comprises polyvinylpyrrolidone.

In some embodiments, the catalyst is a catalyst for dry reforming of methane. In some embodiments, the catalyst precursor solution is formed from components for producing a catalyst for dry reforming of methane.

The structured reactor substrate is at least partially immersed in the catalyst precursor solution, thereby coating at least part of the surface of the substrate with the solution.

In some embodiments, the structured reactor substrate is fully immersed or substantially fully immersed in the catalyst precursor solution.

5 Any suitable technique may be used for immersion of the substrate in the catalyst precursor solution. For example, in some embodiments, the substrate is dip-coated in the solution. A suitable dip-coater is, for example, the Dip-Coater Filmlift FL-1 (MGW Lauda, Königshofen, Germany) with variable dipping and withdrawal velocities. That dip-coater has a clamping support for the substrate/monolith to vertically align with the precursor solution in a
10 container.

During dip-coating, the catalyst precursor solution may if desired be agitated, e.g. frit may be stirred.

During dip-coating, dipping velocity and withdrawal velocity are set at an appropriate speed to ensure adequate coating of the structured reactor substrate. For example, dipping
15 velocity may be in the range of from 25 to 75 cm/min, or about 50 cm/min. Withdrawal velocity may for example be in the range of from 25 to 75 cm/min, or about 50 cm/min.

Multiple immersion cycles (e.g. dip-coating cycles) may be used. In some embodiments, the substrate is at least partially immersed in and withdrawn from the solution a plurality of times, e.g. 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23,
20 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, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100 or more.

The substrate may if desired be held in the solution for a desired period of time.

25 In some embodiments, the structured reactor substrate is immersed (held, if desired) and withdrawn repeatedly for a period of time in the range of from 1 hour to 10 hours, e.g. from 5 to 10 hours, or for about 7 hours.

The immersion step is carried out at a suitable temperature, for example it may be carried out at a temperature in the range of from 10°C to 50°C, or in the range of from 15°C to
30 40°C, or about 25°C, or at ambient temperature.

The coated structured reactor substrate is dried. For example, it may be dried in an oven. The coated substrate may be dried at any suitable temperature, for example it may be dried at ambient temperature or at elevated temperature. For example, it may be dried at a

temperature in the range of from 20°C to 80°C, or from 25°C to 50°C. A drying oven may be used if desired. The drying step may be carried out for a suitable period of time, e.g. it may if desired be carried out for a period in the range of from 1 to 12 hours.

In some embodiments, the substrate is subjected to multiple coating cycles, each coating cycle comprising:

1a) at least partially immersing a conductive structured reactor substrate in a catalyst precursor solution, so as to coat at least part of the surface of the substrate with the solution; and 1b) withdrawing the coated substrate from the solution; wherein 1a) and 1b) are carried out a plurality of times; and

2) drying the coated substrate.

For example, the substrate may be subjected to 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 or more coating cycles. In some embodiments, the substrate is subjected to a number of coating cycles in the range of from 3 to 8.

In some embodiments, each coating cycle is carried out for a period of time in the range of from 5 to 10 hours.

The method of the invention may comprise additional processing steps if desired.

In some embodiments, prior to immersion, the substrate is subjected to pre-treatment to prepare the surface for catalyst coating. For example, the substrate may be contacted with acid, such as nitric acid (e.g. an aqueous solution of nitric acid), e.g. for a period of time in the range of from 6 to 48 hours, e.g. at ambient temperature.

In some embodiments, following treatment with acid, the substrate may be aged in a suitable solvent, e.g. an organic solvent such as acetone. The aging step may be carried out for a suitable period of time, e.g. in the range of from 6 to 48 hours, e.g. at ambient temperature. If desired, following aging, the substrate may be washed, e.g. with water, and/or dried.

In some embodiments, pre-treatment comprises contacting the substrate with aqueous nitric acid, contacting the substrate with acetone, washing the substrate with water, and drying the substrate.

In some embodiments, following immersion of the substrate in catalyst precursor solution, and following drying, the dried coated substrate is subjected to a calcination step. Calcination is carried out using a suitable calcination apparatus, such as a calciner. Calcination may be carried out for example at a temperature in the range of from 200°C to 600°C, or in the

range of from 300°C to 500°C. The calcination step may for example be carried out for a period of time in the range of from 2 to 24 hours, e.g. from 3 to 8 hours.

In some embodiments, the dried coated substrate or calcined coated substrate is subjected to a reduction step by treatment with hydrogen, prior to use. For example, a flow of hydrogen gas may be passed over/through the coated substrate, e.g. at elevated temperature, such as a temperature in the range of from 400 to 500°C, or about 450°C.

In some embodiments, the reduction step is carried out for a period in the range of from 2 to 6 hours, or from 3 to 5 hours, or about 4 hours.

In another aspect, there is provided a catalyst-coated structured reactor produced or producible by a method as defined herein.

It has been found that example catalyst-coated structured reactors produced according to the above methods have comparatively low particle size of active catalyst particles (e.g. NiO particles). It has also been found that example catalyst-coated structured reactors produced according to the above methods can be obtained with a high degree of uniformity in terms of catalyst particle size and/or in terms of dispersion on the surface of the substrate.

In another aspect, there is provided a catalyst-coated structured reactor comprising:

a structured reactor substrate which is formed of an electrically conductive material that is capable of generating heat *via* magnetic induction, and which is coated with a nickel-based catalyst,

wherein the catalyst coating comprises active catalyst (e.g. NiO) nanoparticles having a mean particle diameter in the range of from 20 to 80 nm.

In some embodiments, the catalyst coating comprises active catalyst (e.g. NiO) nanoparticles having a mean particle diameter in the range of from 30 to 70 nm, or from 40 to 60 nm, or about 50 nm.

In some embodiments, at least 50% of the active catalyst (e.g. NiO) nanoparticles have a particle diameter in the range of from 20 to 100nm, or from 20 to 90nm, or from 20 to 80nm, or from 30 to 70nm, or from 40 to 60nm.

In some embodiments, at least 60% of the active catalyst (e.g. NiO) nanoparticles have a particle diameter in the range of from 20 to 100nm, or from 20 to 90nm, or from 20 to 80nm, or from 30 to 70nm, or from 40 to 60nm.

In some embodiments, at least 70% of the active catalyst (e.g. NiO) nanoparticles have a particle diameter in the range of from 20 to 100nm, or from 20 to 90nm, or from 20 to 80nm, or from 30 to 70nm, or from 40 to 60nm.

In some embodiments, at least 80% of the active catalyst (e.g. NiO) nanoparticles have a particle diameter in the range of from 20 to 100nm, or from 20 to 90nm, or from 20 to 80nm, or from 30 to 70nm, or from 40 to 60nm.

5 In some embodiments, at least 90% of the active catalyst (e.g. NiO) nanoparticles have a particle diameter in the range of from 20 to 100nm, or from 20 to 90nm, or from 20 to 80nm, or from 30 to 70nm, or from 40 to 60nm.

In some embodiments, at least 95% of the active catalyst (e.g. NiO) nanoparticles have a particle diameter in the range of from 20 to 100nm, or from 20 to 90nm, or from 20 to 80nm, or from 30 to 70nm, or from 40 to 60nm.

10 In some embodiments, catalyst (e.g. NiO) nanoparticles are substantially uniformly dispersed on the surface of the substrate.

The sphericity of particles may vary. Where a particle is not spherical, the term particle diameter will be understood as referring to being the diameter of a sphere having an equivalent volume to the volume of the particle.

15 Mean particle diameter can be determined using any suitable technique. For example, it may be determined using scanning electron microscopy (SEM). Alternatively, it may be determined using transmission electron microscopy.

SEM and/or TEM may provide two-dimensional images. Where SEM/TEM is used, if an imaged particle is not circular, the term particle diameter will be understood as referring to
20 being the diameter of a circle having an equivalent area to the area of the imaged particle.

In some embodiments, particle diameter is determined using TEM, and using the following protocol:

- 4mg of sample is placed in a 2 mL protein tube, 1.5ml water is added, with the tube then being vortexed and then sonicated to form a colloidal mixture;
- 25 - 1.3µL of the prepared mixture is drop case on to a plasma-cleaned Cu TEM grid coated with holey carbon, and the grid is then dried under inert gas flow.
- TEM imaging is carried out using and FEI Tecnai G2 T20 Twin TEM operating at 200 kV accelerating voltage, with micrographs being taken of groups of particles at an appropriate magnification (e.g. in the range of from 15kx to 80 kx);
- 30 - Micrographs are analysed using an appropriate software package, such as Gatan Digital Micrograph.
 - o A representative range of particles is selected for analysis

- The diameter of particles is determined using the equivalent circle technique, e.g. using the 'oval annotate' function in Gatan Digital micrograph.

In some embodiments, particle diameter is determined using TEM using the methodology described in the examples.

5

Uses of Catalyst-Coated Structured Reactors

Example catalyst-coated structured reactors have been shown to provide strong performance in catalysing chemical transformations. Accordingly, in another aspect, there is provided use of a catalyst-coated structured reactor as defined herein, in a process for producing a chemical product.

10

In some embodiments, the process for producing a chemical product is a process comprising reaction of gaseous reactants. In some embodiments, the process is for producing syngas. In some embodiments, the process is for dry reforming of methane (i.e. reaction of methane and carbon dioxide to produce carbon monoxide and hydrogen).

15

In some embodiments, the process for producing a chemical product is a reverse water gas shift reaction. In some embodiments, the process for producing a chemical product is for steam methane reforming (e.g. reaction of methane with steam to produce hydrogen, carbon monoxide and carbon dioxide). In some embodiments, the process for producing a chemical product is for bi-reforming of methane (e.g. reaction of methane with carbon dioxide and steam to produce syngas with a hydrogen to carbon monoxide ratio of about two). In some embodiments, the process for producing a chemical product is for tri-reforming of methane (a combination of CO₂ reforming, steam reforming and partial oxidation of methane). In some embodiments, the process for producing a chemical product is for CO or CO₂ methanation.

20

In another aspect, there is provided a process for dry reforming of methane, comprising:

25

reacting carbon dioxide and methane in a catalyst-coated structured reactor as defined herein, at elevated temperature, to produce hydrogen and carbon monoxide.

In such a process, a feed of carbon dioxide and a feed of methane is provided to the catalyst-coated structured reactor. Any suitable feed flow ratio (i.e. the ratio of the volume of the feed gases) may be provided. In some embodiments, the feed flow ratio of carbon dioxide to methane is in the range of from 2:1 to 1:2, or in the range of from 1.5:1 to 1:1.5 or about 5:4.

30

The reaction may be carried out at any suitable temperature, for example it may be carried out at a temperature in the range of from 800 to 1000°C, or from 850 to 950°C, or about 900°C.

Magnetic induction heating is typically used. For example, an induction coil may be arranged around the outside of a container containing catalyst-coated structured reactor (e.g. wrapped around it). An example of such a system is the Ambrell Easyheat Induction system.

The reactor is typically insulated from the environment to reduce energy losses.

5 A cooling fluid (such as water) may be used to cool the induction coil during operation, if desired.

Weighted hourly space velocity (WHSV) is the total volumetric feed (in litres) going into a reactor per hour per unit weight of catalyst loaded in the reactor. In some embodiments, the WHSV is in the range of from 4000 to 100000 L/h.kg_{Cat}. In some embodiments, the WHSV
10 is in the range of from 4000 to 5000 L/h.kg_{Cat}. In some embodiments, the WHSV is about 4500 L/h.kg_{Cat}. In some embodiments, the WHSV is in the range of from 10,000 to 30,000 L/h.kg_{Cat}. In some embodiments, the WHSV is about 20,000 L/h.kg_{Cat}. In some embodiments, the WHSV is in the range of from 50,000 to 70,000 L/h.kg_{Cat}. In some embodiments, the WHSV is about 60,000 L/h.kg_{Cat}.

15 In some embodiments, that process achieves at least 30%, or at least 40%, or at least 50%, or at least 60%, or at least 70%, or at least 80% conversion of carbon dioxide.

In some embodiments, that process achieves at least 30%, or at least 40%, or at least 50%, or at least 60%, or at least 70%, or at least 80% conversion of methane.

Any suitable arrangement of reactors may be used in the process. For example, if
20 desired multiple catalyst-coated structured reactors may be used in parallel, each being provided with a flow of reactants. Such an arrangement may facilitate larger scale operations. Such an arrangement may also be useful for maintaining operations during cleaning activities, or for catalyst regeneration and/or replacement. For example, some of the reactors may be in operation, whilst others are offline being cleaned, treated to regenerate catalyst, or replaced.

25 Reaction sampling may be carried out. For example, the reaction temperature can be monitored, e.g. using an optical pyrometer. The apparatus may be configured containing one or more sampling valves pre- and/or post- allowing sampling of reactants and/or products.

The products exiting the reactor can be stored or used, e.g. in further chemical transformations.

30 For example, the products may be subjected to the Fischer-Tropsch process, to produce hydrocarbons and water (e.g. by reaction in a reactor containing a suitable catalyst, such as an iron- or cobalt-based catalyst, and at elevated temperature, for example in the range of from 150 to 300°C).

Accordingly, in some embodiments, the process comprises the step of reacting hydrogen and carbon monoxide to produce one or more hydrocarbons and water.

The present disclosure is further illustrated by the following non-limiting examples.

5 **Examples**

Example 1: Preparation, characterisation and use of catalyst precursor solution-treated structured reactors

EXPERIMENTAL

10 **Fabrication of 3D Printed Monoliths**

Gyroid and octet monolith structures were designed in the nTopology platform. A cylindrical volume was defined with a diameter of 20 mm and height of 50 mm. A unit cell was then defined with either the gyroid or octet structure. The cylindrical volume was then filled with the unit cell and the size and inner wall thickness of the unit cell adjusted to achieve 50%
15 infill. A minimum of 0.4 mm wall thickness was used to ensure printability. The nTopology file was then converted to a meshed .STL file and sliced in Netfabb (Autodesk) with 0.25 um layer thickness.

3D printing was performed on a Concept Laser MLab R (GE), using INCONEL-625 powder (Sandvik) with a 5 – 45 µm particle size distribution. The laser parameters were
20 optimised for maximum density, and were as follows; laser power = 95 W, scan speed = 1050 mm/s, hatch distance = 0.08 mm and layer thickness of 0.025 mm. Printing was conducted under an argon atmosphere, with oxygen content kept below 0.2%.

Catalyst Precursor Solution Preparation

25 To prepare NiO/Ce_{0.8}Gd_{0.2}O_{2-δ} catalyst, nickel nitrate hexahydrate Ni(NO₃)₂·6H₂O 99.99% (Sigma Aldrich) was used as Ni metal precursor. Cerium nitrate hexahydrate Ce(NO₃)₃·6H₂O 99.99% (Sigma Aldrich) and Gadolinium nitrate hexahydrate Gd(NO₃)₃·6H₂O 99.99% (Sigma Aldrich) were used as precursors to prepare mixed oxide catalyst support. Polyvinylpyrrolidone (PVP) (Sigma Aldrich) was used as a binding agent, Potassium hydroxide
30 KOH ACS reagent ≥85% (Sigma Aldrich) was used for adjusting the basicity of the support and co-precipitation. 12 wt.% Ni and 88% (80% CeO₂-20% Gd₂O₃) mixed oxide support was synthesised using co-precipitation method. To synthesise 0.2M catalyst solution, calculated

amount 2.34 g of Nickel nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added in milli-q water (193.8 mL). After constant stirring for about 30 minutes at room temperature (20 °C), 10.91 g of Cerium nitrate hexahydrate $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 99.99% trace metals basis (Sigma Aldrich) and 2.53 g of Gadolinium nitrate hexahydrate $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 99.99% trace metals basis (Sigma Aldrich) were added in the same beaker. The pH of the solution was checked through Hannah pH meter after 30 minutes (3.5 pH). To adjust the basicity of the support, KOH was added in adjusted amount for the pH to achieve value of 9.5. The solution was stirred for 30 minutes and heated at 80 °C for 4 hours on a hot plate. To adjust the viscosity of the solution, water soluble Polyvinylpyrrolidone (PVP) was added 5 wt.% into the solution. This precursor solution is then used for the dip-coating procedure of monoliths. Mass before and after the coatings were calculated and the monoliths were calcined at 300 °C for 2 hours with 2°C/min ramp up and then to 500 °C with 2°C/min ramp up. Coated monolith was then introduced to quartz tube for the reaction to take place.

To prepare Ni/SBA-15 catalyst, measure 68.011 mL of 37 wt% Hydrochloric Acid solution (12.1784M, univAR™) in measuring beaker. Measure out 346.17 mL of Milli-Q water and add it to the HCl to make 2M HCl solution. The HCl solution was then placed inside a Schott bottle, and 13.810g of P123 Pluronic was placed inside the solution while being stirred vigorously at 40 °C for 24 hours. 32.710 mL of reagent grade TEOS Tetraethyl orthosilicate (reagent grade, 98% Sigma Aldrich) was then filled inside a burette and added dropwise to the solution, and the solution was left stirring vigorously at 40 °C for 24 hours. 5.945 g Nickel nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 99.99% (Sigma Aldrich) was measured and placed inside the Schott bottle. 110 mL of 2M KOH was added to co-precipitate and adjust the pH of the precursor solution. The pH was adjusted to 9.5 to 10 and solution was kept at stirring and heating at 80 °C for 4 hours under reflux. Polyvinylpyrrolidone (PVP) was then added (6.666 g) to 133.3 mL of Milli-Q water (5 wt.% PVP) into the solution and kept stirring overnight.

To prepare Ni/MgO catalyst solution, Add 238.785 mL of Milli-Q Water to the Schott Bottle. Weigh out 55.983 g of Magnesium Nitrate Hexahydrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ACS reagent, 99% (Sigma Aldrich) and add to the Schott Bottle. Constantly stir while under heating at 80 °C. Check initial pH of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution in Schott bottle using pH strip (pH = 5). Weigh out 5.945 g of Nickel nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 99.99% (Sigma Aldrich) and add to the heated mixture. Add 140 mL solution of 1M KOH ACS reagent ≥85% (Sigma Aldrich) to

the solution and then wait for 5 mins. Check pH of solution using pH strip (pH = 10). Place in an oil bath under constant stirring at 80 °C. Wait for 10 mins under constant stirring, then check for pH. Add 133 mL of 5wt% PVP to the solution.

- 5 To prepare Ni/MgO-MCM-41 Sandwiched catalyst, abovementioned Ni/MgO procedure was followed to coat Ni/MgO active catalyst layer. MCM-41 solution was separately synthesised to sandwich the active layer of Ni/MgO catalyst. MCM-41 solution was prepared 360 mL of milli-q water was added to the schott bottle. 7.2 g of Hexadecyltrimethylammonium bromide (CTAB, BioXtra, $\geq 99\%$ Sigma Aldrich) was added to the schott bottle and stirred until
- 10 the solution was homogeneous. 24 mL of Ammonia solution 32%, univAR™ was added to the mixture and stirred for 15 minutes. 30 mL of TEOS Tetraethyl orthosilicate (reagent grade, 98% Sigma Aldrich) was added to a burette and added dropwise to the solution under stirring. Leave the solution under stirring overnight.

15 **Pre-treatment of the INCONEL-625 Monoliths**

- INCONEL-625 monoliths were pre-treated with 20 v/v% HNO₃ (Nitric Acid) aqueous solution. The nitrification was done for 24 hours followed by ageing the monoliths in acetone for 24 hours. The monoliths were washed with milli-q water several times and pressure cleaned with compressed air. The monoliths were washed again with water and kept under oven-drying
- 20 for 24 hours at 100 °C. The monoliths were then cooled down and weighed using weighing balance.

Procedure for the Dip-Coating of the INCONEL-625 monolith

- Dip-coating technique involved a dip-coater (Dip-Coater Filmlift FL-1 (MGW
- 25 Lauda, Königshofen, Germany) with variable dipping and withdrawal velocities. The dip-coater has a clamping support for the substrate/monolith to vertically align with the precursor solution in the beaker. The solution in the 250 mL beaker was under constant magnetic stirring at 500 RPM. The dipping velocity was set at 50 cm/min and withdrawal velocity was set at 50 cm/min. The dipping time was 7 hours for the to increase the coating mass and enhanced wetting time.
- 30 The concentration of the solution was kept approximately constant for each coating cycle. 8 cycles of coating were performed for both type of the geometries. Mass before and after the coating were calculated. Volume difference of precursor solution being evaporated or getting into the channels of monolith was noted before and after each coating.

Catalyst Characterisation Techniques

Precursor solution based coated catalyst and slurry based coated catalyst were exposed to X-ray diffraction analysis using Rigaku Miniflex powder diffractometer with mono-chromatized CuK α radiation ($\lambda = 0.154$ nm) at 40 kV and 15 mA to investigate the structure, metal crystal phases and crystal size. The crystallography of the catalyst was confirmed by X-ray diffraction analysis (XRD) using Rigaku Miniflex600 XRD. The 2θ range of 10° – 90° with a step size of 0.10° and speed of 5 deg/min were used. Gas product concentration was measured quantitatively with gas chromatography using Shimadzu 2014 GC-MS. CHNS analysis was conducted using Thermo Scientific FlashSmart CHNS analyser to identify the fresh and spent NiO/Ce_{0.8}Gd_{0.2}O_{2- δ} catalyst for Carbon, Hydrogen, Nitrogen and Sulphur content of samples. FEI Quanta 3D Dual Beam Microscope was used for Scanning Electron Microscopy using EBSD and ETD detectors to analyse the morphology and uniformity of coating onto the monoliths. Micromeritics 3Flex-nitrogen porosimetry was used to calculate the BET surface area of the fresh and spent NiO/Ce_{0.8}Gd_{0.2}O_{2- δ} catalyst.

Procedure for Determining Particle Size from TEM Micrographs.

Sample Preparation

4 mg of powder sample was placed in a 2mL protein tube. 1.5mL Milli-Q ultrapure water was added to the tube. The tube was vortexed for two minutes before being batch sonicated for 15 minutes. The powder did not completely disperse into a colloidal solution and larger particles settled to the bottom of the tube quickly.

A Cu TEM grid coated with holey carbon was plasma cleaned for 20 seconds before 1.3 μ L of the prepared solution was drop cast onto the grid. The prepared solution was shaken by hand and the 1.3 μ L volume was taken from the lower third of the protein tube. The grid was then dried under gentle N₂ gas flow. The TEM sample was prepared the same day it was imaged.

TEM Imaging

The FEI Tecnai G2 T20 Twin TEM, operating at 200kV accelerating voltage, was used to image the samples. At low to moderate magnifications (15kx – 80kx) micrographs of groups of particles were taken.

Particle Size Analysis

Micrographs were viewed and analysed in the Gatan Digital Micrograph software package. From each micrograph a range of particles were selected for analysis.

The particles' morphology was somewhat inhomogeneous, but could be approximated to spherical if averaged across all particles. As such, each selected particle was approximated as a circle using the 'oval annotate' function in Gatan. The diameter of that circle was then recorded as the approximate size of the particle.

The sample means were calculated along with the standard deviation.

Catalytic Activity Measurements

DRM reaction was carried out at a feed ratio of 5:4 CO₂:CH₄. Coated gyroid monolith without wall is denoted by GWW (Gyroid Without Wall) and the gyroid monolith with wall is denoted by GW (Gyroid Walled). The 3D printed INCONEL-625 monolith reactor basically comprises of Ni, Cr, Mo and Fe. This highly stable, corrosion-resistant monolith reactor has been printed in Gyroid unit cell structure. One reactor was made with wall and another reactor was made without wall. The monolithic INCONEL-625 reactors have been made in 50 cm in length and 20 cm in diameter. The wall thickness for monolith reactor with wall was 2 cm.

Ambrell Easyheat Induction system was used to perform the experiments. The coil wrapped the quartz tube reactor with monolith sitting at the middle of the quartz tube. The catalyst was reduced in situ at 450 °C for 4 hours with Hydrogen (H₂) while providing 32 A of electric current. For both the reactors the Amperage of current varied due to change in structural properties which affect coupling of the material with current. After reduction, more current was provided to raise the temperature to 900 °C which is thermodynamically feasible temperature range for the reaction to take place. CO₂ and CH₄ were introduced into the quartz tube with 5:4 CO₂:CH₄ feed flow ratio. 4500 L/h.kg_{cat} weight hourly space velocity (WHSV) was used for the reaction. Cooling water was constantly provided for the cooling of the coil. The reactor was well insulated with glass wool to avoid any energy losses. The experiment was run with sampling after ever 1h. Temperature of the reactor was continuously measured using optical pyrometer at different lengths of the monolith reactor. Reactant conversions were calculated by the eq (5), where R can be any reactant species (CO₂ or CH₄) [6] ,

$$X_{(R)} (\%) = \left(\frac{F_{Rin} - F_{Rout}}{F_{Rin}} \times 100 \right) \quad (5)$$

H₂/CO ratio and the product yield (mol/kg_{cat}.h) were calculated by the following equations (6-7) respectively [6],

$$\text{H}_2/\text{CO Ratio} = \left(\frac{F_{\text{H}_2\text{out}}}{F_{\text{COout}}} \right) \quad (6)$$

and

$$\text{Yield (mol/kg}_{\text{cat}}\text{.h)} = \left(\frac{F_{P\text{out}}}{\text{Amount of catalyst coated (kg)}} \right) \quad (7)$$

Where P can be any product specie (H₂ or CO), R can be any reactant specie (CO₂ or CH₄), F_{in} and F_{out} are molar flowrates (μmol/min) of the species going in and out of the reactor respectively.

10 Results and Discussion

Catalyst coating deposition and specific loading

It was observed that the GWW monolith showed excellent characteristics by depositing almost 4.08 g of catalyst with a significant higher specific catalyst loading. This is due to the influence of a 2 mm wall in GW monolith that creates a barrier in wetting and hence, lower deposition and specific loading is observed. Whilst the GW monolith was satisfactory, it was observed in case of the walled monolith Figure 4(a); capillary action was prominently taking place restricting the precursor solution to fully draw into the channel voids. Surface tension between a liquid and the solid surface of a monolithic material causes a liquid, such as a solvent, to be drawn into the microchannels of the material. The increased surface area-to-volume ratio in microchannels amplifies this effect and causes a higher capillary force [7].

Catalytic performance for dry reforming of methane

The reaction studies showed that the reactant conversion, H₂/CO ratio and product yield were significantly higher in case of GWW as compared to GW. The reaction were run at a same weighted space hourly velocity of 4500 L/h.kg_{Cat}. Catalyst deposition in case of GWW was 4.08 g with a specific catalyst loading of 0.788 g/cm² after 8 cycles of coating, whereas in case of GW, 1.38 g of catalyst was coated after completing 8 cycles of coating. GWW showed a high conversion of 86.3% and 98.5% for CO₂ and CH₄ respectively as compared to GW where it was possible to achieve 62% conversion for CO₂ and 36.5% for CH₄. This is mainly due to the major side reaction of Reverse Water Gas Shift Reaction eq. (2). which depends on the

different feed ratios of the reactant gases. Higher CO₂ conversion in case of GW could be due to unreacted methane and could be due to poor methane activation, pore blockage and reduced active surface area. The catalyst was active and stable in both cases with 42 h of activity in case of GWW and showed no signs of deactivation. In addition to this, no pressure drop was detected across the monolith gyroid reactors.

XRD analysis

The spectra in Figure 8. show peaks relating to cubic GDC (Gadolinium Doped Ceria) solid solution (JCPDS-PDF No. 75-0161) [8]. XRD of precursor solution coated NiO/Ce_{0.8}Gd_{0.2}O_{2-δ} and slurry coated NiO/Ce_{0.8}Gd_{0.2}O_{2-δ} were analysed. NiO supported on Gadolinium doped Ceria slurry obtained by suspending the powder catalyst into water followed by addition of the binder, show sharp peaks of GDC support and NiO peaks are evident at the relevant 2θ region. In case of the slurry coated catalyst, crystallite size of NiO is 22.5 nm while the crystallite size of the Ce-Gd solid solution support is 7.5 nm using Scherrer Equation. Contrary to this, no NiO peaks were seen with the NiO/Ce_{0.8}Gd_{0.2}O_{2-δ} precursor coated catalyst. The crystallite size of GDC support was calculated as 10.1 nm in case of the precursor coated catalyst with no evident NiO peak. It might be due to high dispersion of NiO over the CeO₂ support and additionally NiO could be in the amorphous form. XRD of precursor solution coated NiO/Ce_{0.8}Gd_{0.2}O_{2-δ} and slurry NiO/Ce_{0.8}Gd_{0.2}O_{2-δ} were analysed. NiO supported on Gadolinium doped Ceria slurry obtained by suspending the powder catalyst into water followed by addition of the binder, show sharp peaks of GDC support and NiO peaks are evident at the relevant 2θ region. With the slurry coated catalyst, crystallite size of NiO is 22.5 nm while the crystallite size of the Ce-Gd support is 7.5 nm. Weak or no NiO peaks were seen with the NiO/Ce_{0.8}Gd_{0.2}O_{2-δ} precursor coated catalyst. The crystallite size of GDC support was calculated as 10.1 nm in case of the precursor coated catalyst with no evident NiO peak. Absence of any peaks belonging to Gd₂O₃ compared to the host CeO₂ lattice (5.410 Å), further confirms the formation of Ce_{0.8}Gd_{0.2}O_{2-δ} (GDC) solid

Textural and morphological properties (SEM Analysis)

Fresh and spent catalyst show clear difference in their structure morphology, due to greater exposure to the gas flow and long-time on-stream activity, structure of the spent catalyst has changed and caused it to look more like a sponge with voids as evident from Figure 9(b). This is justified from the surface area and pore size analysis. The BET surface area of the

catalyst dropped from 18.56 m²/g to 1.84 m²/g. The textural and morphological analysis of the coated catalyst can be observed from Figure 9. It is evident from Fig 9(c) and Fig 9(e) that the catalyst solution has well impregnated into the channels of gyroid monolith. Additionally, from Figure 9, catalyst can be seen on the substrate at the interior walls of the monolith. This could be due to enhanced deposition of the precursor solution within the voids of the monolith. However, colour contrast imaging can exhibit catalyst particle grown on the wall. As the material of the monolith is INCONEL-625 containing Ni, BSED detector and ETD detector might not illustrate a colour gradient. Catalyst was stable and abrasion resistant to a high extent. This makes the catalyst more stable and provides great interaction between the catalyst and substrate itself. No evident signs of coking were observed in the morphological studies of this catalyst. Both GWW and GW monoliths showed homogeneity in catalyst growth and provided great deposition of the catalyst without blocking the channels of gyroid geometry. Coking was not observed in this analysis as the topology of the catalyst did not show any graphitic carbon (needles, carbon whiskers, nanotubes or onions) in the imaging. Overall, great deposition, uniformity and homogeneity of the catalyst was observed in the imaging of coated structured reactor.

CHNS Analysis of the Fresh and Spent Catalysts

CHNS analysis was performed to analyse the carbon, hydrogen, nitrogen and sulphur content in the fresh and spent catalysts. The catalyst was recovered from the GWW and GW monoliths after completion of reaction studies while the catalyst was still active and stable. It was observed that there was no significant coke deposition on the recovered catalyst. Literature suggests that in previous studies, catalyst showed deactivation after even few hours, time on stream. Whilst in this study, catalyst showed promising catalytic activity and stability even after 42 h time on stream. PVP is composed of long chain hydrocarbons, primarily consisting of carbon content. After calcination process, PVP decomposes between a temperature range of 250 °C to 600 °C depending up on its molecular weight [9]. Catalyst was calcined at 550 °C which is in the range of PVP decomposition, however, some might have not decomposed which results in 0.32% C in the fresh catalyst.

Table 1. CHNS analysis of fresh and spent catalyst

Fresh Catalyst	Spent Catalyst
Carbon %	Carbon %
0.32	1.04

Temperature and Power profile of Monoliths

Gyroid monoliths were exposed to high temperatures to analyse their heat and power profiles with respect to time. It was observed that the monolith without wall took just a little over 100 s to achieve 1000 °C temperature which can be seen from Figure 10(a). Contrary to this, almost 250 s were taken by the Gyroid without wall monolith to achieve the same conditions. Both monoliths successfully achieved 1000 °C temperature within 4 minutes time. Since the generated eddy currents in a solid material will be more concentrated and produce more heat per unit volume compared to a porous material, the heating rate of a solid wall geometry will typically be higher than that of a porous geometry. However, a porous material's precise heating rate will also be influenced by its porosity, pore size distribution, and electrical conductivity in both the solid and fluid phases [10]. The effectiveness of magnetic induction heating is also be impacted by the geometry of a solid wall or porous material. Our study demonstrates that a thicker solid wall may take longer to heat through entirely than a thinner or no wall. This is brought on by the eddy currents' requirement to travel a greater distance. Similar to this, a porous geometry that is more complicated and has a greater surface area to volume ratio than one that is simpler and has a lower surface area to volume ratio could experience more heating. It depends on the presence of conductive elements that can produce eddy currents, magnetic induction heating is not successful for all materials. Additionally, the alternating magnetic field's frequency can have an impact on the effectiveness of heating, with higher frequencies typically producing faster heating but also more energy losses as a result of electromagnetic interference [11-13].

Power profile showed the trend that monolith without the boundary wall consumes more power and couples less efficiently as compared to the walled monolith, as the solid wall couples much efficiently with the induction coil. From Figure 10(b) it is noted that 500 W of power was taken by GW to achieve 1000 °C mark as compared to 585 W taken by GWW monolith, hence making GW more energy efficient.

Conclusions

This study demonstrates the use of clean and sustainable source of energy for dry reforming of methane reaction that is conventionally run using firebox which is run using natural gas / CH₄. Magnetic induction heating has proven to be a great source of energy for DRM reaction as it couples greatly with the INCONEL-625 alloy and couples power efficiently. The findings show that both geometries of gyroid structure i.e. with wall and without wall perform very well with induction heating system. Use of a coated catalyst monolith reactor is an efficient way of carrying out DRM reaction as it does not promote coke formation and allows zero pressure drop against high throughput of reactant gases. With normalized 4500 L/h.kg_{cat} WHSV, it was possible to achieve a high conversion for CO₂ and CH₄ (86.3% and 98.5% respectively) with GWW monolith. The influence of wall shows better energy efficiency; however, it decreases exposed area of the monolith reactor and does not allow high catalyst deposition. In addition to this, the walled monolith provides minimal contact of gases with the catalyst due to solid boundary wall that hinders the wetting tendency of the monolith during coating cycles. Overall magnetic induction heating is an excellent way of energy for DRM reaction to produce syn gas using coated reactors.

Example 2: Particle analysis of samples which were a) surface coated by immersion in a catalyst precursor solution of NiO/Ce_{0.8}Gd_{0.2}O_{2-δ}, b) surface coated with a slurry of NiO/Ce_{0.8}Gd_{0.2}O_{2-δ}, or c) fresh powdered catalyst.

TEM and Electron diffraction for NiO catalyst with CeO₂-Gd₂O₃ supports

Precursor Coated Catalyst:

The precursor sample consisted of dense aggregates of ~20-40nm diameter nanoparticles and lower concentration groups of larger ~20-100nm diameter nanoparticles. Selected area electron diffraction (SAED) patterns were taken for both aggregates and lower density groupings. SAED 1, taken from a lower density grouping, gave a diffraction pattern dominated by the crystal planes of NiO (Figure 11a). SAED 2, taken from an aggregate of smaller particles, gave reflections for support structures (CeO₂ primarily), but no indication of NiO (Figure 11b).

Lattice analysis of the precursor sample agrees with the SAED patterns: all larger particles (ranging between 20-100nm diameter) examined were composed of NiO. Figure 12

shows one of the groups of NiO particles at low magnification and a single particle at high magnification. Aggregates, such as the area examined in SAED 2, were not investigated in HRTEM as the stacking of particles makes it very difficult to image the lattices of single crystals.

In summary: the precursor sample is not uniform with aggregates of support nanostructures forming while NiO nanoparticles remained separate, dispersed through the sample. NiO nanoparticles were roughly spherical without significant morphological control. The size ranged between 20-50 nm for single crystal NiO nanoparticles, while some NiO nanoparticles appear to have fused together to create larger structures up to 150nm across.

Slurry Coated Catalyst

The slurry sample consisted primarily of large aggregates (Figure 13a) with some smaller clusters of particles (Figure 13b). The majority of particles fall between 10-20nm in diameter.

SAED was taken in three areas (two aggregates and a large cluster). As can be seen in Figure 14, these diffraction patterns do not indicate the presence of NiO at all.

Lattice fringe imaging was conducted for multiple particles from small clusters. Only one cluster displayed interplanar spacings consistent with NiO. This cluster, along with the lattice spacing analysis, is shown in Figure 15. Every other lattice fringe was consistent only with the support structures.

Based on lattice fringe imaging and the SAED patterns obtained, it is clear that very little NiO is present in the slurry sample. Some very small particles (~2-5nm diameter) are likely NiO, but these particles make up a small proportion of the sample.

SEM for NiO catalyst with CeO₂-Gd₂O₃ supports

Precursor Coated Catalyst:

SEM images are shown in Figure 16. Potential Z-contrast in background aggregates of small particles. This matches NiO particles found in TEM. Large particles (up to ~30um diameter) of support structure. No large particles of NiO were observed in the precursor coated catalyst. Particles are observed to be more dispersed and much more uniform than those observed in the slurry-coated catalyst.

Slurry Coated Catalyst:

SEM images are shown in Figure 17. Many larger particles are formed in case of the slurry-coated catalyst. NiO is forming into large particles, discrete particles between $\sim 10 \mu\text{m}$ to $\sim 50 \mu\text{m}$ diameter. CeO₂ and Gd₂O₃ are indistinguishable from z-number contrast. However, NiO particles can be seen distinguished by the potential Z-contrast in the background.

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Fresh Powdered Catalyst:

SEM images are shown in Figure 18. Fresh powder catalyst particles are in the range of $2 \mu\text{m}$ to $100 \mu\text{m}$. Particles fused together to form larger particles of around $100 \mu\text{m}$ or greater. SEM images are taken using BSED and they show Z-contrast in the particles. Ni having a smaller atomic number of 28 as compared to Cerium 58 and Gadolinium 64. It shows a darker contrast compared to the Gadolinium doped ceria support. Darker particles in the SEM images belong to NiO and they are within the range of $2 \mu\text{m}$ to $100 \mu\text{m}$.

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Table 2. NiO particle size comparison in the NiO/Ce_{0.8}Gd_{0.2}O_{2- δ} catalyst

Precursor Coated Catalyst (nm)	Slurry Coated Catalyst (μm)	Fresh Powder Catalyst (μm)
20-100	10-50	2-100

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TEM analysis of the precursor coated catalyst illustrated that the particle size of NiO are nanoparticles ranging from 20-100 nm in diameter and the lattice analysis of the precursor sample agrees with the SAED patterns: all larger particles (ranging between 20-100 nm diameter) examined were made up of NiO. In case of the slurry coated catalyst, larger particles of NiO were observed which were not been able to analysed in the TEM analysis due to larger particle size of NiO. Particle size of slurry coated catalyst were analysed using BSED imaging of sample using SEM. Z contrast exhibited darker NiO particles compared to the support particles and the NiO particles were in the range of $10\text{-}50 \mu\text{m}$. In case of the fresh powder catalyst, particles were clustered and agglomerated and showed a particle size of $2\text{-}100 \mu\text{m}$ in diameter. These particles were observed in the SEM (BSED) imaging having a Z-contrast compared to the support particles.

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Conclusions:

Nanoparticles of NiO are uniformly present in the precursor-coated sample with average particle size $\sim 50 \text{ nm}$. The size of most of these NiO particles ranges from 20-100 nm in diameter. In slurry coated catalyst, NiO was not detected in TEM analysis, this is due to the

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micron range particles which do not suspend on the TEM grind. From SEM analysis it is evident that the slurry-coated sample resulted in NiO particles of 10-50 μm despite of the same loading as the precursor-coated sample. The particle size observed in the fresh powder catalyst range from 2 μm to 100 μm . These particles aggregated to form large particles of around 100 μm in diameter. This concludes that the particles made up from the precursor solution show more dispersion and are in nanoparticle range compared to the slurry coated catalysts which have larger particle size and lower dispersion.

Example 3: Catalyst coating of different structured reactor designs.

Gyroid Monolith

A gyroid monolith was printed with an outer wall of 2 mm and an inner diameter of 10mm. The total surface area of the monolith was 6756 mm². This monolith was dip-coated with NiO/GDC precursor solution for 7 hours and it deposited 222.9 mg of the catalyst in 3 coating cycles. Each cycle consisted of coating and drying. At the end of the coating cycles, the monolith was calcined. The catalyst showed excellent adhesion and homogeneity across the monolith. The monolith was printed on Concept laser Mlab with 90x90x80mm-built capacity. Images of the printed monolith, and after coating, are shown in Figure 19. Gyroid showed a slightly higher amount of catalyst deposition than octet and Voronoi monoliths, comparing first three coating cycles (discussed below).

Octet Monolith

An octet monolith was printed with an outer wall of 2 mm and an inner diameter of 10mm. The total surface area of the monolith was 7021 mm². This monolith was dip-coated with NiO/GDC precursor solution for 7 hours and it deposited 346.7 mg of the catalyst in 8 coating cycles. Each cycle consisted of coating and drying. At the end of the coating cycles, the monolith was calcined. Coating cycles were increased to get an estimate of the monolith depositing more catalyst with stability and avoiding pore blockage. The catalyst showed excellent adhesion and homogeneity across the monolith and did not show any pore blockage. The monolith was printed on Concept laser Mlab with 90x90x80mm-built capacity. Images of the printed monolith, and after coating, are shown in Figure 20.

Voronoi Monolith

A Voronoi monolith was printed with an outer wall of 2 mm and an inner diameter of 10mm. The total surface area of the monolith was 6423 mm². This monolith was dip-coated with NiO/GDC precursor solution for 7 hours and it deposited 232.2 mg of the catalyst in 4 coating cycles. Each cycle consisted of coating and drying. At the end of the coating cycles, the monolith was calcined. The catalyst showed excellent adhesion and homogeneity across the monolith. The monolith was printed on Concept laser Mlab with 90x90x80mm-built capacity. Images of the printed monolith, and after coating, are shown in Figure 21.

Catalyst deposition versus number of coating cycles is shown for the 3 monoliths in Figure 22. The octet monolith was dipped with 5h coating time and 7h coating time to verify the influence of dipping time. Longer dipping time provided improved results. The gyroid monolith had the highest loading after the 3rd coating cycle.

Example 4: Catalyst coating of structured reactors using different catalysts

In addition to the NiO/GDC (NiO/Ce_{0.8}Gd_{0.2}O_{2-δ}) catalyst, other catalysts such as Ni/SBA-15 and Ni/MgO were coated onto the substrate. The monolith was gyroid having an inner diameter of 20mm and a length of 50mm. It was observed that catalyst loading with Ni/SBA-15 and Ni/MgO was uniform, adhered very well and performed excellently in catalytic activity, with the Ni/MgO catalyst showing the best activity results of the two catalysts at comparable Weight Hourly Space Velocities (WHSVs). The monoliths were printed on Concept laser Mlab with 90x90x80 mm-built capacity. Figure 23 shows the catalyst-coated monoliths.

A further catalyst-coated structured reactor was prepared. A sandwiched Ni/MgO-MCM-41-coated monolith was prepared. This is shown in Figure 24. The catalytic reactor proved to be the best candidate in terms of catalytic activity, stability and resistance to coking. The catalyst showed a high surface area of 349m²/g having mesoporous size. This provides nil pressure drop, and has been tested at 100,000 L.h⁻¹kg⁻¹_{cat}. 99% conversion of both reactants was achieved in the DRM process using the catalytic reactor until WHSV was 40,000. At WHSV 100,000, 87% and 83% conversion were achieved for CO₂ and CH₄ respectively. The monolith was printed on Concept laser Mlab with 90x90x80mm-built capacity.

Catalyst deposition versus number of coating cycles is shown for the monoliths in Figure 25. Lower amounts of catalysts were loaded with the experiments involving additional catalysts, to achieve higher weight hourly space velocity (WHSV). With lower loading, and keeping flow rate constant, it is possible to achieve high WHSV.

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Example 5: Catalytic performance for dry reforming of methane – further catalysts

Experiments to assess performance of additional catalyst-coated structured reactors were carried out using similar conditions to those as for Example 1.

Ni/SBA-15 Catalyst

Ni/SBA-15 catalyst showed reasonable activity and stability for 12 h time on stream and showed a conversion of 59.02% for CH₄ and 64.93% conversion for CO₂ at 6000 L/h.kg_{cat} of WHSV. Results are shown in Figure 26. The catalyst did not show any signs of coking, however, other MgO-based catalysts illustrated a higher catalytic activity at relatively higher WHSVs.

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Ni/MgO Catalyst

Coated Ni/MgO gyroid monolith was exposed to the dry methane reforming reaction. 0.535 g of catalyst was coated onto the monolith. Various WHSVs were tested, the DRM reaction was carried out at a feed ratio of 5:4 CO₂:CH₄. The results were shown in Figure 27. The catalyst exhibited stability throughout the 42 h run and did not show any signs of coking. 85.1% CO₂ and 97.6% CH₄ conversion were achieved. CH₄ conversion is often higher than CO₂ conversion at lower WHSVs. This is due to the fact that at lower WHSV, the reactant's residence time in the catalyst bed is longer, giving the reaction more time to proceed. Throughout the series of reactions, the H₂/CO ratio is almost 0.97, however, it decreased at a greater WHSV because a dominating Reverse Water Gas Shift reaction was taking place, which produced more CO and consumed more CO₂. Through the series of reactions, a negligible pressure drop of 207 Pa (1.55 mmHg) was noted. The overall mole balance indicates no evidence of obvious coking. Ni/MgO catalyst achieved a high yield of 1800 mol.kg⁻¹_{cat}.h⁻¹ of CO and nearly 1400 mol.kg⁻¹_{cat}.h⁻¹ for H₂. This catalyst performed better than the Ni/SBA-15 and the Ni/GDC catalysts.

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Ni/MgO – MCM-41 Sandwiched Catalyst

Sandwiched catalyst using MCM-41 as a high surface area mesoporous support outperformed all other tested catalysts and provided a high surface area of 349 m²/g. This catalyst was stable at 100000 L/h.kg_{cat} WHSV and exhibited a consistent conversion of CO₂ and CH₄. This catalyst managed to achieve nearly 99.69% conversion for CH₄ and 98.53% for CO₂. The results are shown in Figure 28. No signs of coking were observed through the mole balance and the catalyst was stable for more than 80 h time on stream. Compared to the Ni/MgO catalyst, the sandwiched catalyst showed more than twice the amount of yield of the product gas. Sandwiched catalyst provided a high yield of 3650 mol.kg⁻¹_{cat}.h⁻¹ of CO and nearly 3315 mol.kg⁻¹_{cat}.h⁻¹ for H₂.

Example 6: Kinetic Parameter Estimation

The estimation and optimisation of kinetic parameters were conducted using MATLAB R2023b software based on ordinary differential equations. For kinetic model parametric study, the reaction was carried out on a range of different temperatures (800 °C, 850 °C and 900 °C) in a kinetically controlled regime. The flow rate was increased to 100,000 L.h⁻¹.kg_{cat}⁻¹ to proceed a faster reaction. The reaction was carried out with 5:4 CO₂:CH₄ feed flow ratio with high reactant concentrations to aid the kinetically control regime. Kinetically controlled regimes typically develop when the reaction kinetics are significantly faster than the rates of mass transfer. Essentially, the chemical reaction itself is the rate-limiting step [14].

The reaction rate equation proposed by Richardson and Paripatyadar employed a Langmuir-Hinshelwood rate expression, implemented for this study [15, 16]. Estimation and optimisation of the reaction kinetic parameters for the DRM reaction were based on the following reactions:



The differential equations governing species transport through the reactor were numerically integrated under steady-state conditions utilising the Runge–Kutta method of the fourth order on MATLAB software [17]. The five essential reaction rates have been as specified as follows.

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$$r_1 = \frac{k_1 K_{CO_2,1} K_{CH_4,1} P_{CH_4} P_{CO_2}}{(1 + K_{CO_2,1} P_{CO_2} + K_{CH_4,1} P_{CH_4})^2} \left(1 - \frac{(P_{CO} P_{H_2})^2}{K_{P_1} (P_{CH_4} P_{CO_2})} \right) \quad (\text{Eq 13})$$

$$r_2 = \frac{k_2 K_{CO_2,2} K_{H_2,2} P_{CO_2} P_{H_2}}{(1 + K_{CO_2,2} P_{CO_2} + K_{H_2,2} P_{H_2})^2} \left(1 - \frac{(P_{CO} P_{H_2O})}{K_{P_1} (P_{CH_4} P_{CO_2})} \right) \quad (\text{Eq 14})$$

$$r_3 = \frac{k_3 K_{CH_4,3} \left(P_{CH_4} - \frac{P_{H_2}^2}{K_{P_3}} \right)}{\left(1 + K_{CH_4,3} P_{CH_4} + \frac{1}{K_{H_2,3}} P_{H_2}^{1.5} \right)^2} \quad (\text{Eq 15})$$

$$r_4 = \frac{\frac{k_4}{K_{H_2O,4}} \left(\frac{P_{H_2O}}{P_{H_2}} - \frac{P_{CO}}{K_{P_4}} \right)}{\left(1 + K_{CH_4,4} P_{CH_4} + \frac{1}{K_{H_2O,4}} \frac{P_{H_2O}}{P_{H_2}} + \frac{1}{K_{H_2,4}} P_{H_2}^{1.5} \right)^2} \quad (\text{Eq 16})$$

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$$r_5 = \frac{\frac{k_5}{K_{CO,5} K_{CO_2,5}} \left(\frac{P_{CO_2}}{P_{CO}} - \frac{P_{CO}}{K_{P_5}} \right)}{\left(1 + K_{CO,5} P_{CO} + \frac{1}{K_{CO,5} K_{CO_2,5}} \frac{P_{CO_2}}{P_{CO}} \right)^2} \quad (\text{Eq 17})$$

The reaction rate constant is denoted as k_i , while the thermodynamic equilibrium constants and partial pressures species i are represented as K_i and P_i , respectively. The kinetic parameters that were utilised in the current investigation are detailed in Table 3. Reaction rates are provided in $[\text{mol.kg}^{-1}.\text{s}^{-1}]$, and partial pressures in Pa.

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The continuity equations for species are the following,

$$\frac{dX_{CH_4}}{dz} = \frac{\rho_b \omega L}{F_{CH_4}^\circ} (r_1 + r_3) \quad (\text{Eq 18})$$

$$\frac{dX_{CO_2}}{dz} = \frac{\rho_b \omega L}{F_{CO_2}^\circ} (r_1 + r_2 + r_5) \quad (\text{Eq 19})$$

$$\frac{dX_{CO}}{dz} = \frac{\rho_b \omega L}{F_{CH_4}^\circ} (2 \times r_1 + r_2 + r_4 + 2 \times r_5) \quad (\text{Eq 20})$$

$$\frac{dX_{H_2}}{dz} = \frac{\rho_b \omega L}{F_{CH_4}^\circ} (2 \times r_1 - r_2 + 2 \times r_3 + r_4) \quad (\text{Eq 21})$$

$$\frac{dX_{H_2O}}{dz} = \frac{\rho_b \omega L}{F_{CH_4}^0} (r_2 - r_4) \quad (\text{Eq 22})$$

Here, $F_{CH_4}^0$ and $F_{CO_2}^0$ are the initial molar flow rates of the reactant gases, CH_4 and CO_2 , respectively. X_i represents the conversion of reactant species, i.e. CH_4 and CO_2 , where X_i is the yield for CO , H_2 , and H_2O .

The sum of least squares method is a vital tool in parametric optimisation, specifically when curve fitting and regression analysis are involved. Parametric models, which are articulated as functions with specific parameters requiring optimisation, are utilised in this particular context. The sum of squared errors (SSE), which represents the cumulative squared differences between observed data points and model predictions, is utilised to formulate the objective function. The fundamental optimisation problem attempts to determine the optimal parameter values by minimising this objective function. Diverse methods can be employed to solve this issue, such as iterative approaches like gradient descent for more intricate models or normal equations for linear models. In contrast to the analytical solution provided by the normal equations, gradient descent employs a numerical methodology. It is imperative to evaluate the model's fit post-optimization utilising R-squared and other relevant metrics to ascertain its efficacy in accurately reflecting the underlying data. The sum of least squares method offers a methodical approach to parameter refinement in parametric models, thereby improving their capacity to predict the results [18, 19].

As illustrated in Table 3, the values that changed significantly from the reported literature value were k_1 , k_2 and k_4 . All other parameters were subjected to a fit with least error from the experimental data set. This interprets the significance of the reaction rates of DRM, RWGS and gasification reaction for our kinetic parameters. The activation energies and pre-exponential factors varied from the reported values in Table 3. The activation energies were lower than the literature reported catalyst except the k_1 value which was measured slightly higher than the reported model value, whereas, the pre-exponential factors were generally higher than the literature reported values except k_1 and k_4 values. The optimised parameters are a better fit with our data and they show an inverse trend to the model parameters based on literature.

Despite optimisation, the underestimation of kinetic model values may be a result of a number of factors that were not adequately evaluated during the optimisation procedure. A significant contributing factor is a reaction mechanism in the kinetic model, which may omit

critical reactions or pathways, resulting in an underestimate of conversion values. In addition, the underestimation of the model may result from defects in determining reaction rate constants or excessive sensitivity to these parameters during optimisation. Inadequate consideration of fluctuations in temperature and pressure conditions can potentially compromise the precision of predictions, especially when the model fails to incorporate non-linear adjustments to account for these influences. Mass transfer limitations, including diffusion concerns, may contribute to underestimation if not sufficiently accounted for in the model. Furthermore, substantial discrepancies may arise due to errors in estimating particular parameters during optimisation, which could render the model sensitive to such parameters. Inadequate representation of the system's complexities, uncertainties in experimental data, and the model's structure's complexity all contribute to the underestimation difficulty [20, 21].

Table 3. Thermodynamic constants and rate constants

Parameter (This Work)	Value	Parameter (Model)[9]	Value
k_1	$1.28 \times 10^6 \exp \frac{-105555}{RT}$	k_1	$1.29 \times 10^6 \exp \frac{-102065}{RT}$
k_2	$0.567 \times 10^6 \exp \frac{-72222}{RT}$	k_2	$0.35 \times 10^6 \exp \frac{-81030}{RT}$
k_3	$7.00 \times 10^3 \exp \frac{-58333}{RT}$	k_3	$6.95 \times 10^3 \exp \frac{-58893}{RT}$
k_4	$4.78 \times 10^9 \exp \frac{-157333}{RT}$	k_4	$5.55 \times 10^9 \exp \frac{-166397}{RT}$
k_5	$1.56 \times 10^{15} \exp \frac{-231111}{RT}$	k_5	$1.34 \times 10^{15} \exp \frac{-243835}{RT}$
$K_{CO_2,1}$	$2.61 \times 10^{-2} \exp \frac{37500}{RT}$	$K_{CO_2,1}$	$2.61 \times 10^{-2} \exp \frac{37641}{RT}$
$K_{CH_4,1}$	$2.60 \times 10^{-2} \exp \frac{40600}{RT}$	$K_{CH_4,1}$	$2.60 \times 10^{-2} \exp \frac{40684}{RT}$
$K_{CO_2,2}$	$0.58 \exp \frac{9200}{RT}$	$K_{CO_2,2}$	$0.5771 \exp \frac{9262}{RT}$
$K_{H_2,2}$	$1.50 \exp \frac{6000}{RT}$	$K_{H_2,2}$	$1.494 \exp \frac{6025}{RT}$
$K_{CH_4,3}$	$0.22 \exp \frac{-550}{RT}$	$K_{CH_4,3}$	$0.21 \exp \frac{-567}{RT}$
$K_{H_2,3}$	$5.2 \times 10^7 \exp \frac{-133000}{RT}$	$K_{H_2,3}$	$5.18 \times 10^7 \exp \frac{-133210}{RT}$
$K_{H_2O,4}$	$4.7 \times 10^{-6} \exp \frac{97500}{RT}$	$K_{H_2O,4}$	$4.73 \times 10^{-6} \exp \frac{97770}{RT}$
$K_{CH_4,4}$	$3.50 \exp \frac{0}{RT}$	$K_{CH_4,4}$	$3.49 \times \exp \frac{0}{RT}$
$K_{H_2,4}$	$1.80 \times 10^{13} \exp \frac{-216000}{RT}$	$K_{H_2,4}$	$1.83 \times 10^{13} \exp \frac{-216145}{RT}$
$K_{CO,5}$	$7.50 \times 10^{-6} \exp \frac{100500}{RT}$	$K_{CO,5}$	$7.34 \times 10^{-6} \exp \frac{100395}{RT}$
$K_{CO_2,5}$	$2.80 \times 10^7 \exp \frac{-104000}{RT}$	$K_{CO_2,5}$	$2.81 \times 10^7 \exp \frac{-104085}{RT}$
K_{P_1}	$6.8 \times 10^{14} \exp \frac{-260000}{RT}$	K_{P_1}	$6.78 \times 10^{14} \exp \frac{-259660}{RT}$
K_{P_2}	$55.8 \times \exp \frac{-36500}{RT}$	K_{P_2}	$56.4971 \times \exp \frac{-36580}{RT}$
K_{P_3}	$3.0 \times 10^5 \exp \frac{-84500}{RT}$	K_{P_3}	$2.98 \times 10^5 \exp \frac{-84400}{RT}$
K_{P_4}	$1.38 \times 10^7 \exp \frac{-125000}{RT}$	K_{P_4}	$1.38 \times 10^7 \exp \frac{-125916}{RT}$
K_{P_5}	$1.94 \times 10^9 \exp \frac{-168500}{RT}$	K_{P_5}	$1.9393 \times 10^9 \exp \frac{-168527}{RT}$

Since the sandwiched Ni/MgO@MCM-41 catalyst outperformed all other catalysts on stream activity and remained stable without any signs of coke formation, its reaction kinetics

were investigated in a kinetically controlled regime. The reaction was run with 5:4 ratio of CO₂:CH₄ diluted in Ar (CO₂=9.5%, CH₄=7.5%, Ar=83%). The feed was diluted with Argon to keep the reactant concentrations sufficiently low for the estimation of intrinsic reaction kinetics for DRM on the structured reactor. Figure 29 (a) shows that CO₂ conversion was higher than the CH₄ at all studied temperatures, and displayed a slightly lower conversion at reduced temperatures of 850 °C and 800 °C. CH₄ conversion showed a sharper decreasing trend with the temperature. The H₂/CO ratio kept lowering as the temperature reduced, which confirms the lower yield of H₂, making the RWGS (r₂) reaction dominant at all temperatures as opposed to the others. As all reactions, r₁-r₅, produce CO, its yield was higher than H₂, consumed in the RWGS (Eq. 9) having the highest reaction rate at all temperatures.

The model was based on existing kinetic parameters [17] and the deviation from the experimental values was evident from the model CO₂ and CH₄ conversions. These parameters (Table 3) were optimised for our catalyst based on the sum of least squares parametric estimation. It can be seen from Figure 29 (b), that after the parametric optimisation, the CH₄ model conversion fits reasonably well with our experimental values. However, the model under-predicts the CO₂ conversion by approximately 5-15%. The model deviates more at 800 °C compared to the higher temperatures.

Optimised kinetic parameters in this work are compared with the literature values in Table 4. Rate constants, k₂, k₄, and k₅ were significantly higher than the literature (335%, 138%, and 385%, respectively) at 800 °C. The catalyst in this work is more active for the RWGS reaction (r₂) and the carbon gasification reactions (r₄ and r₅), especially at lower temperatures, but marginally smaller rate constant for r₁. This supports the lack of coke formation observed here.

Table 4 compares the results from this work against the literature values at similar reaction conditions. This work demonstrates high conversion at much higher space velocities than previously reported. Moreover, the Ni/MgO@MCM-41 catalyst was stable for at least 120 h on-stream after which it was collected to carry out post-reaction characterisation.

Table 4. Comparison of rate constants with literature [17]

	Temperature	k_1 (s ⁻¹)	k_2 (s ⁻¹)	k_3 (s ⁻¹)	k_4 (s ⁻¹)	k_5 (s ⁻¹)
This Work	800°C	9.3	172.8	10.1	104.7	8750.2
	850°C	15.8	247.8	13.5	229.6	27730.6
	900°C	25.5	344.6	17.7	471.0	79651.3
From [17]	800°C	13.9	39.7	9.4	44.0	1805.3
	850°C	23.1	59.6	12.7	101.0	6096.5
	900°C	36.8	86.2	16.6	215.9	18558.5
% Difference	800°C	-33%	335%	7%	138%	385%
	850°C	-32%	316%	7%	127%	355%
	900°C	-31%	300%	7%	118%	329%

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CLAIMS

1. A method of making a catalyst-coated structured reactor, comprising
at least partially immersing a structured reactor substrate which is formed of an
5 electrically conductive material that is capable of generating heat *via* magnetic induction, in a
catalyst precursor solution, thereby coating at least part of the surface of the substrate with the
solution;
withdrawing the coated substrate from the solution; and
drying the coated substrate;
10 thereby providing a catalyst-coated structured reactor.
2. The method as claimed in claim 1, wherein the substrate is at least partially immersed in and
withdrawn from the solution a plurality of times.
- 15 3. The method as claimed in claim 1 or 2, wherein the substrate is dip-coated in the solution.
4. The method as claimed in any of claims 1 to 3, wherein the substrate is subjected to multiple
coating cycles, each coating cycle comprising:
1a) at least partially immersing a conductive structured reactor substrate in a catalyst
20 precursor solution, so as to coat at least part of the surface of the substrate with the
solution; and 1b) withdrawing the coated substrate from the solution; wherein 1a) and
1b) are carried out a plurality of times; and
2) drying the coated substrate.
- 25 5. The method as claimed in claim 4, wherein each coating cycle is carried out for a period of
time in the range of from 5 to 10 hours.
6. The method as claimed in any of claims 1 to 5, wherein the dried coated substrate is subjected
to a calcination step.
- 30 7. The method as claimed in any of claims 1 to 6, wherein the dried coated substrate or calcined
coated substrate is subjected to a reduction step by treatment with hydrogen.

8. The method as claimed in any of claims 1 to 7, wherein the substrate is made of a nickel-based alloy.

5 9. The method as claimed in claim 8, wherein the substrate is made of Inconel 625 alloy or C22 alloy.

10. The method as claimed in any of claims 1 to 9, wherein prior to immersion, the substrate is subjected to pre-treatment to prepare the surface for catalyst coating.

10 11. The method as claimed in claim 10, wherein pre-treatment comprises
contacting the substrate with aqueous nitric acid,
contacting the substrate with acetone,
washing the substrate with water, and
drying the substrate.

15

12. The method as claimed in any of claims 1 to 11, wherein the substrate is produced by 3D printing.

13. The method as claimed in any of claims 1 to 12, wherein the substrate comprises a gyroid
20 structure.

14. The method as claimed in any of claims 1 to 13, wherein the substrate does not have a circumferential wall.

25 15. The method as claimed in any of claims 1 to 14, wherein the catalyst which is coated on the substrate is a catalyst for dry reforming of methane.

16. The method as claimed in claim 15, wherein the catalyst is a nickel-based catalyst.

30 17. The method as claimed in claim 16, wherein the catalyst is or comprises Ni/SBA-15, Ni/MgO and NiO/Ce_{0.8}Gd_{0.2}O_{2-δ}, optionally wherein the catalyst is of the formula NiO/Ce_{0.8}Gd_{0.2}O_{2-δ}.

18. The method as claimed in claim 17, wherein the catalyst is Ni/MgO, which is sandwiched between coatings of MCM-41.

19. The method as claimed in any one of claims 1 to 18, wherein the catalyst precursor solution
5 comprises an aqueous solution of metal salts.

20. The method as claimed in claim 19, wherein the catalyst precursor solution is formed from cerium nitrate hexahydrate, gadolinium nitrate hexahydrate and nickel nitrate hexahydrate.

21. The method as claimed in claim 20, wherein the catalyst precursor solution comprises a
10 viscosity adjuster, optionally polyvinylpyrrolidone.

22. A catalyst-coated structured reactor produced or producible by a method of any of claims 1
to 21.

23. A catalyst-coated structured reactor comprising:

a structured reactor substrate which is formed of an electrically conductive material that
is capable of generating heat *via* magnetic induction, and which is coated with a nickel-based
catalyst,

20 wherein the catalyst coating comprises NiO nanoparticles having a mean particle
diameter in the range of from 20 to 80 nm.

24. The catalyst-coated structured reactor as claimed in claim 23, wherein the nanoparticles of
NiO have mean particle diameter in the range of from 40 to 60 nm.

25. The catalyst-coated structured reactor as claimed in claim 23 or 24, wherein the mean
particle diameter is determined using scanning electron microscopy (SEM).

26. The catalyst-coated structured reactor as claimed in any of claims 23 to 25, wherein NiO
30 nanoparticles are substantially uniformly dispersed on the surface of the substrate.

27. Use of a catalyst-coated structured reactor as claimed in any of claims 22 to 26, or as defined
in any of claims 1 to 21, in a process for producing a chemical product.

28. A process for dry reforming of methane, comprising:

reacting carbon dioxide and methane in a catalyst-coated structured reactor as claimed in any of claims 22 to 26, or as defined in any of claims 1 to 21, at elevated temperature, to
5 produce hydrogen and carbon monoxide.

29. The process as claimed in claim 28, wherein the feed flow ratio of carbon dioxide to methane is about 5:4.

10 30. The process as claimed in claim 28 or 29, wherein the reaction is carried out at a temperature in the range of from 800 to 1000°C, optionally about 900°C.

31. The process as claimed in any of claims 28 to 30, wherein the weight hourly space velocity (WHSV) is in the range of from 4000 to 100000 L/h.kg_{Cat}, optionally in the range of from 4000
15 to 5000 L/h.kg_{Cat}, or optionally about 4500 L/h.kg_{Cat}, or optionally in the range of from 10,000 to 30,000 L/h.kg_{Cat}, or optionally about 20,000 L/h.kg_{Cat}, or optionally in the range of from 50,000 to 70,000 L/h.kg_{Cat}, or optionally about 60,000 L/h.kg_{Cat}.

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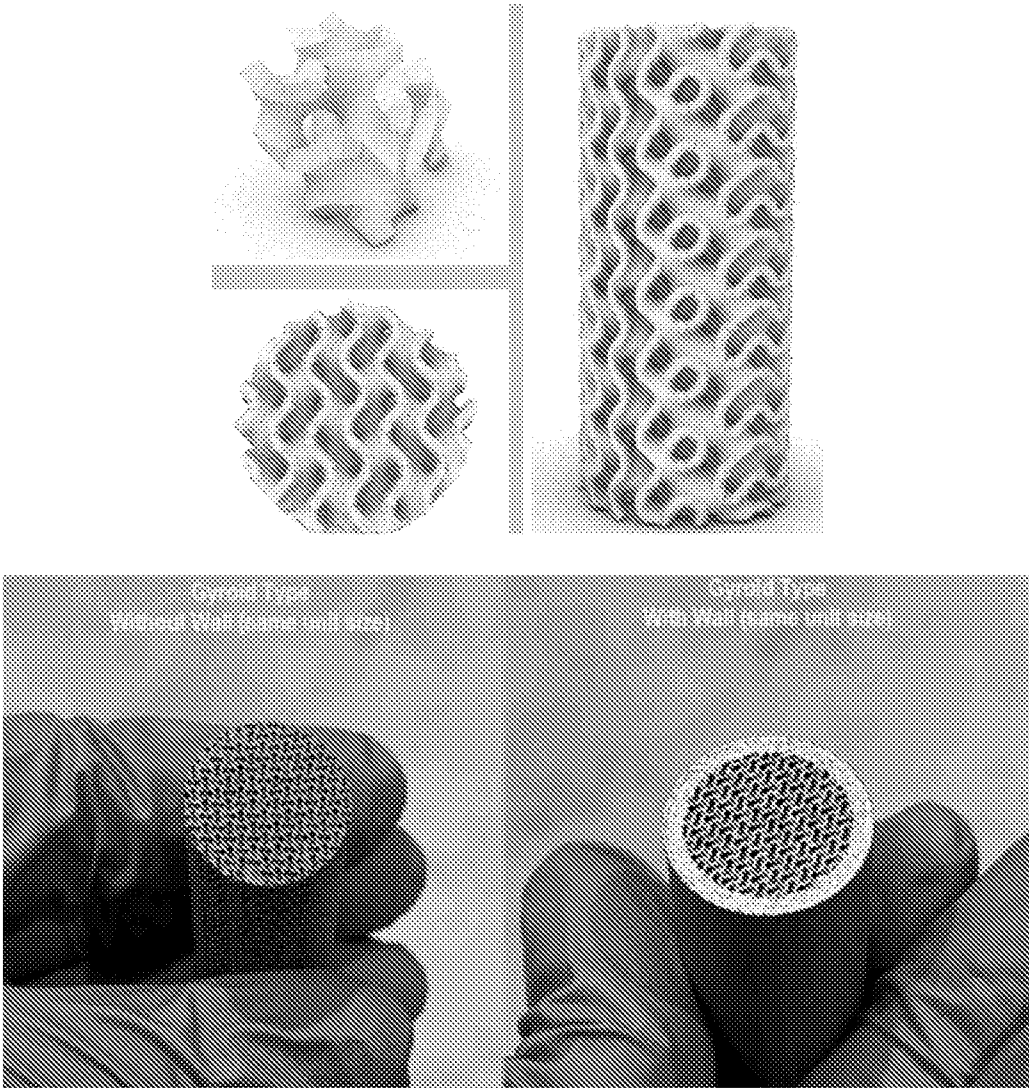


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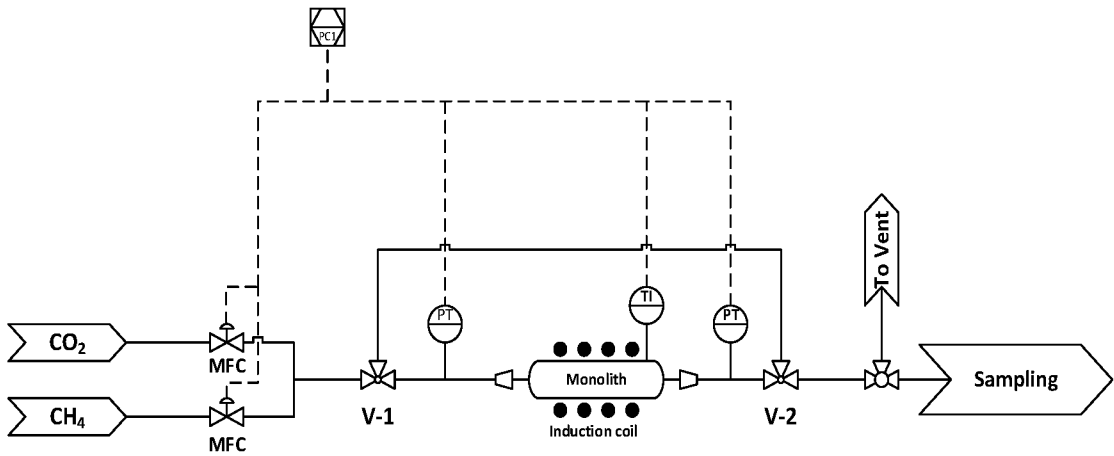


Figure 2

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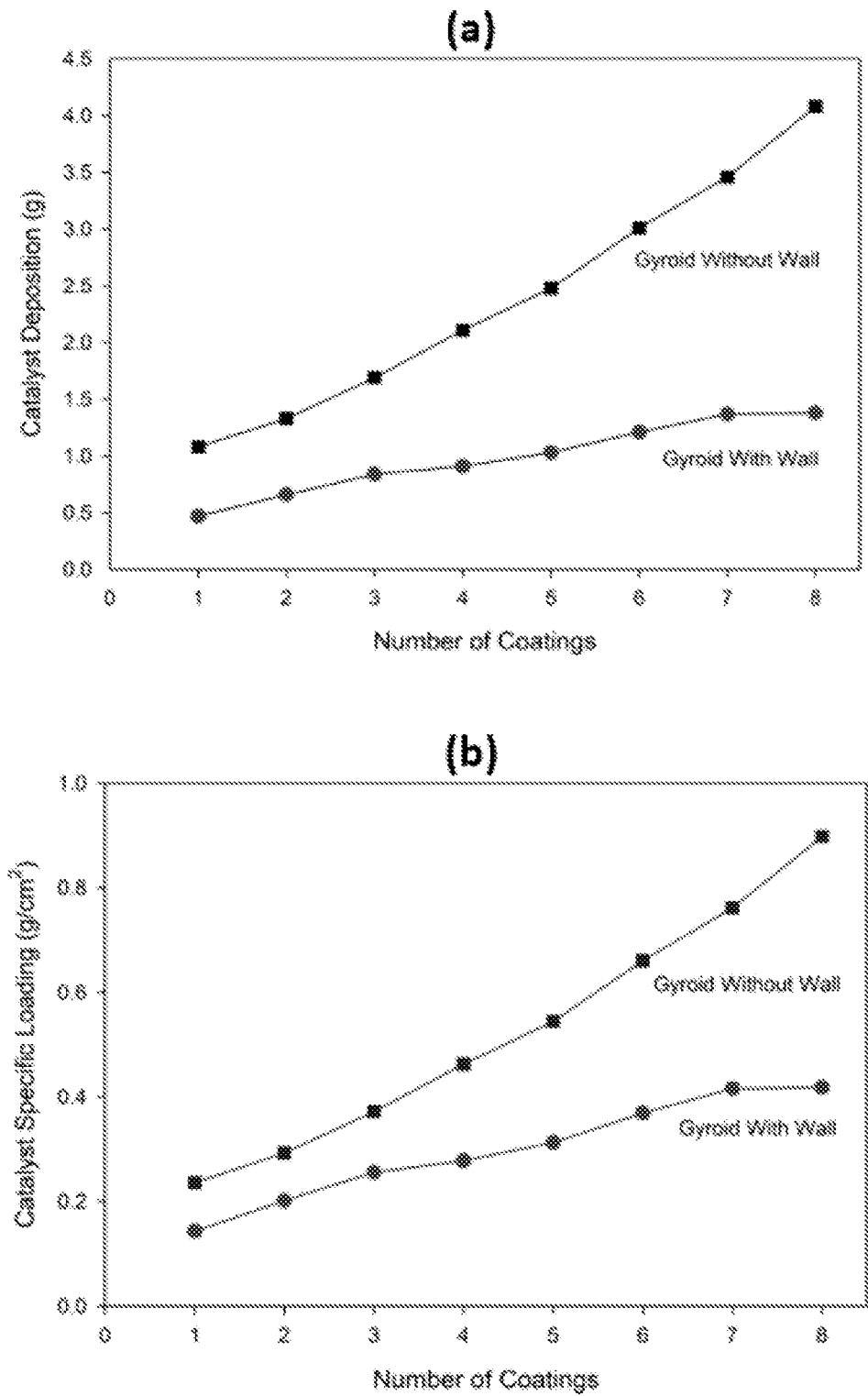


Figure 3

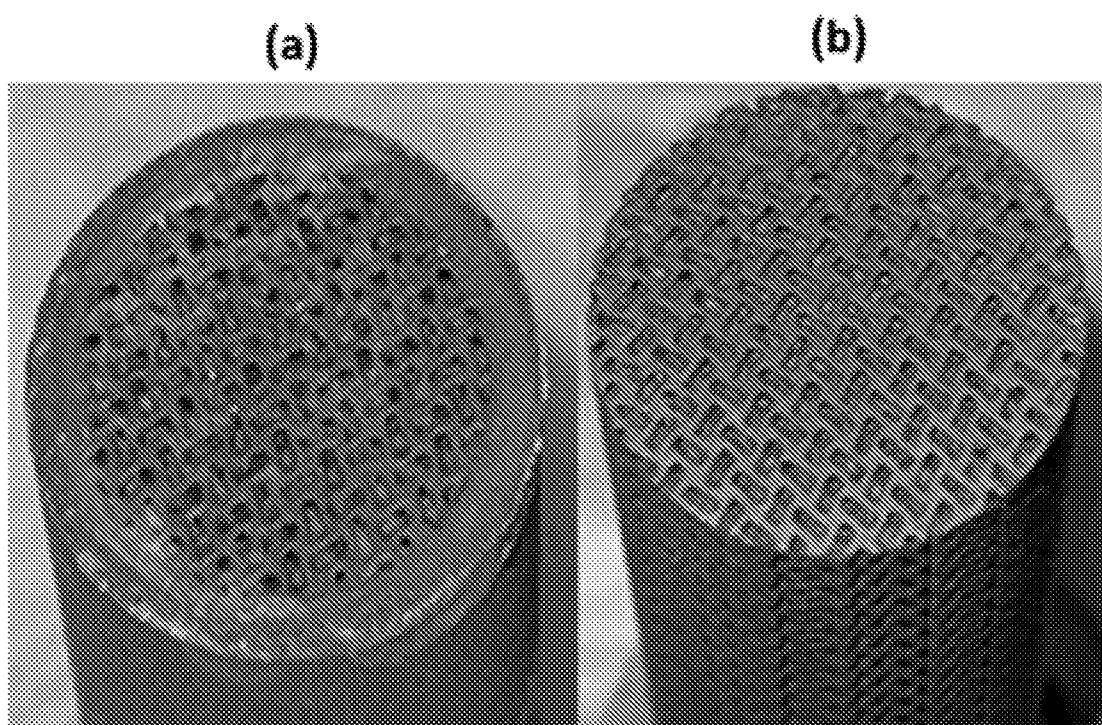


Figure 4

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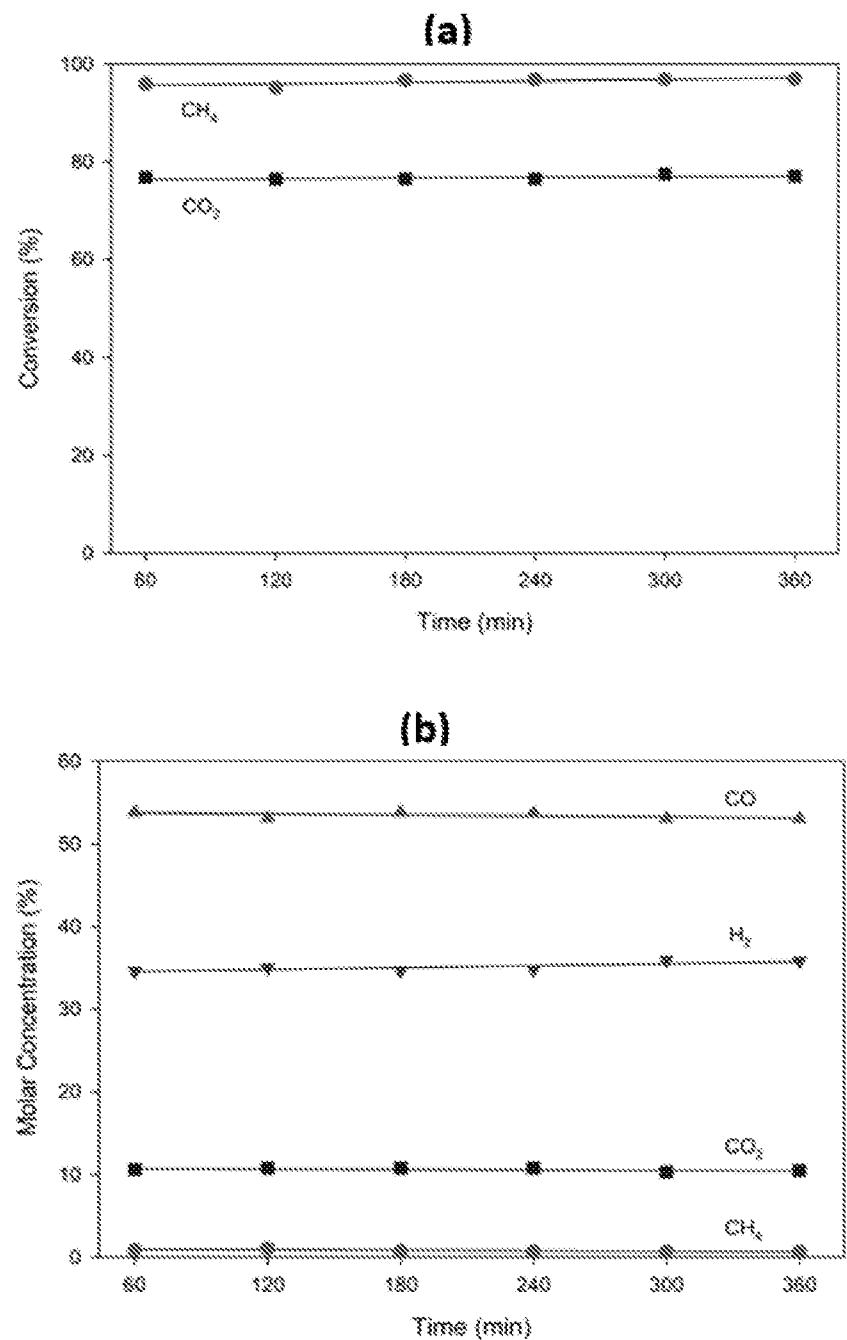


Figure 5

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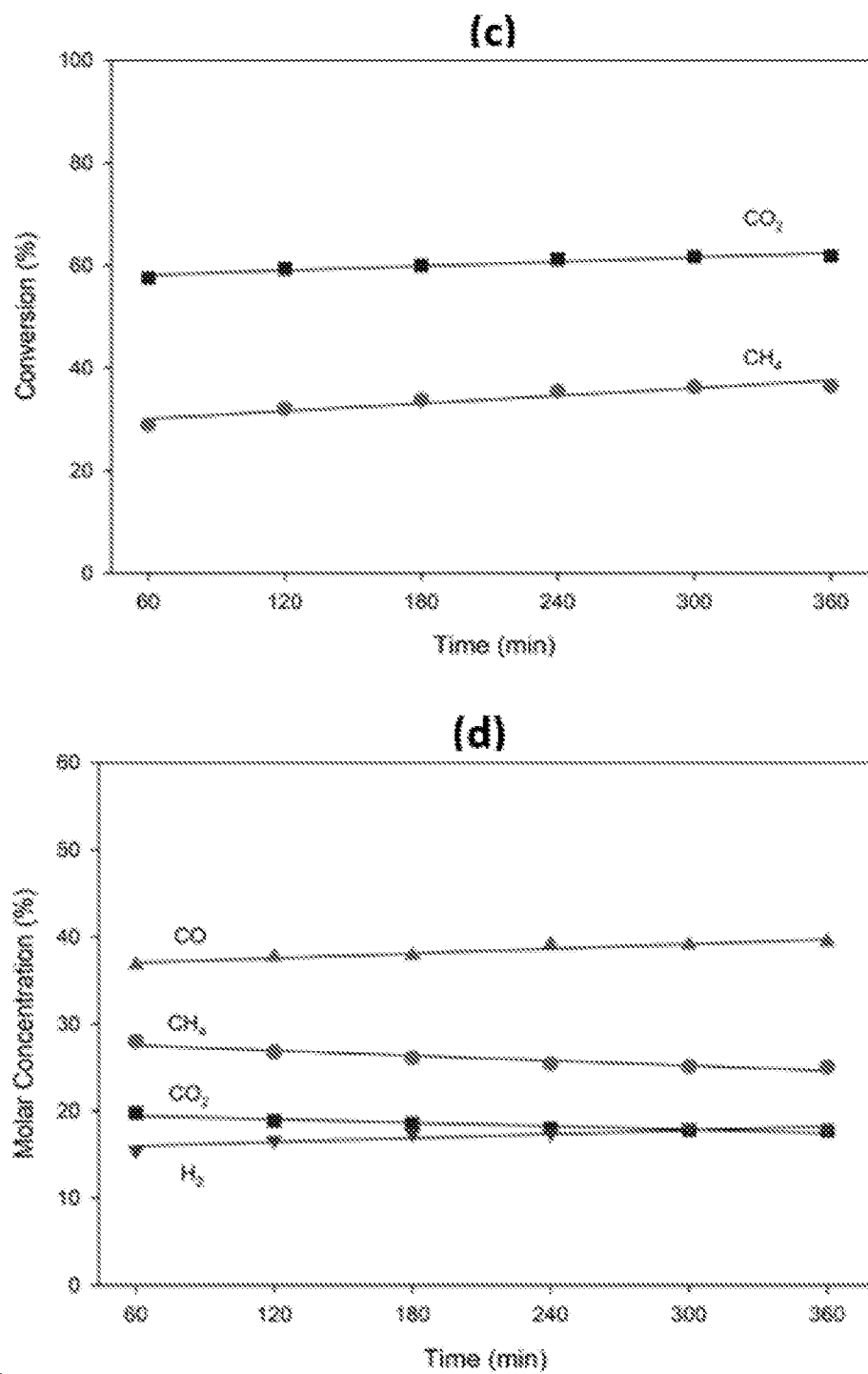


Figure 5 Continued

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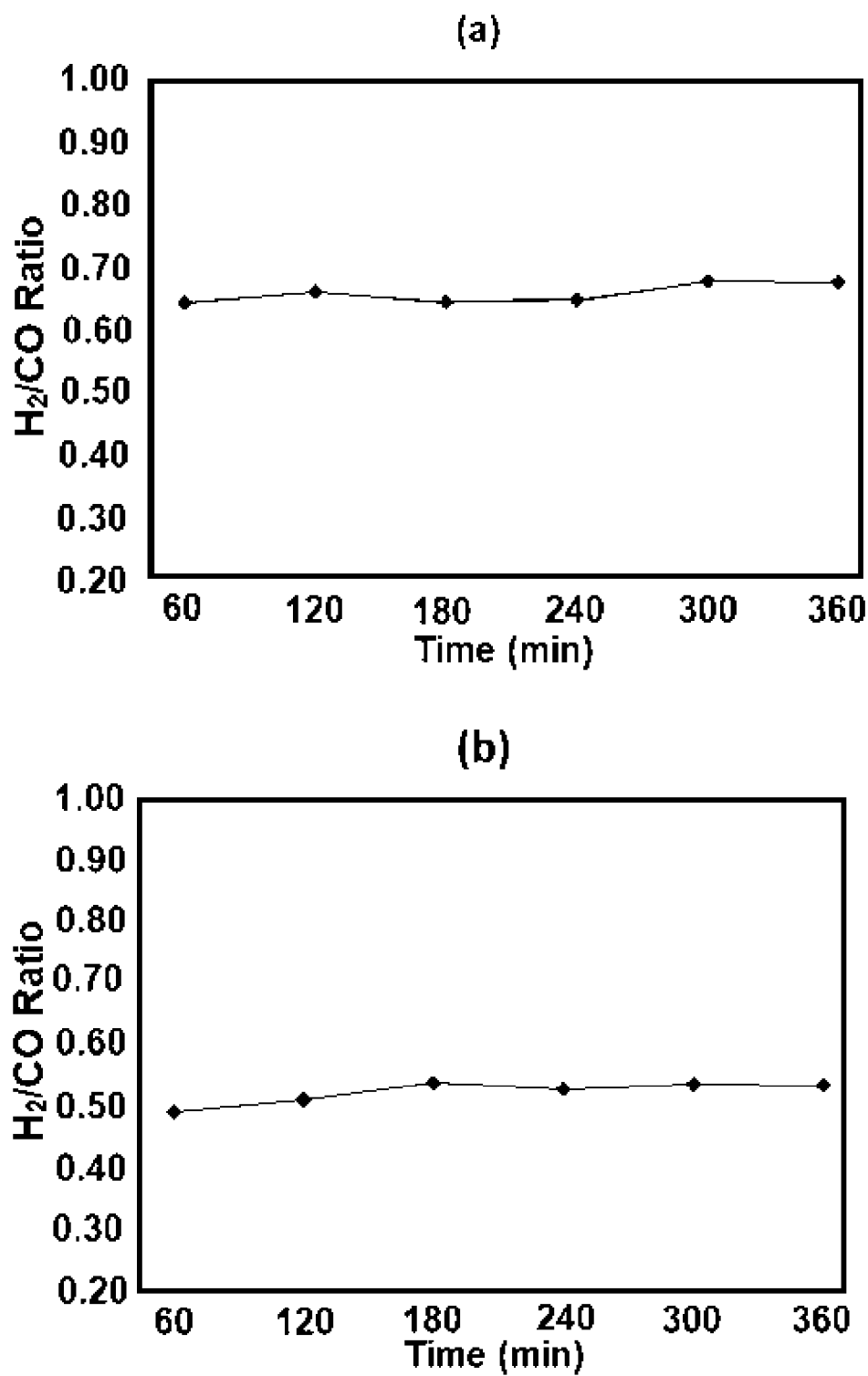


Figure 6

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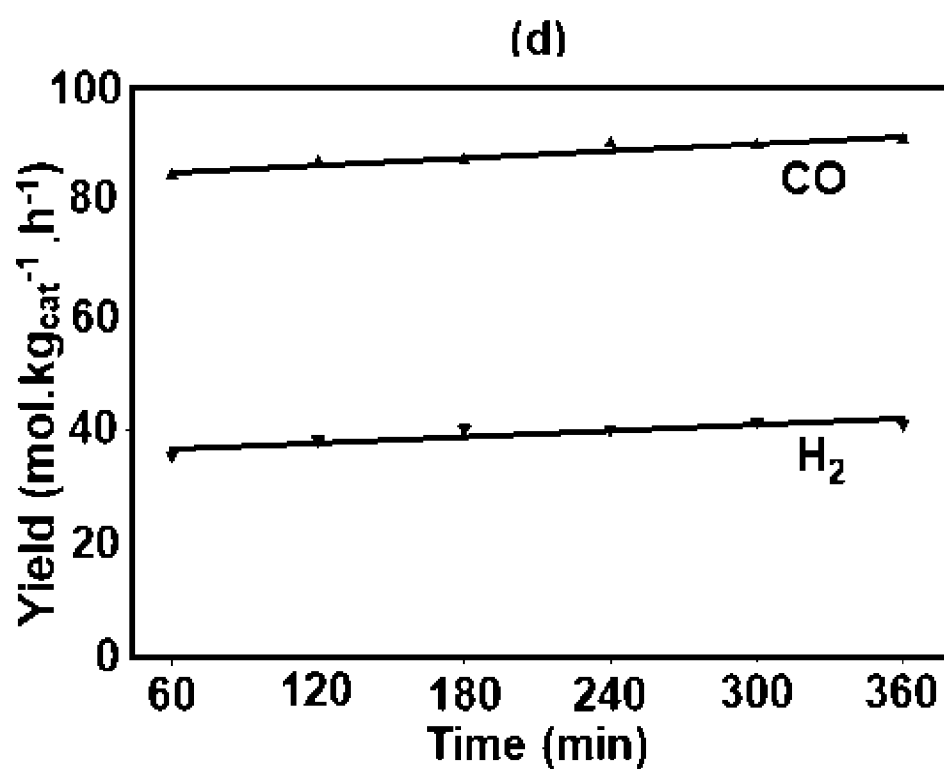
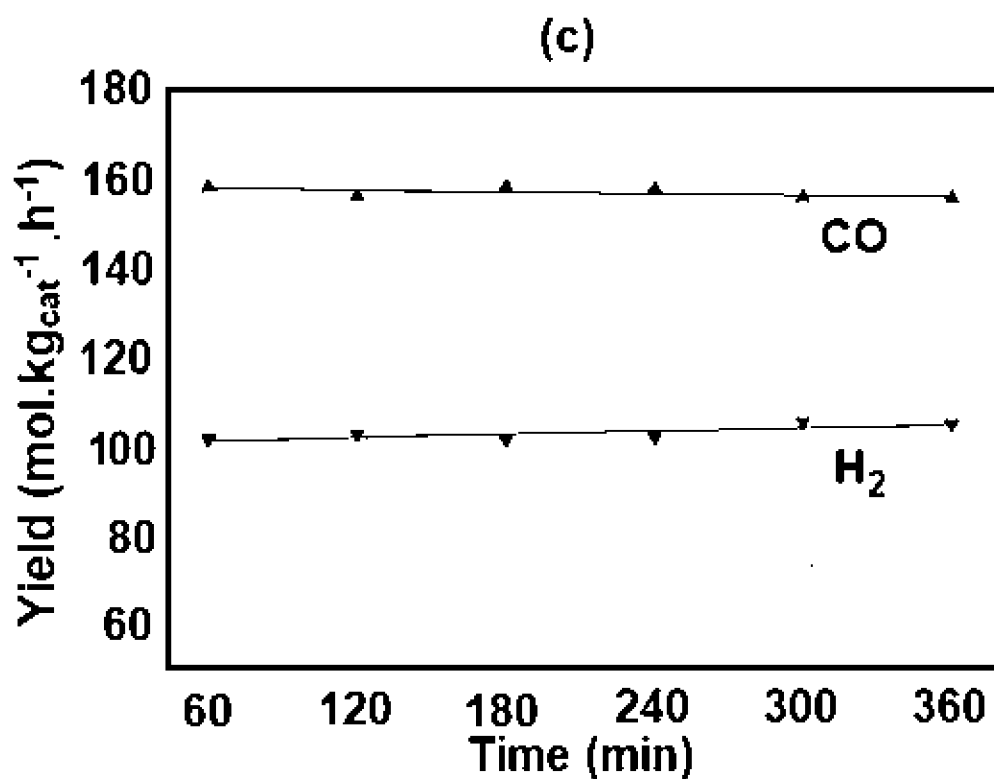


Figure 6 Continued

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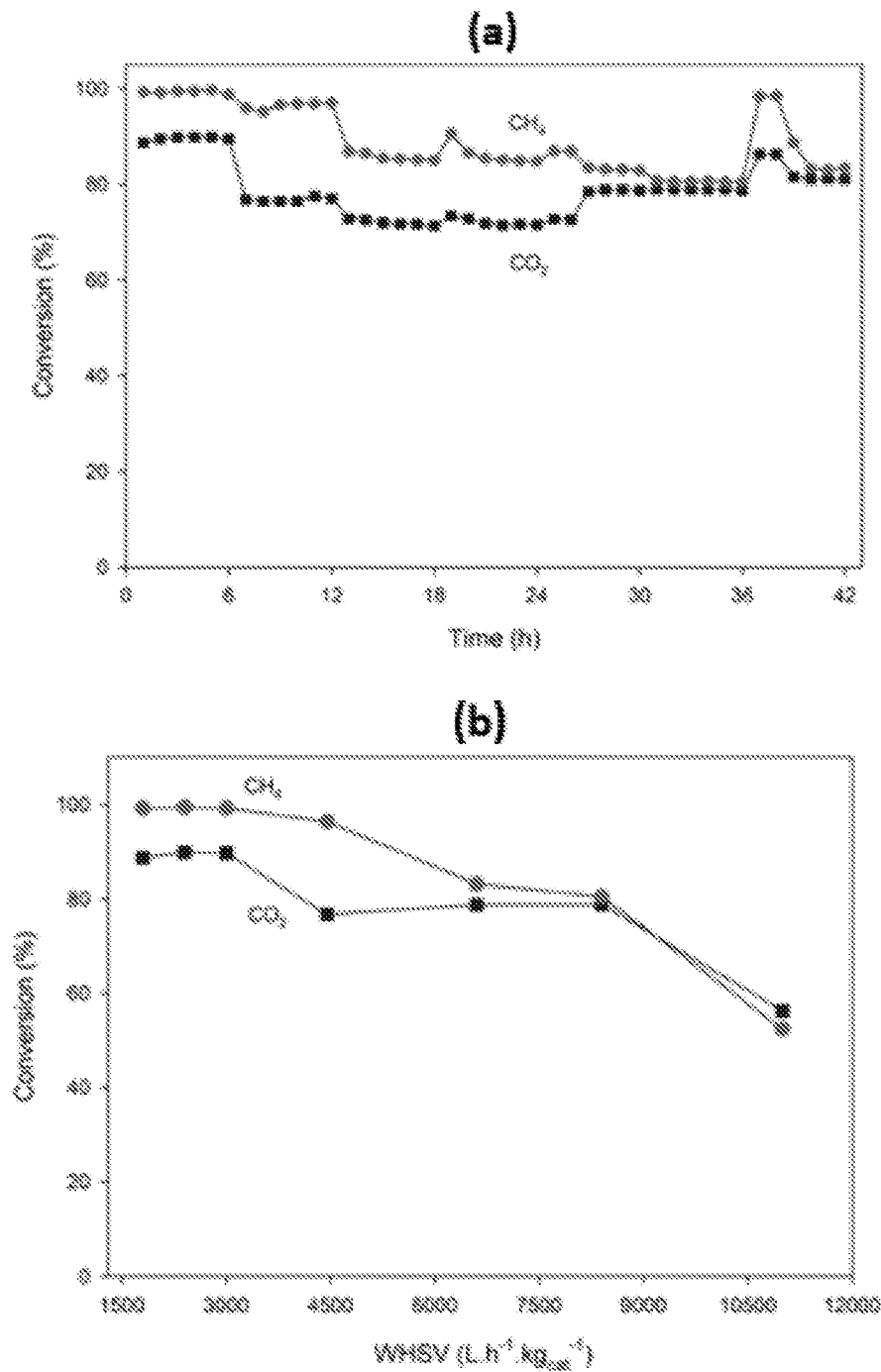


Figure 7

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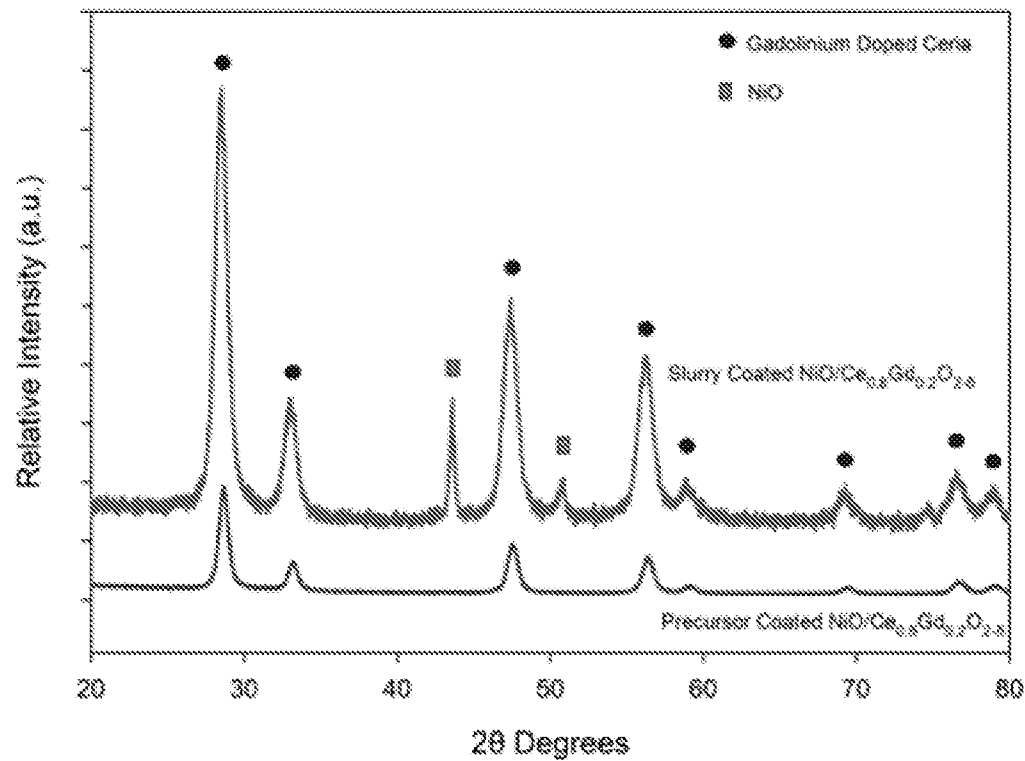


Figure 8

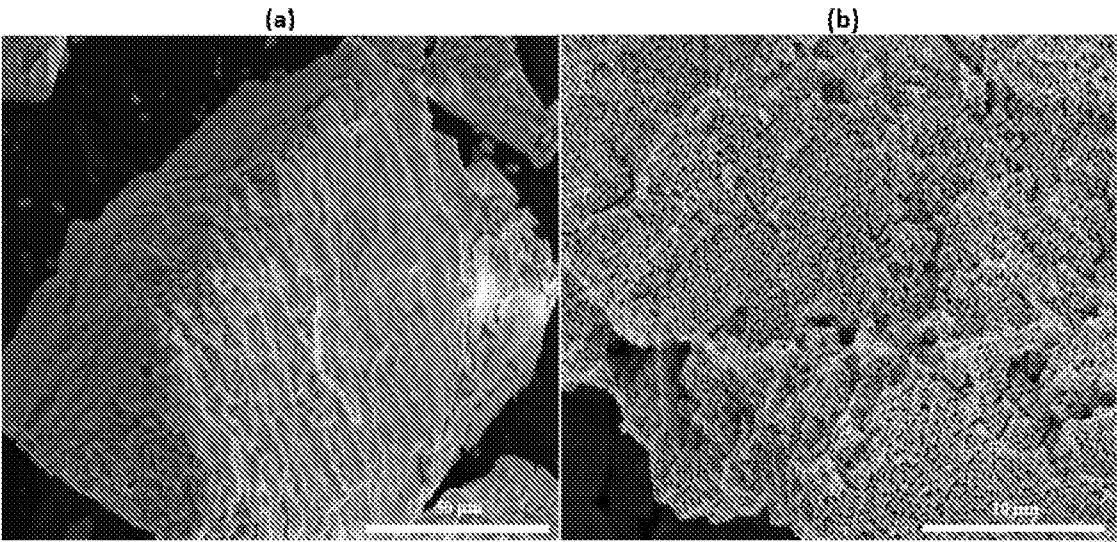


Figure 9

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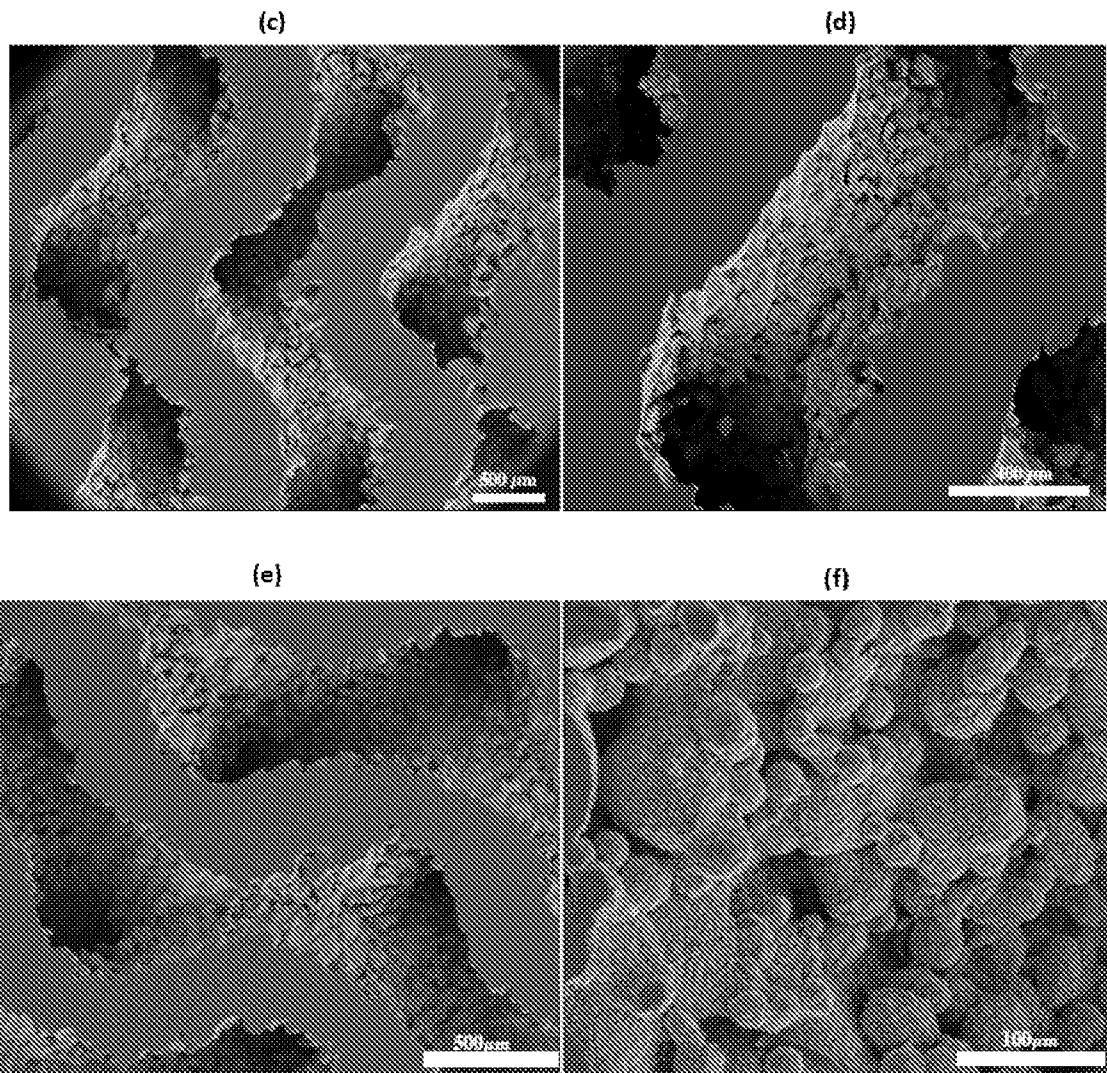


Figure 9 Continued

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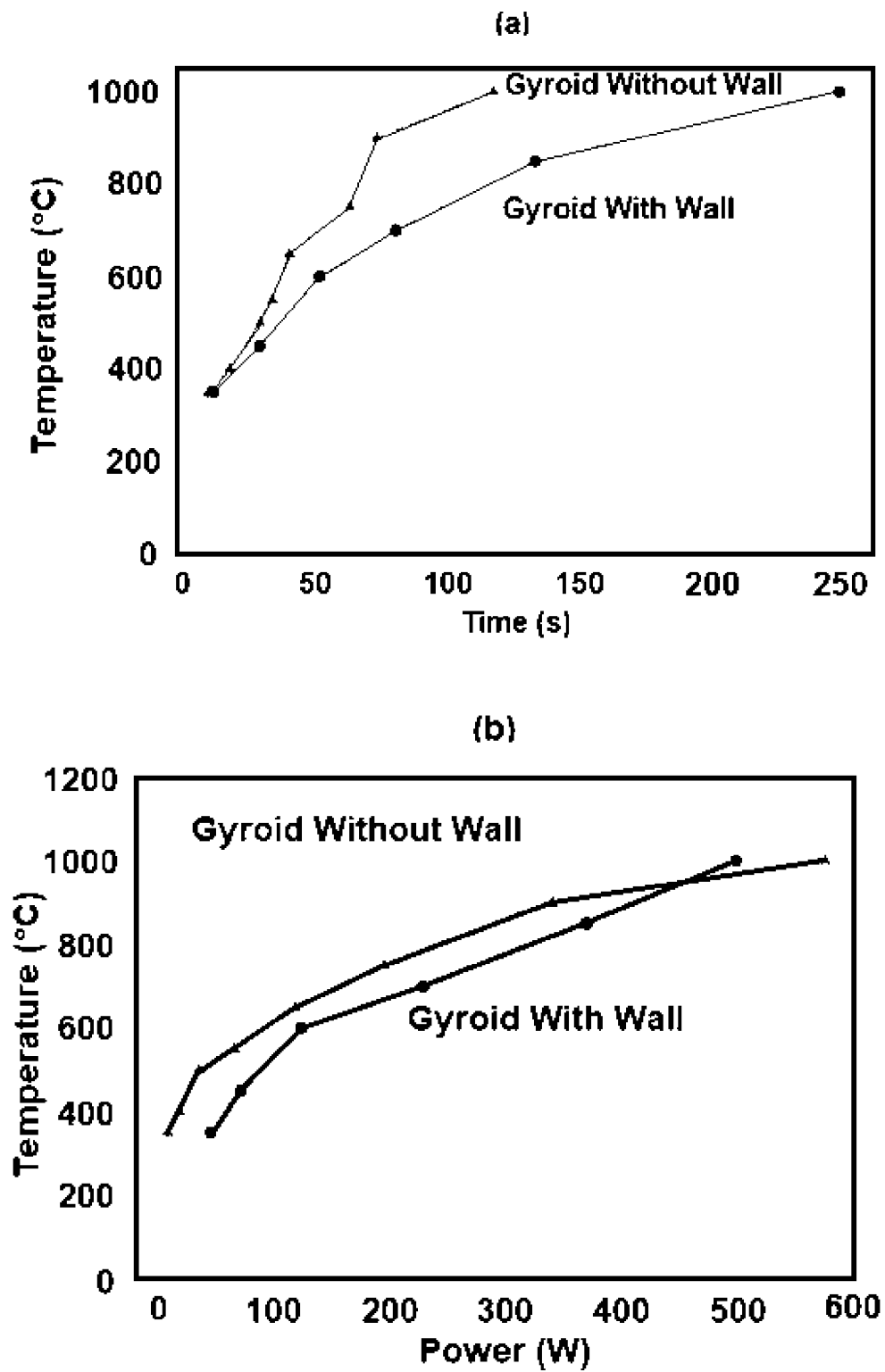


Figure 10

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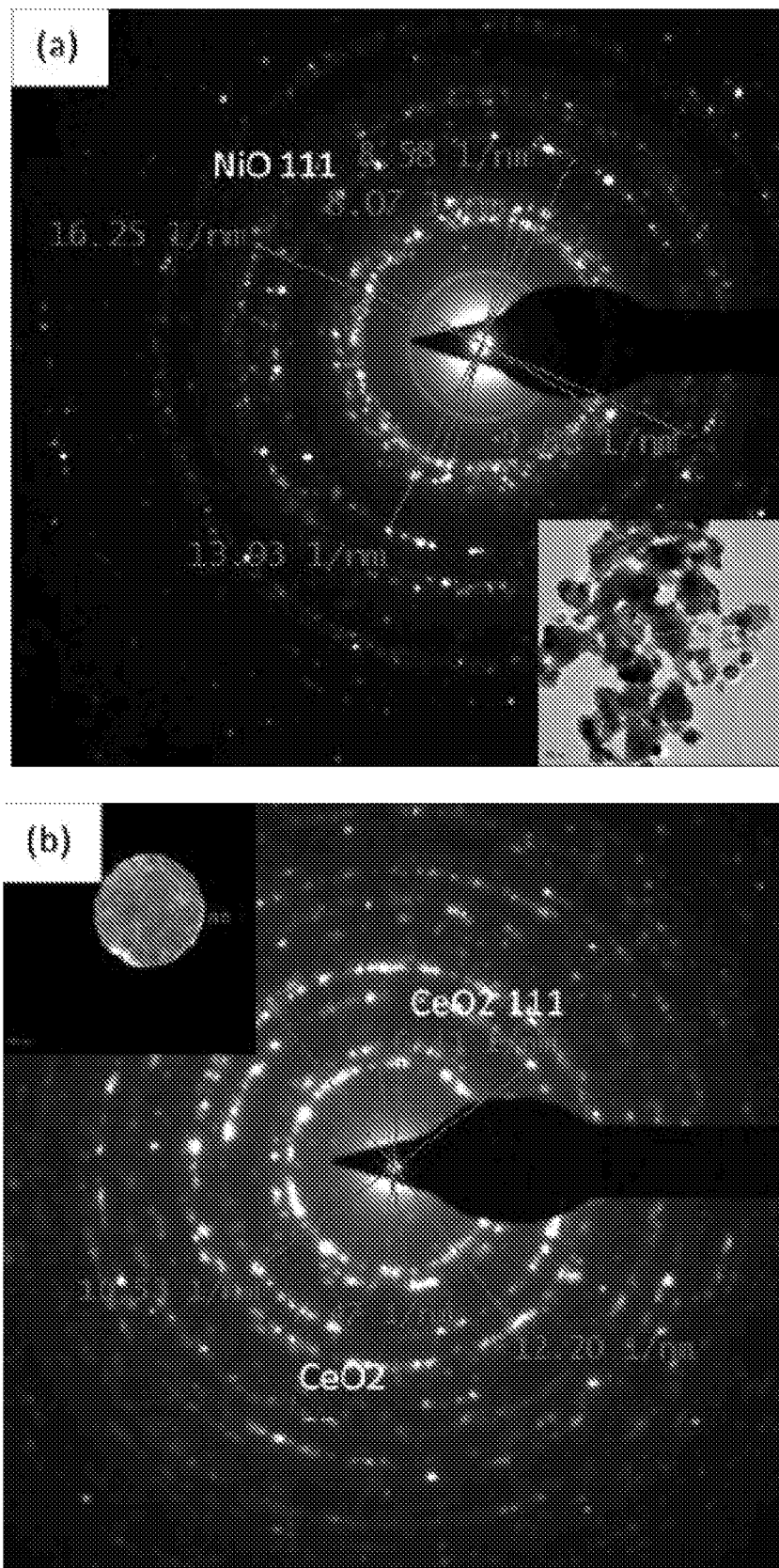


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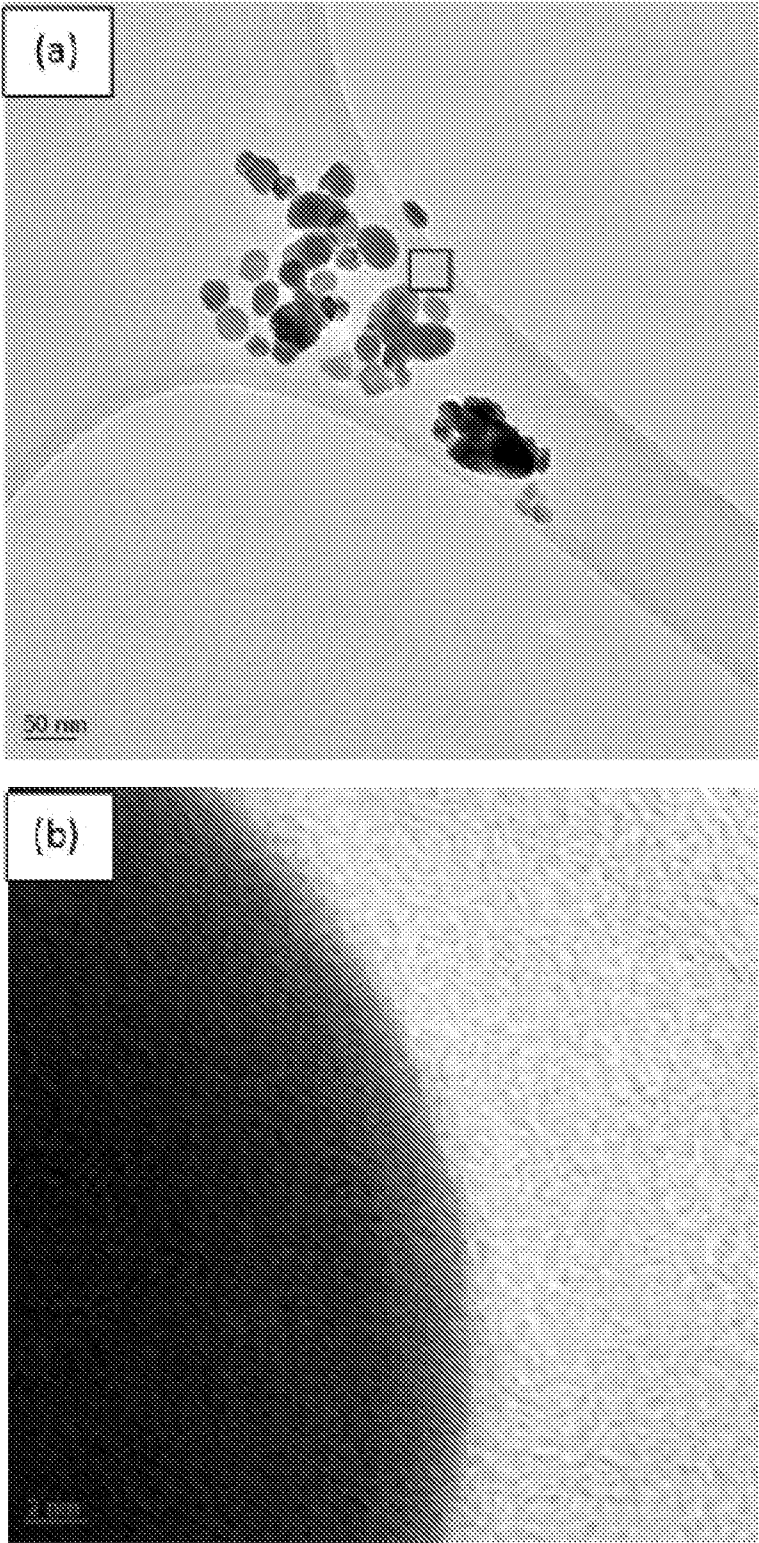


Figure 12

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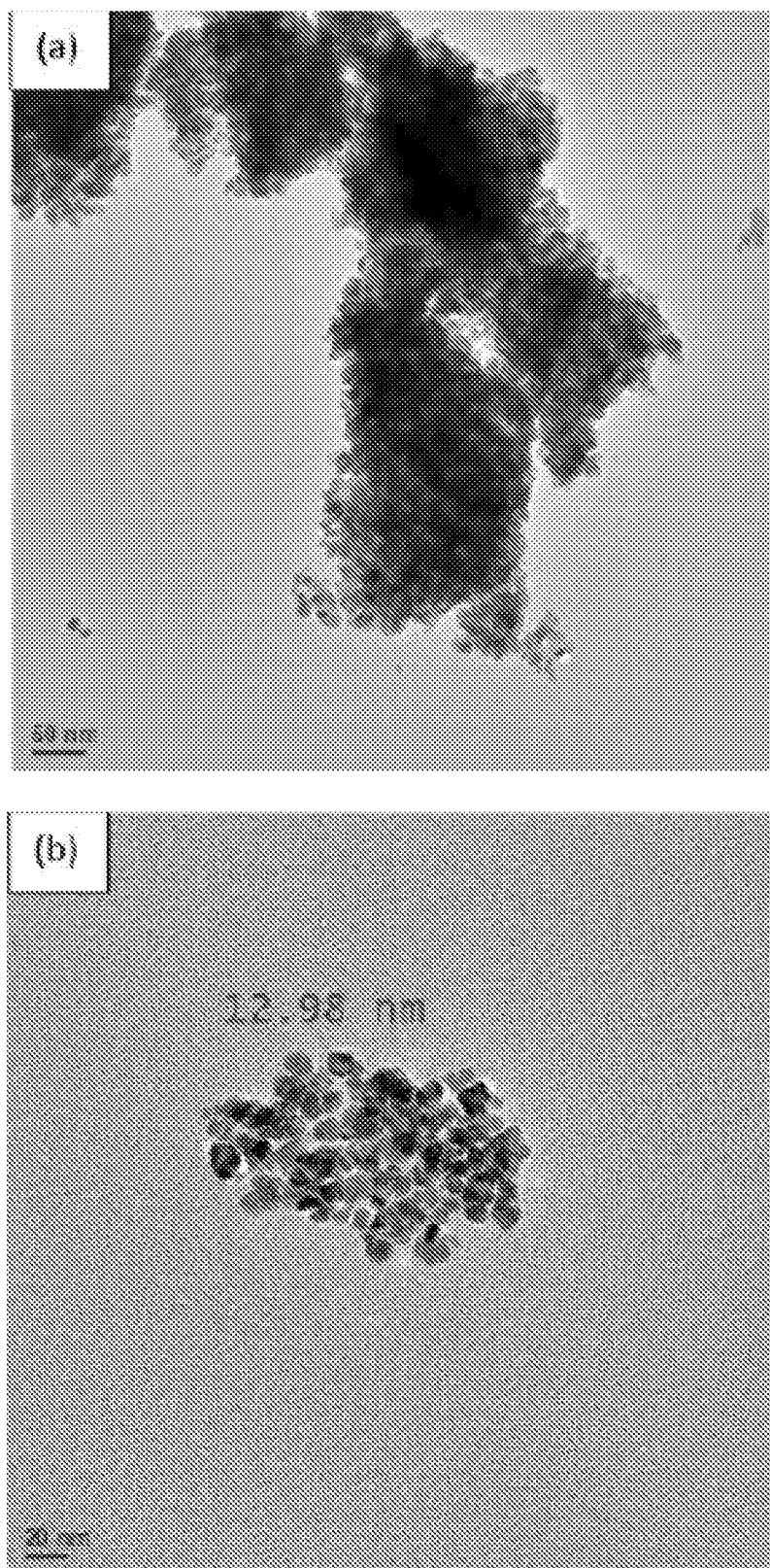


Figure 13

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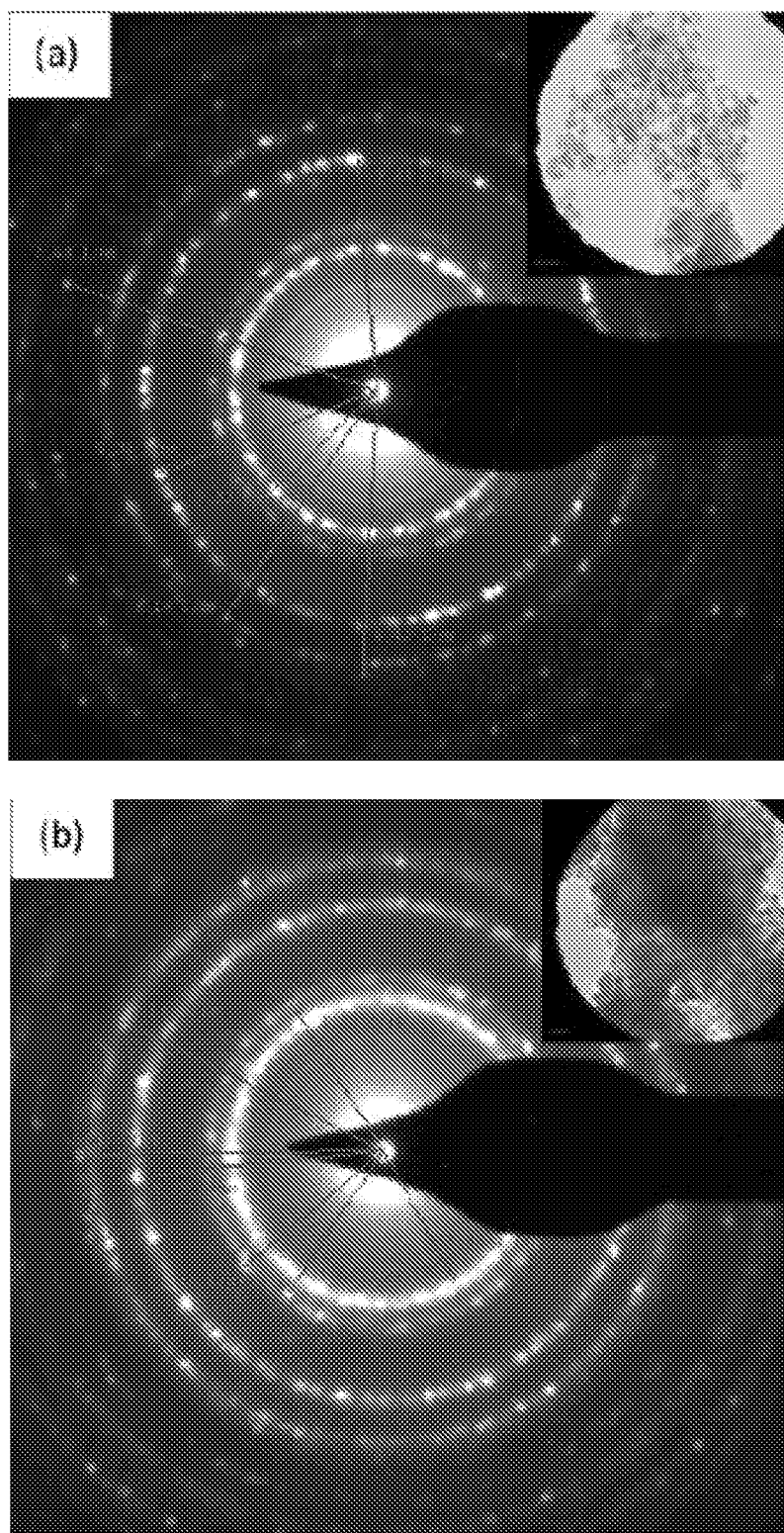


Figure 14

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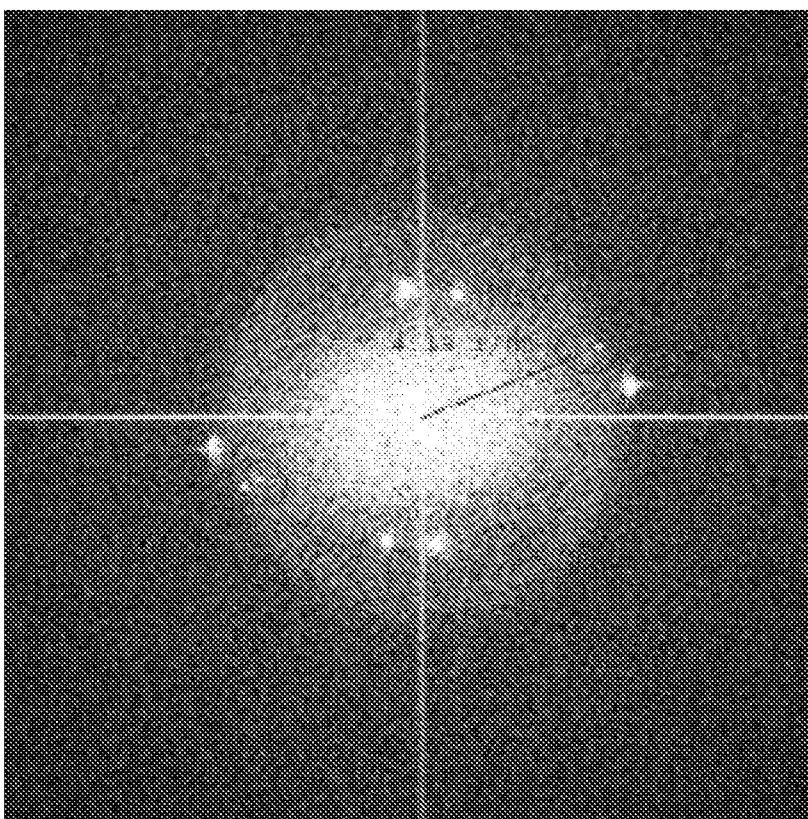
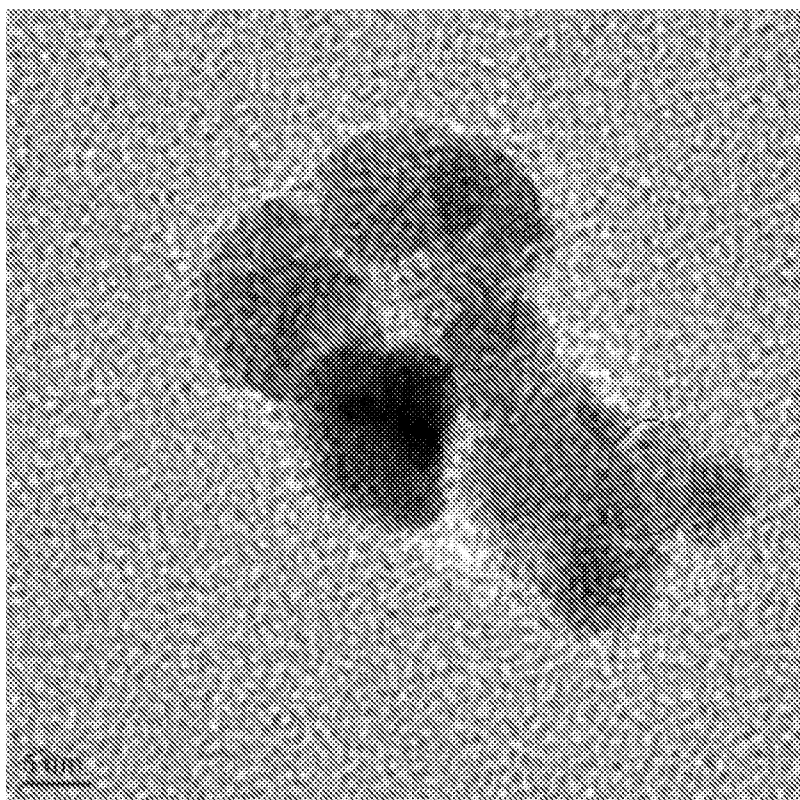


Figure 15

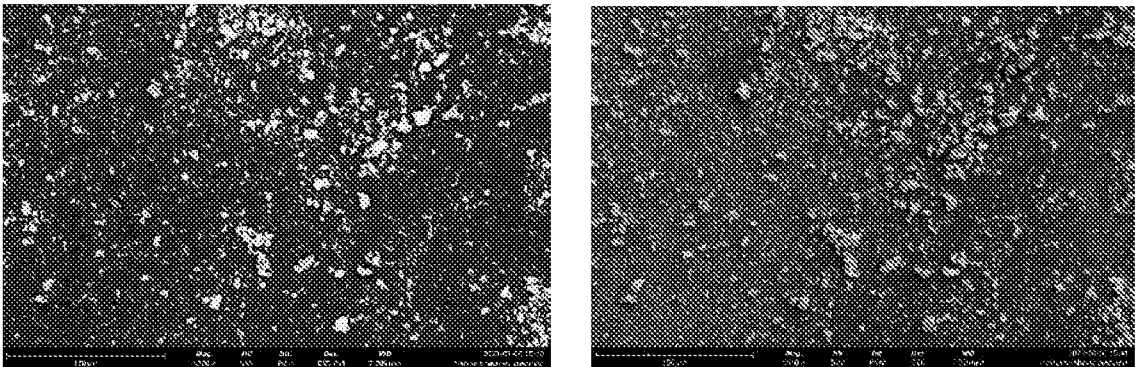


Figure 16

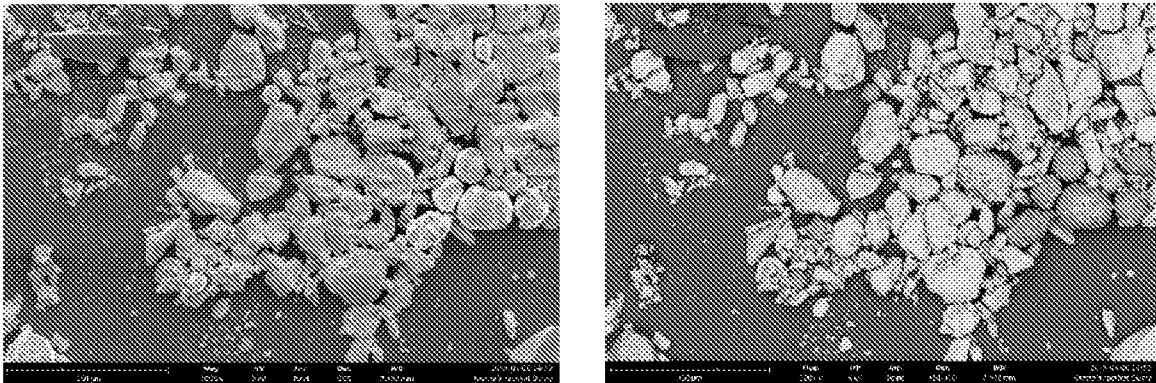


Figure 17

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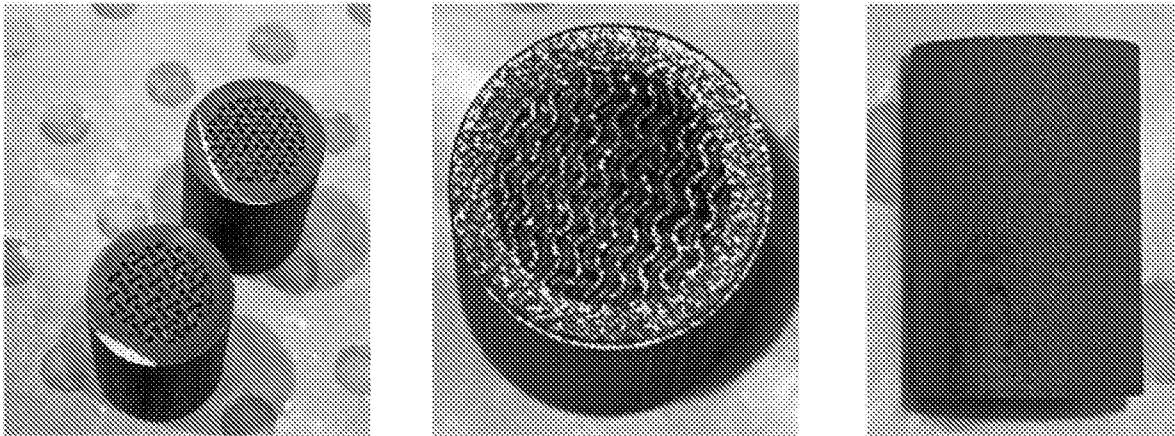


Figure 19

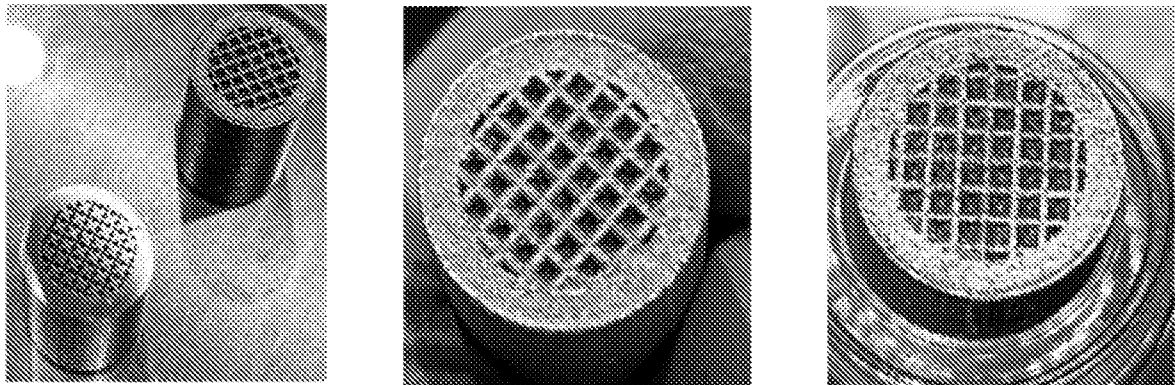


Figure 20

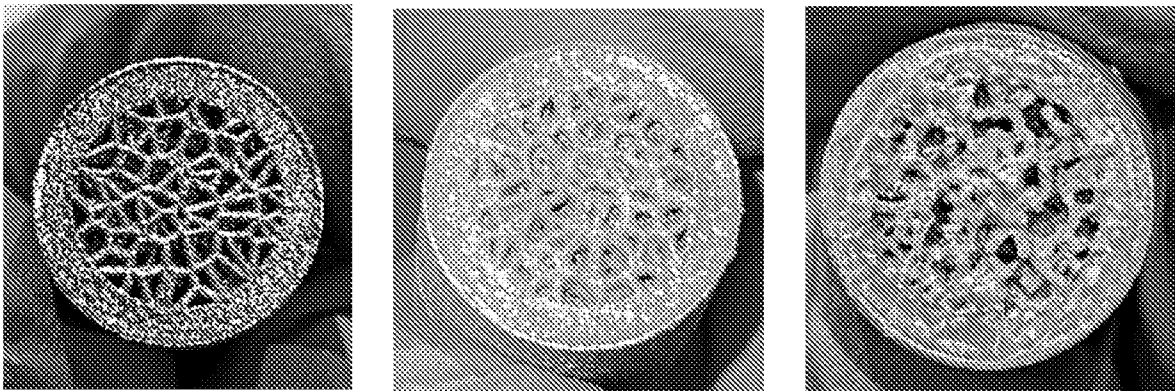


Figure 21

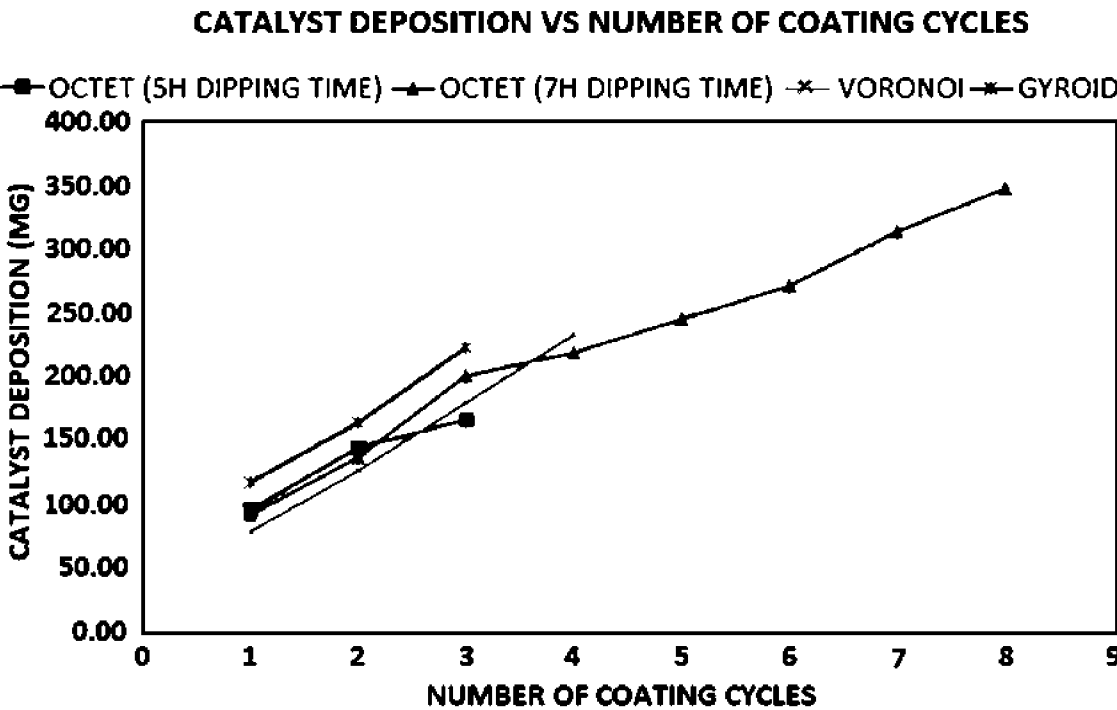


Figure 22

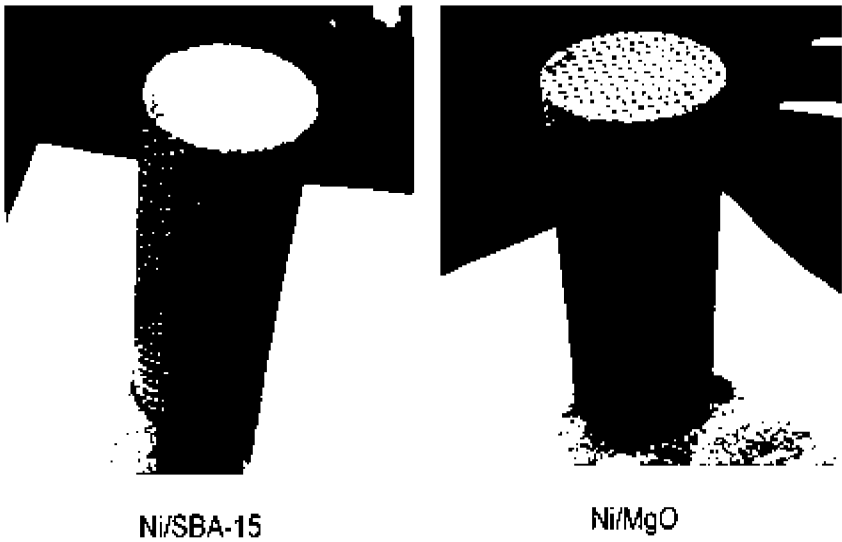


Figure 23



Ni/MgO-MCM41 Sandwiched Monolith

Figure 24

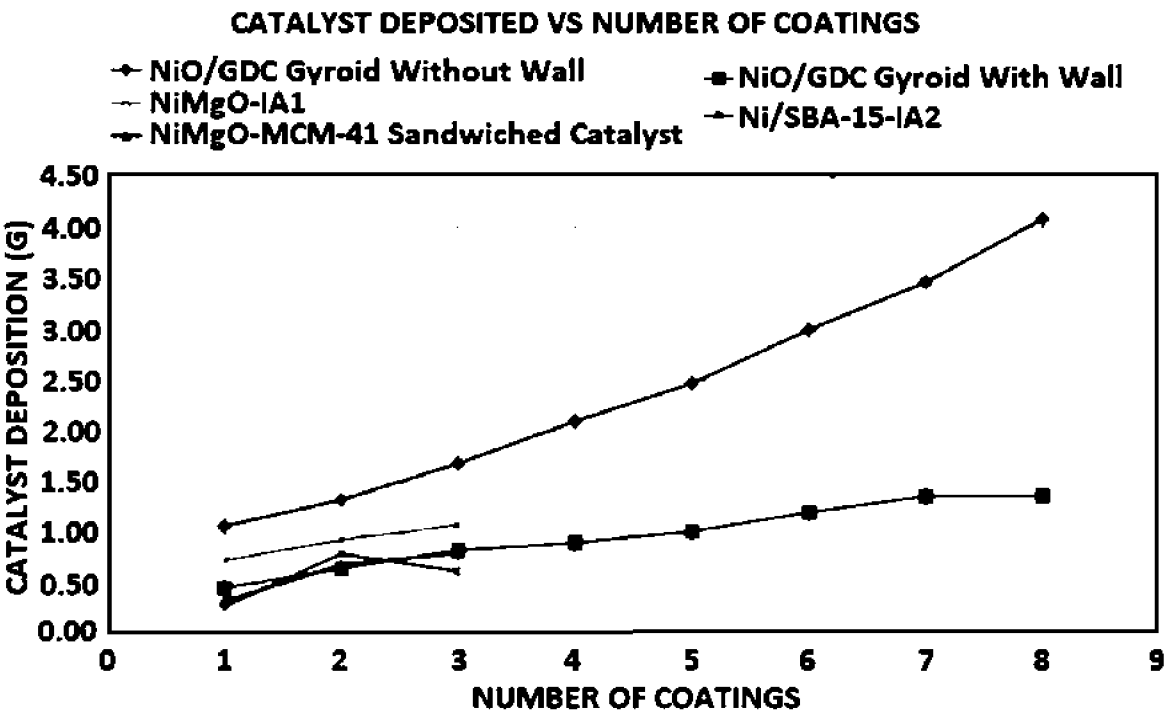


Figure 25

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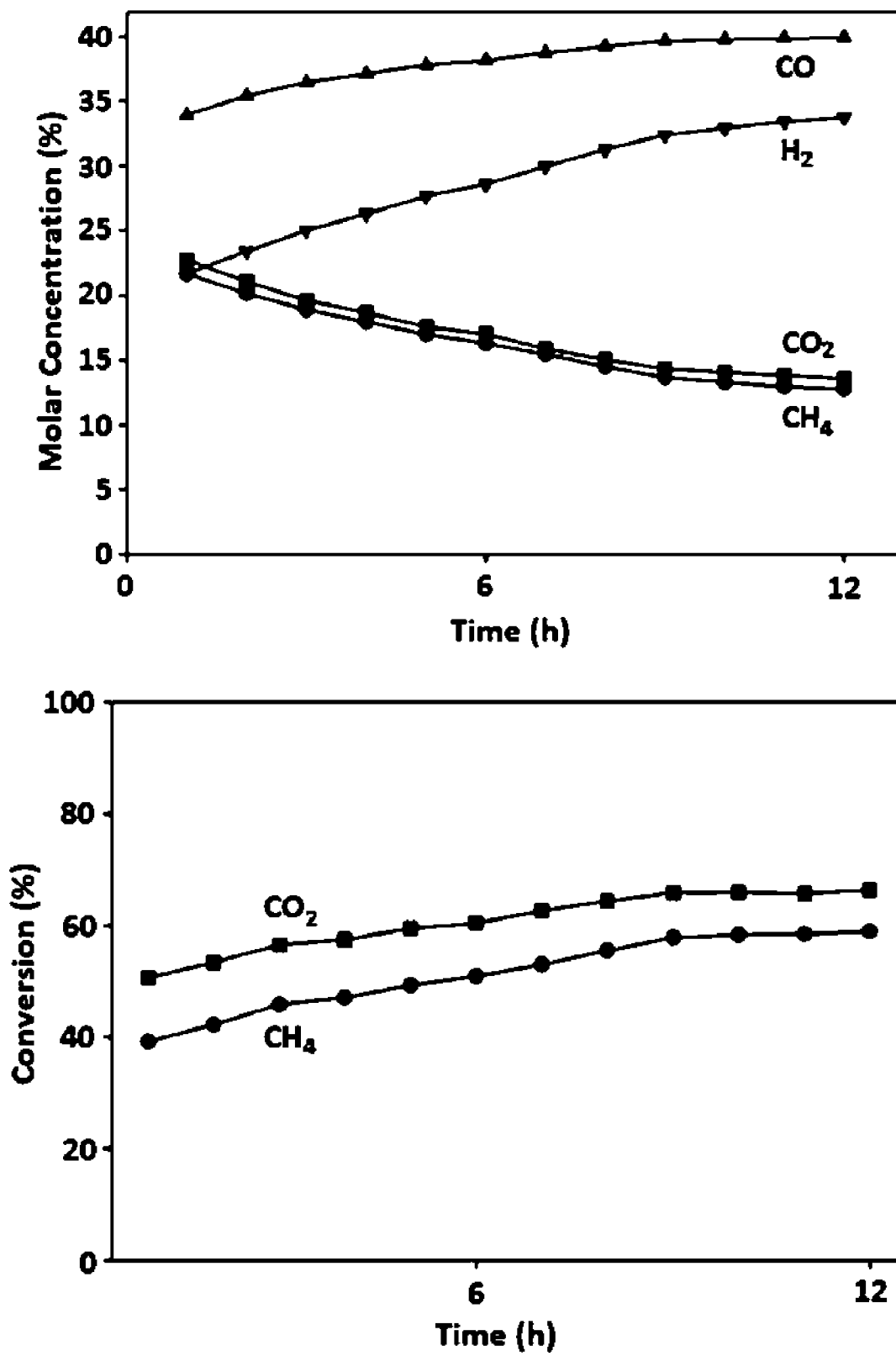


Figure 26

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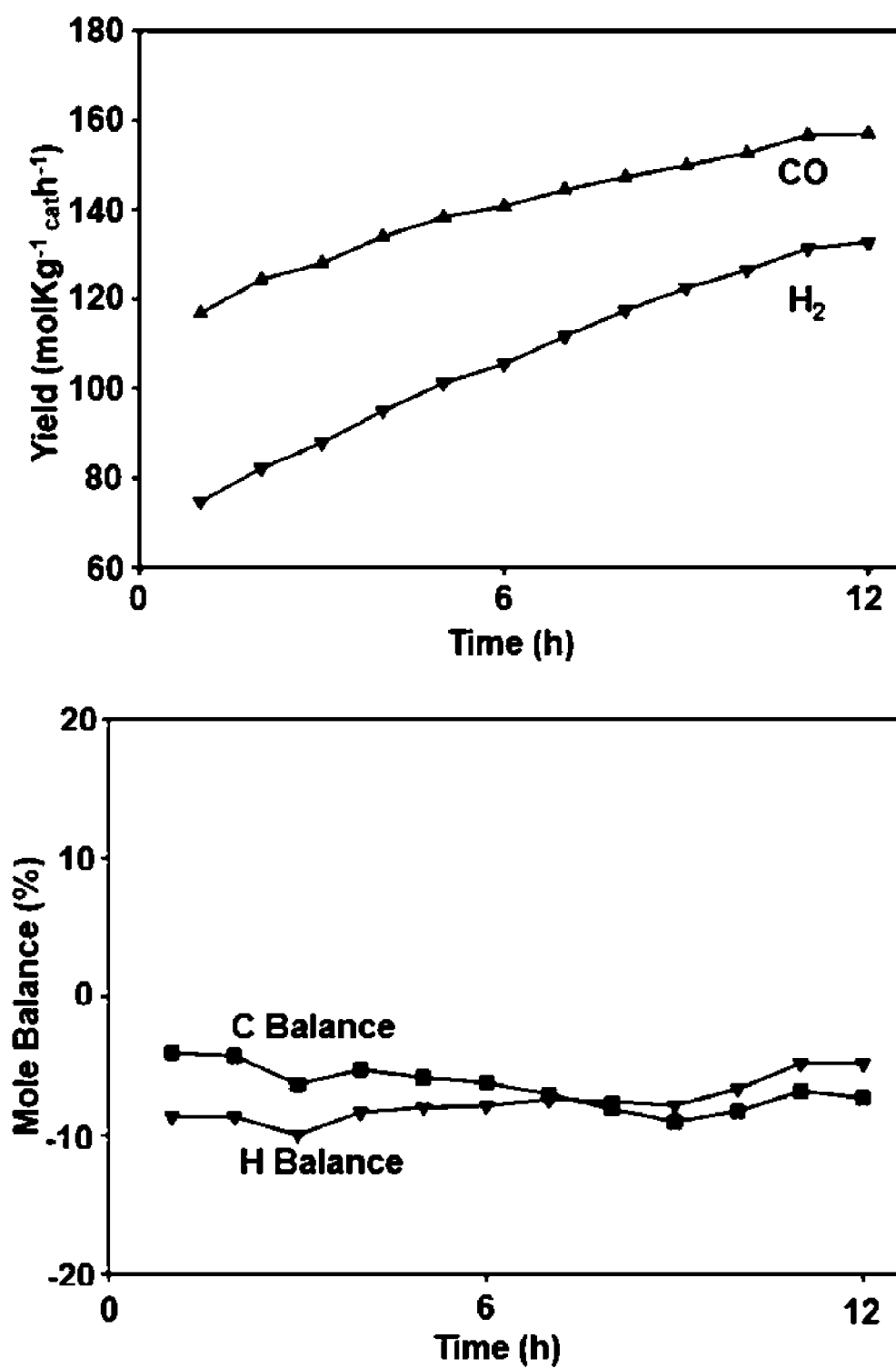


Figure 26 Continued

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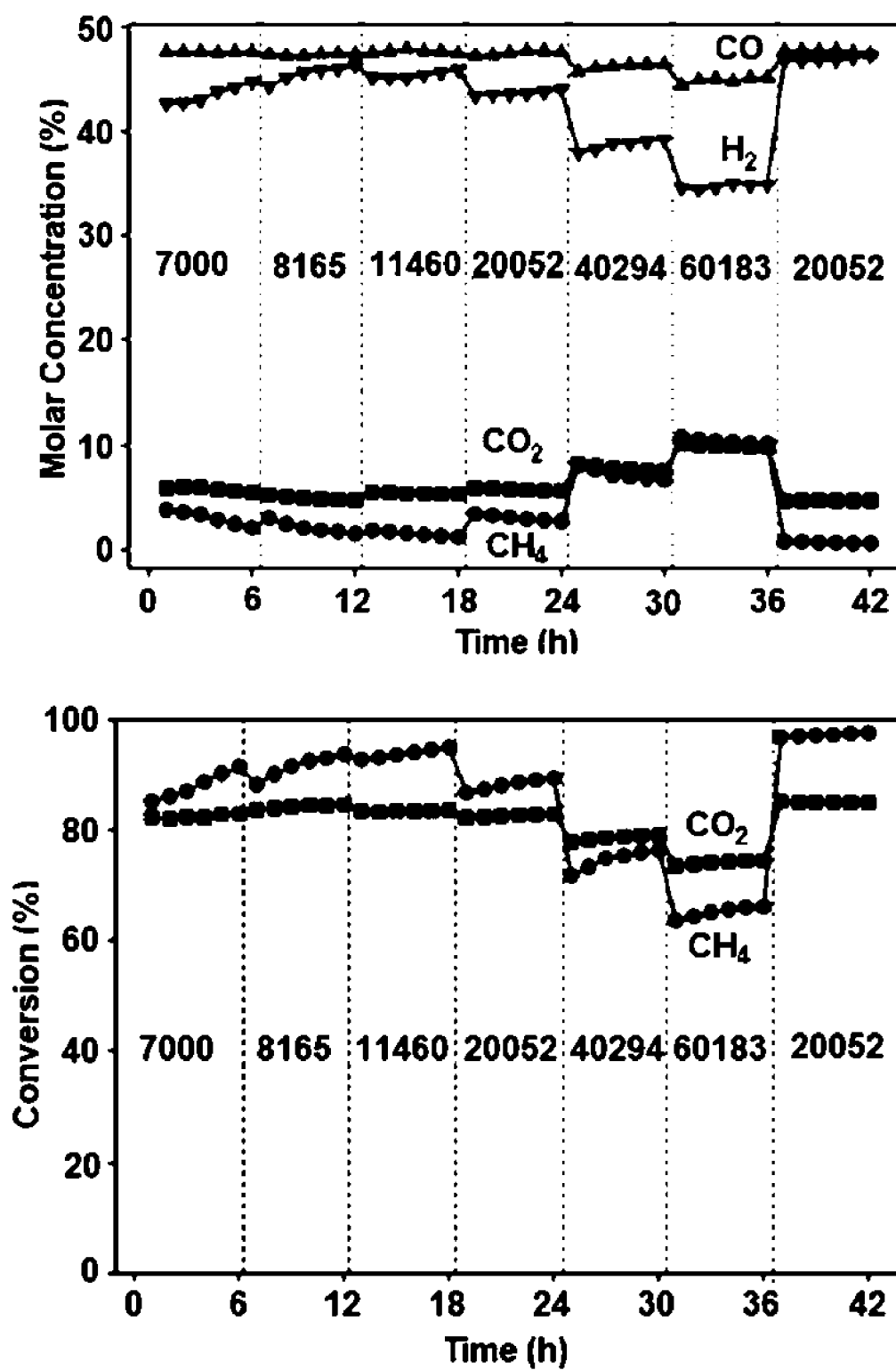


Figure 27

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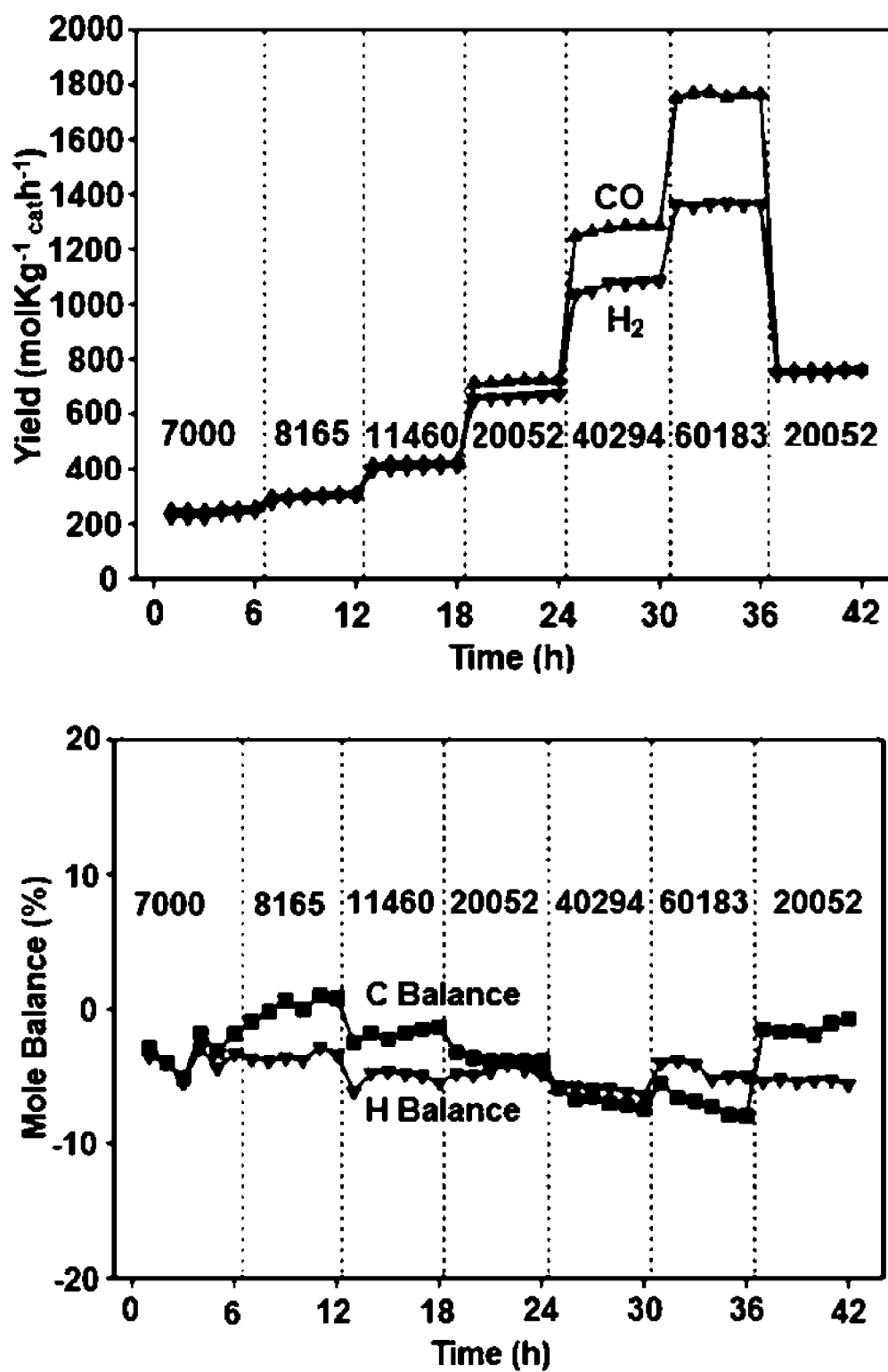


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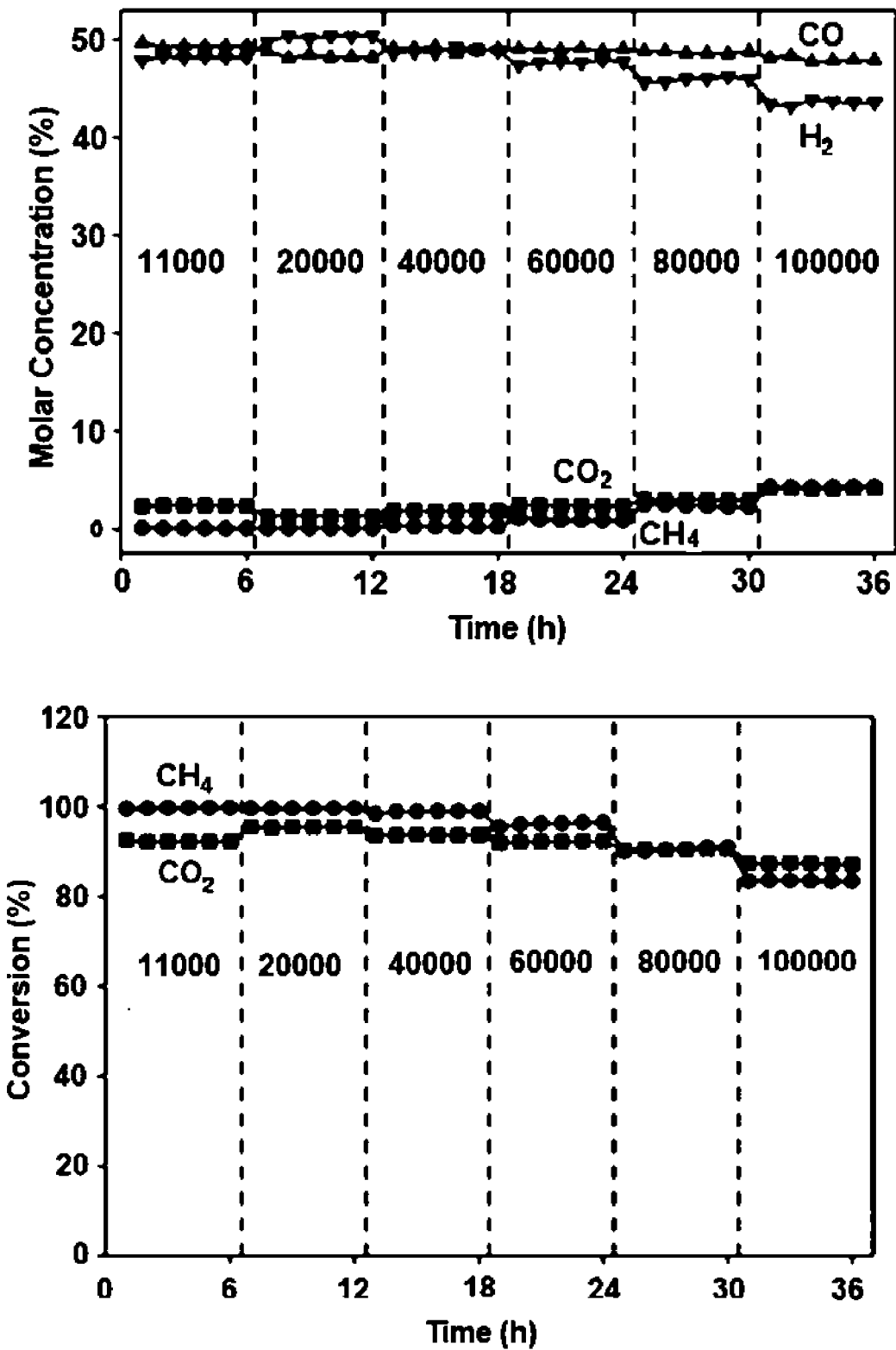


Figure 28

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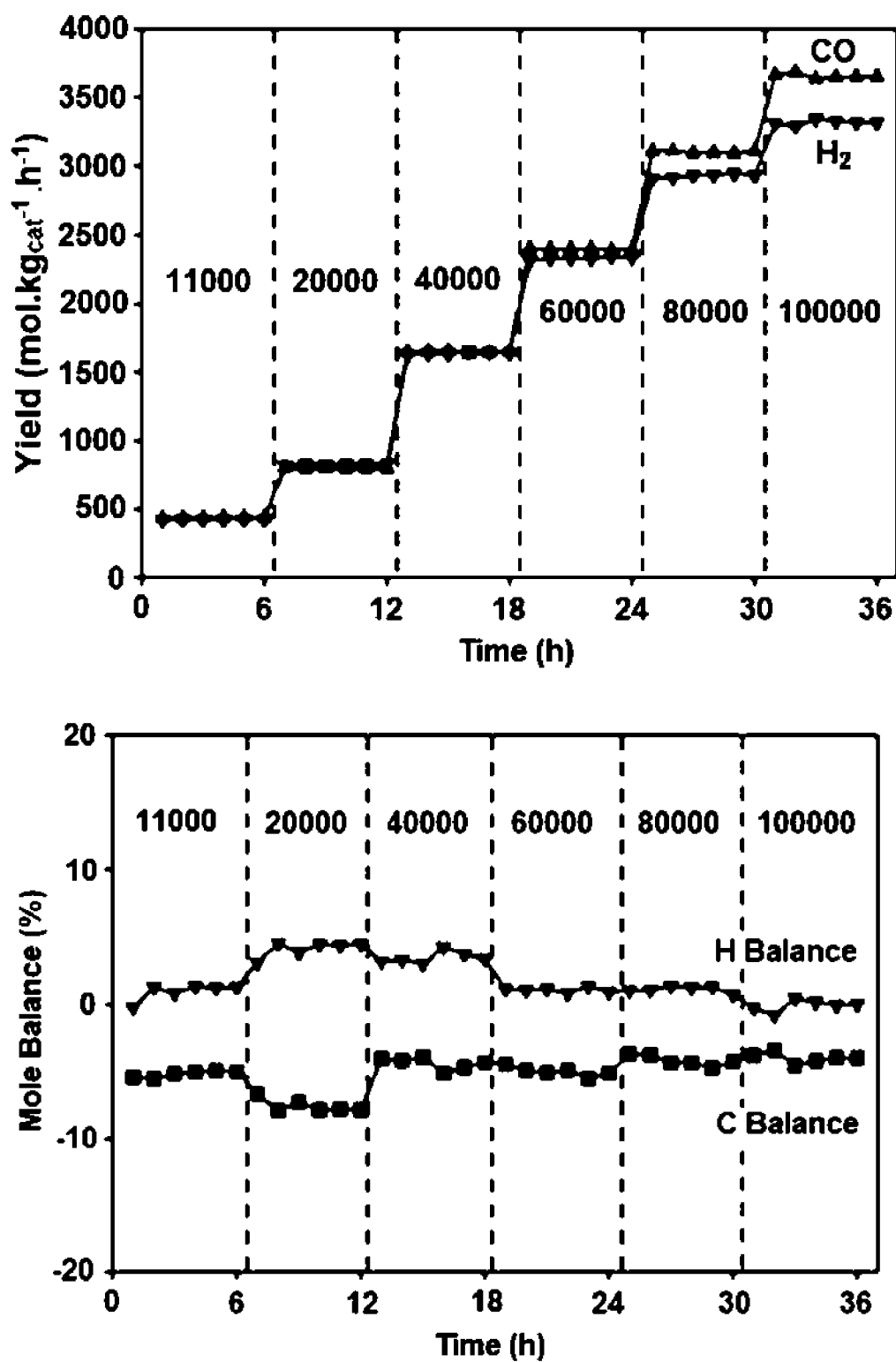


Figure 28 Continued

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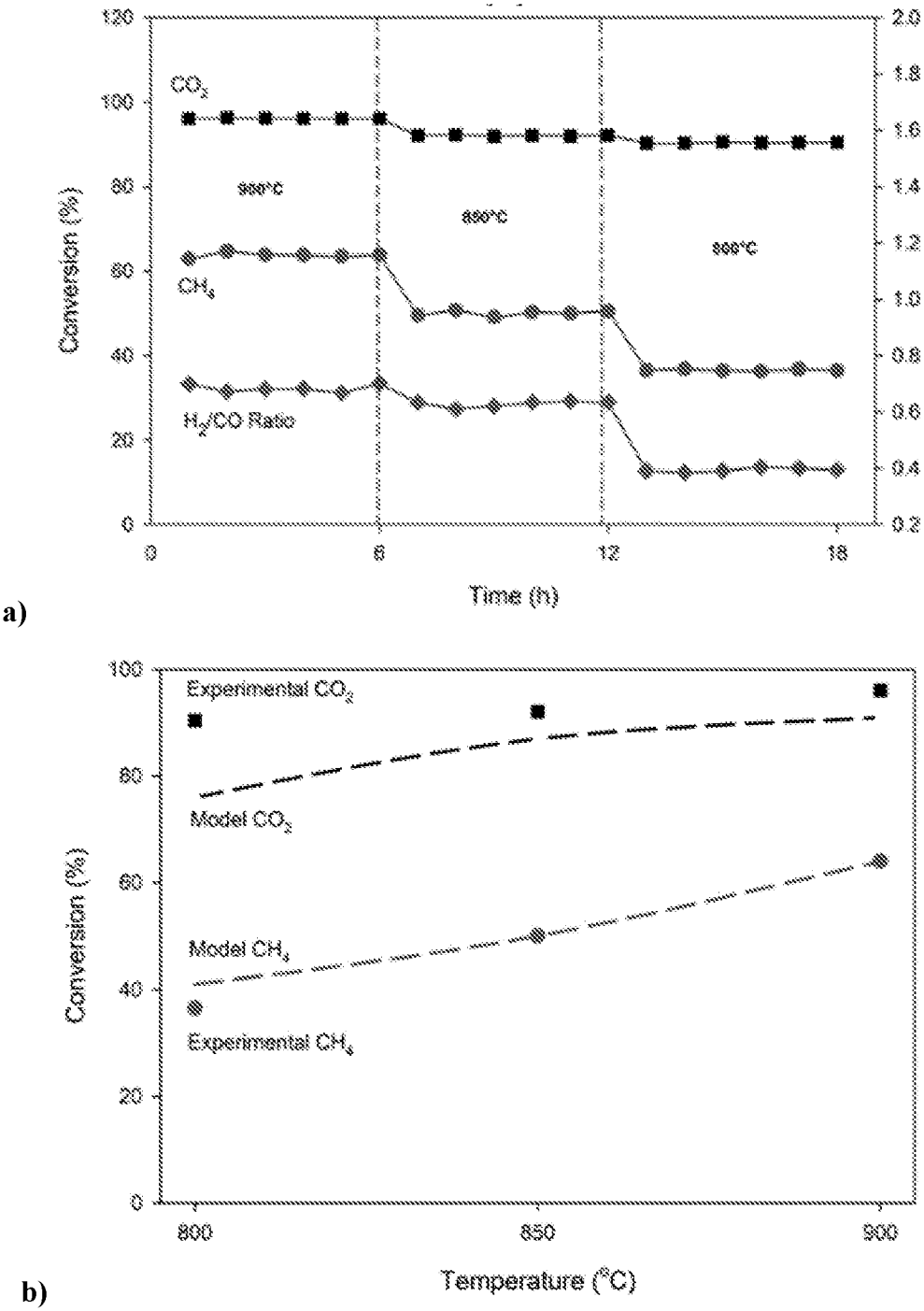


Figure 29

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2024/050871

A. CLASSIFICATION OF SUBJECT MATTER

B01J 8/02 (2006.01) B01J 23/755 (2006.01) C01B 3/26 (2006.01)

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)

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)

Databases: PATENTW, CAPLUS, Espacenet, Google Search/Patents/Scholar,**IPC/CPC symbols:** B01J (8/02, 23/755, 2208/026, 2208/00433), C10B (3/26, 2203/1241, 2203/1058)**Keywords:** SABATIER, DRY, METHANE, REFORM, CO₂, METHANATION, HYDROGEN, SYNGAS, CONVERT, BIOGAS, SUBSTRATE, SUPPORT, MONOLITH, STRUCTURE, CATALYST, HIGH CURIE, INDUCTION, MAGNETIC, FERROMAGNETIC, CONDUCTER, HONEYCOMB, CORRUGATED, GAUZE, FOAM, POROUS, FIBRE, MESH, LATTICE, GYDROID, SHEET, COAT, DEPOSIT, SOLUTION, SLURRY, AEQUOUS, MIXTURE, BLEND, IMMERSE, DIP COAT, DIPPED, SOAK, IMBIBE, SUBMERGED, NICKEL, NI, NiO, OXIDE and other like terms**Applicant/inventor(s):** HILL, Matthew; TANKSALE, Akshat; SADIQ, Muhammad Munir; ASMAT, Hamza; DJUMAS, Lee; MONASH UNIVERSITY;

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

☒ 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	"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
"D" document cited by the applicant in the international application	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search
8 October 2024Date of mailing of the international search report
08 October 2024

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INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2024/050871
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2023068497 A1 (LG CHEM, LTD.) 27 April 2023, viewed as a machine translation, obtained from espacenet pg 2, pg 3 para 3 and 8, pg 7 para 16; examples	1-31
X	WO 2018178312 A1 (VITO NV) 04 October 2018 para [0032]; examples	1, 3, 6, 7, 12, 14-16, 22 and 27
X	WO 2015106634 A1 (ECO ENVIRONMENTAL ENERGY RESEARCH INSTITUTE LIMITED) 23 July 2015 examples 1-9	1-4, 6, 14-16, 19, 22 and 27
A	WO 2019069169 A1 (UNIV QATAR) 11 April 2019	
A	CN 108654592 A (HUAZHONG UNIVERSITY OF SCIENCE AND TECHNOLOGY) 16 October 2018, viewed as a machine translation, obtained from espacenet	
A	CN 104998649 A (SHANGHAI UNIVERSITY) 28 October 2015, viewed as a machine translation, obtained from espacenet	
A	CN 104707614 A (SHANGHAI JIAO TONG UNIVERSITY) 17 May 2015, viewed as a machine translation, obtained from espacenet	
A	Valérie, M., 'Review on Methods to Deposit Catalysts on Structured Surfaces', 2006, <i>Applied Catalysis A</i> , vol 315, pp. 1-17 <DOI: ff10.1016/j.apcata.2006.08.031>	
A	Ghosh, S. et al., 'Magnetically Induced CO2 Methanation In Continuous Flow Over Supported Nickel Catalysts with Improved Energy Efficiency', 2022, <i>ChemSusChem</i> , vol 16, no 1 <DOI: 10.1002/cssc.202201724>	

Form PCT/ISA/210 (fifth sheet) (July 2019)

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:
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including
2. ☐ Claims Nos.:
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:
3. ☐ Claims Nos.:
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:

See Supplemental Box for Details

1. ☐ As all required additional 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 additional fees, this Authority did not invite payment of 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.

Supplemental Box

Continuation of: Box III

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Invention 1: Claims 1 to 22 and 28-31 (in part) are directed to a method of making a catalyst-coated structured reactor and a process for dry reforming of methane. The feature of the specific method steps to make the catalyst-coated reactor is specific to this group of claims.
- Invention 2: Claims 23-27 and 28-31 (in part) are directed to a catalyst coated structured reactor and a process for dry reforming of methane. The feature of the catalyst coated structured reactor comprising a catalyst coating further comprising NiO nanoparticles having a mean particle diameter in the range of from 20 or 80 nm, is specific to this group of claims.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a priori*.

With regard to method claims 1-22 and catalyst-coated structured reactor *per se* claims 23-27, the process must be specially adapted to produce the claimed product in order to satisfy the requirements of unity. The process is considered to be specially adapted for the manufacture of a product if it inherently results in the product. However, the method of claim 1 lacks specific features regarding the catalyst precursor solution (present specification, example 2) which lead to a NiO nanoparticle with a mean particle diameter in the range of from 20 to 80 nm, being an inherent result of said method. Consequently, claim 1-22 and claim 23-27 are not unified *a priori*.

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2024/050871	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
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End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.			