



# Recent advances on gas-phase CO<sub>2</sub> conversion: Catalysis design and chemical processes to close the carbon cycle

G. Torres-Sempere<sup>1</sup>, L. Pastor-Perez<sup>1,2</sup>, J. A. Odriozola<sup>1,2</sup>,  
J. Yu<sup>3</sup>, F. J. Duran-Olivencia<sup>4</sup>, L. F. Bobadilla<sup>1</sup> and  
T. R. Reina<sup>1,2</sup>

## Abstract

Chemical CO<sub>2</sub> recycling in the gas phase constitutes a straightforward approach for effective CO<sub>2</sub> conversion to added-value products like syngas or synthetic methane. In this scenario, some traditional processes such as the dry and bi-reforming of methane, the CO<sub>2</sub> methanation and the reverse water-gas shift have gained a renewed interest from the CO<sub>2</sub> utilisation perspective. Indeed, these reactions represent flexible routes to upgrade CO<sub>2</sub> and their application at an industrial scale could substantially reduce CO<sub>2</sub> emissions. The bottleneck for the implementation of these processes at the commercial level is the development of highly active and robust heterogeneous catalysts able to overcome CO<sub>2</sub> activation and deliver sufficient amounts of the upgrading products (*i.e.* syngas or synthetic natural gas) at the desired operating conditions. This review paper gathers the most recent advances in the design of new catalytic formulations for chemical CO<sub>2</sub> recycling in the gas phase and constitutes an overview for experts and newcomers in the field to get fundamental insights into this emerging branch of low-carbon technologies.

## Addresses

<sup>1</sup> Inorganic Chemistry Department & Material Science Institute, University of Seville-CSIC, Av. Americo Vesputio 49, Sevilla, 41092, Spain

<sup>2</sup> Department of Chemical and Process Engineering, University of Surrey, Guildford, GU2 7XH, United Kingdom

<sup>3</sup> State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, 430074, Wuhan, China

<sup>4</sup> Departamento de Ingeniería, Universidad Loyola Andalucía, Avda. de Las Universidades s/n, 41704, Seville, Spain

Corresponding authors: Reina, T.R. ([t.ramirezreina@surrey.ac.uk](mailto:t.ramirezreina@surrey.ac.uk)); Bobadilla, L.F. ([bobadilla@icmse.csic.es](mailto:bobadilla@icmse.csic.es))

Current Opinion in Green and Sustainable Chemistry 2022, 36:100647

This review comes from a themed issue on **CO<sub>2</sub> capture and chemistry (2022)**

Edited by **Ben J. Anthony, Lunbo Duan, Fabio Montagnaro, Zhenyu Sun and Qiang Wang**

Available online 18 June 2022

For complete overview of the section, please refer the article collection - **CO<sub>2</sub> capture and chemistry (2022)**

<https://doi.org/10.1016/j.cogsc.2022.100647>

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## Keywords

CO<sub>2</sub> conversion, Global warming, Catalysis, Reforming, Methanation, Reverse water-gas shift.

## Introduction

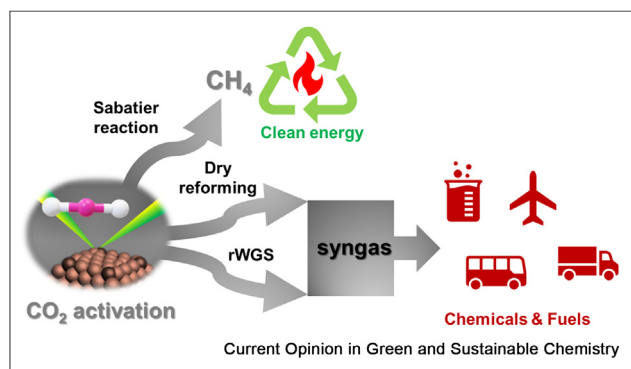
The constant society industrialisation along with the population increase has imposed a surplus in the energy demand around the world. Almost 85% of this energy demand is currently supplied by fossil fuels (natural gas, coal and crude oil) with a heavy carbon footprint [1]. The need for greenhouse gas emissions reduction causing global warming; the change of the actual linear economy to a circular model for a smarter use of natural resources, makes the CO<sub>2</sub> valorisation technologies a cornerstone to enable the transition towards a low-carbon future.

In the last decades, several approaches have been developed targeting CO<sub>2</sub> capture and CO<sub>2</sub> valorisation at an industrial scale. Among the studied alternatives, gas-phase CO<sub>2</sub> conversion represents a direct route for CO<sub>2</sub> upgrading to added-value products [2]. In this sense, there are three main routes for the gas-phase CO<sub>2</sub> conversion: reverse water-gas shift (rWGS), dry reforming of methane (DRM) and CO<sub>2</sub> methanation, also called the Sabatier reaction (Figure 1). All these three processes share the need for a highly active and selective catalyst enabling the activation and subsequent conversion of a highly stable molecule: CO<sub>2</sub>.

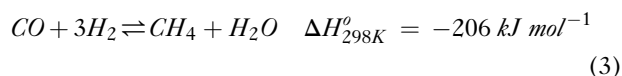
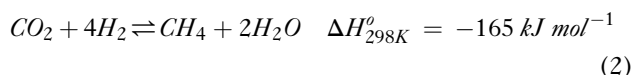
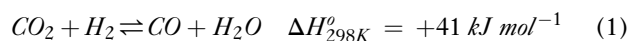
## Gas-phase CO<sub>2</sub> conversion reactions rWGS

The rWGS is an endothermic reaction in which CO<sub>2</sub> is reduced to CO (Eq. (1)). At low temperatures, there are also other favoured reactions that compete with rWGS such as the Sabatier reaction (Eq. (2)) and CO methanation (Eq. (3)), both exothermic [3]. Therefore, the formation of CO is favoured at high temperatures (typically over 700 °C). Based on these premises, a thermally stable, selective and highly active catalyst is needed for this reaction. This is something that the catalysis community has already engineered [4].

Figure 1



Gas-phase CO<sub>2</sub> valorisation strategies: rWGS, DRM and Sabatier reaction.



However, recently a new challenge for rWGS catalysts has been proposed namely the design of low-temperature (LT) rWGS catalysts. This process is often studied at temperatures below 600 °C, considering LT processes that take place at temperatures ranging between 300 and 500 °C, being the CO<sub>2</sub> equilibrium conversion limited to 23% at 300 °C and 1 MPa. This way the reaction can be coupled to downstream processes such as Fischer–Tropsch and methanol synthesis. Indeed, in terms of process integration, it is highly desirable to design LT rWGS systems allowing optimal heat and energy integration. Such a LT rWGS catalyst would represent a disruptive step-ahead when an industrial scale is required resulting in a remarkably advantageous and economically favourable process [5].

#### Novel strategies for LT rWGS catalysts design

Not only the active phase but also the right support and promoter are especially essential for the LT rWGS process. A summary of the most relevant strategies can be found in Table 1 and some interesting examples are described in more detail below.

#### ■ Bimetallic alloy formation

Certain types of metallic promoters can be used to form an alloy with the active phase by its complete reduction.

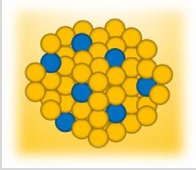
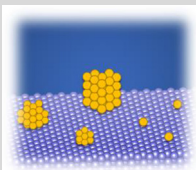
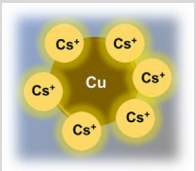
The formation of this alloy can completely change properties such as H<sub>2</sub> dissociation, CO<sub>2</sub> adsorption or C–O cleavage [6]. Cu-based catalysts are a promising option for rWGS due to their high activity, selectivity and economic viability. Furthermore, the presence of Cu influences rWGS to start at low temperatures (165 °C) [7]. Based on this principle, different catalysts have been tested on rWGS using Cu to form bimetallic alloys. Yang et al. [8] studied Fe–Cu/Al<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> catalysts with different Fe/Cu ratios. There was a clear dependence on the Fe/Cu ratio in terms of catalytic performance, presenting the bimetallic alloy with better results than the monometallic catalysts because of a synergetic effect of the active sites. The addition of Fe-enhanced Cu dispersion, while the presence of Cu improved the reducibility of FeO<sub>x</sub> species. This highlights the importance of Fe–Cu interaction in the activation of CO<sub>2</sub>. Furthermore, both CO<sub>2</sub> conversion and H<sub>2</sub> activation were increased due to the presence of multiple active sites: metallic Cu, Cu–FeO<sub>x</sub> interfacial sites and Cu-rich ceria. Finally, CO selectivity was also enhanced in the bimetallic system because of the formation of the Cu<sup>+</sup>–O<sub>v</sub>–Ce<sup>3+</sup> complex, resulting in the active sites for CO formation.

#### ■ Tuning metal-support interaction

Metal-support interfacial sites are of great relevance for rWGS reaction. Hence, this interaction can be adjusted to maximize the metal-support interfacial sites leading to superior CO<sub>2</sub> conversion and CO selectivity. Interfacial site maximization can be achieved by obtaining small and highly dispersed particles of the metal active phase. This is controlled by adjusting pretreatments and changing support properties [9]. Chen et al. [10] studied the effects of surface defects and strong metal-support interaction (SMSI) over Pt/TiO<sub>2</sub> catalysts. TiO<sub>2</sub> nanosheets were pre-treated in dry air, hydrogen and ammonia, resulting in bulk and surface defects due to H and N and obtaining Pt/TN-A, Pt/TN-H and Pt/TN-N, respectively. Oxygen vacancies and N-species promote the dispersion of Pt species over the catalysts' surface. Furthermore, Pt species and SMSI also promote TiO<sub>2</sub> reduction to generate more defects in both surface and bulk of the catalyst. CO<sub>2</sub> is adsorbed on those defects generating intermediates that easily decompose to CO, while Pt particles dissociate H<sub>2</sub> molecules to recover bulk and surface defects. These catalysts presented almost 100% selectivity towards CO at temperatures as low as 300 °C where the side reactions (*i.e.* methanation) are dominant. Even though the CO<sub>2</sub> conversion level is far from equilibrium at this temperature, the full selectivity towards rWGS in this temperature range is a highly commendable result opening new avenues for research when an LT rWGS is targeted. Actually, in an attempt to increase CO<sub>2</sub> conversion for LT Pt-based systems, N-doping is an

Table 1

## Summary of design strategies for low-temperature rWGS catalysts.

Strategies	Advantages	Drawbacks
<p><i>Formation of bimetallic alloys</i></p> 	<ul style="list-style-type: none"> <li>■ Optimal electronic and redox properties</li> <li>■ Higher catalytic activity</li> <li>■ Enhanced reducibility</li> </ul>	<ul style="list-style-type: none"> <li>■ Increase of the catalyst cost</li> </ul>
<p><i>Tuning metal-support interaction</i></p> 	<ul style="list-style-type: none"> <li>■ SMSI effect</li> <li>■ Higher dispersion of active sites (<i>single-atoms</i>)</li> </ul>	<ul style="list-style-type: none"> <li>■ Increase in the catalyst production energy</li> </ul>
<p><i>Alkali metals as promoter</i></p> 	<ul style="list-style-type: none"> <li>■ Enhanced basic properties</li> <li>■ High CO selectivity</li> <li>■ Optimal electron transfer for CO<sub>2</sub> activation</li> </ul>	<ul style="list-style-type: none"> <li>■ Decrease of specific surface area</li> <li>■ Partially blockage of metallic sites</li> </ul>

efficient strategy. Pt/TN-N catalysts present enhanced catalytic performance due to the larger availability of bulk Ti<sup>3+</sup> sites, that also replenish both bulk and surface defects under reduction atmosphere, enhancing the overall catalytic behaviour. In any case, the understanding and careful control of the SMSI effect seems crucial for the design of high-performing LT-rWGS catalysts.

#### ■ Alkali metals as promoters

Alkali metals can enhance significantly the catalytic activity and selectivity of some catalytic systems by changing the electronic environment of the active sites [11]. Varvoutis *et al.* [12] studied the effect of Cs in a CuO/CeO<sub>2</sub> catalyst, observing that the addition of the alkali metal leads to a decrease in CO<sub>2</sub> conversion but favours CO selectivity. The reduction of CO<sub>2</sub> conversion was attributed to the consecutive diminution in the surface area with the increased amount of Cs, resulting in less active sites for the activation of CO<sub>2</sub>. Moreover, the addition of Cs also increases the number of basic sites on the surface of the catalysts, evidencing a correlation between this property and the improved CO selectivity. Our team pioneered the addition of Cs as

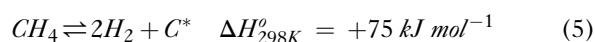
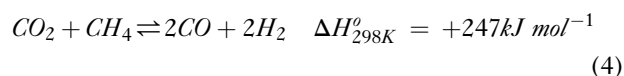
rWGS catalysts promoter over Mo<sub>2</sub>C catalyst, achieving CO<sub>2</sub> conversions of almost 20% and CO selectivity of 100% at 400 °C [13]. Among the alkali promoters, Caesium has a big atomic radius being a very electro-positive element. The later favours electron donation to CO<sub>2</sub> antibonding orbitals thus facilitating C–O activation and the subsequent reaction.

#### DRM

Syngas consists of a mixture of CO and H<sub>2</sub>, and its importance resides in the numerous valuable compounds that can be synthesised from syngas (*i.e.* dimethyl ether, alcohols or hydrocarbon fuels and waxes). Syngas is normally produced via reforming reactions, which are distinguished from each other depending on the oxidant used, the H<sub>2</sub>/CO molar ratio produced and thermodynamics and kinetic trends [7]. DRM (Eq. (4)) has attracted a huge interest due to the simultaneous elimination of two main greenhouse gas [14]. The effluent of the DRM reactor yields syngas with a molar H<sub>2</sub>/CO ratio close to 1 which is ideal for hydroformylation reactions and can also be fed in a Fischer–Tropsch synthesis unit opening direct routes for CO<sub>2</sub> conversion to synthetic fuels [15]. In addition, DRM is a suitable process to upgrade biogas mixtures coming from anaerobic digestion of bio-waste since biogas mainly consists of CH<sub>4</sub> and CO<sub>2</sub> [16]. Hence the

smart design of highly effective DRM catalysts represents one of the challenges of catalysis for a circular economy.

DRM is an endothermic reaction (Eq. (4)) needing temperatures around 900 °C to reach acceptable syngas production. At this temperature, catalytically active metal sites deactivate due to sintering. Furthermore, at this temperature, methane decomposition (Eq. (5)) is also favoured, promoting carbon deposition on the surface of the catalysts [16]. It is crucial to hinder carbon deposition in order to obtain long-term operations [17].



The type of active metal centres, promoters and supports used as well as the structure and the synthesis method of the catalyst are the essential parameters for the design of any catalyst. For DRM, noble metals such as Rh, Ru, Pd, Pt and Ir are the most used displaying high conversions and resistance to coke formation. However, the scarcity and market price of noble metals pushes the catalysis community to find alternatives, being Ni the one presenting better result [18]. However, Ni typically suffers from sintering and coking, hence the question is: can we design sintering and coking-tolerant Ni-based catalysts? Fairly promising advances have taken place in this regard in recent years. A summary of the effective strategies can be found in Table 2.

#### Novel strategies for Ni-based catalysts optimization

As mentioned before, Ni-based catalysts are the most promising materials for DRM reactions. This is due to its large abundance, low cost and high catalytic activity for this process. The successful performance of Ni-based catalyst strongly depends on its dispersion and small particle size [19]. Herein, we assess the most attractive and recently developed strategies for achieving optimal Ni DRM catalysts.

#### ■ Fine-tuning the electronic environment of nickel to prevent coking and sintering

Azancot et al. [20,21] investigated the effect of potassium in a Ni/MgAl<sub>2</sub>O<sub>4</sub> catalyst evidencing via FTIR spectroscopy new active centers for DRM: Mg–O–K and Ni–O–K sites. Mg–O–K sites have strong basicity,

promoting the adsorption of CO<sub>2</sub> molecules and forming carbonate species that evolve to CO via rWGS, as this adsorption is considered the critical step for this reaction. Meanwhile, the Ni–O–K interaction seems to reduce CO dissociation over Ni particles, preventing the formation of coke in the active phase. Alkaline and 3d transition metal mixed oxides exhibit metallic character (zero band-gap) allowing CO<sub>2</sub> and CH<sub>4</sub> dissociation but inhibiting CO adsorption. Furthermore, this new active site promotes the gasification of carbonaceous species via reverse Boudouard reaction. These alternatives identified reforming phases open new opportunities for Ni-based reforming catalysts.

#### - Protecting nickel in a core/yolk@shell structure

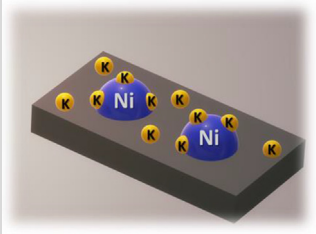
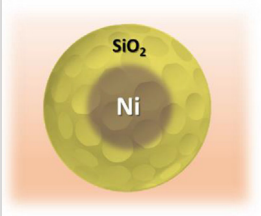
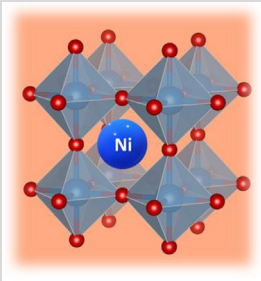
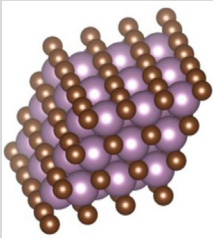
The encapsulation of metal nanoparticles (NPs), especially with yolk@shell structures, seems to be a promising method for the prevention of sintering and coke formation over catalysts. Yolk@shell are structures derived from core@shells, consisting of a porous shell material recovering the NPs, keeping a void between both. Yolk@shell prevents NPs aggregation while allowing reactants to diffuse in and out through the nanoporous channels of the structure [22]. Furthermore, yolk@shell structures are also responsible for the increase in the catalytic activity due to higher local partial pressures inside these complexes, acting as nano-reactors. Price et al. [23] studied a Ni@SiO<sub>2</sub> catalysts, where Ni particles are covered by a SiO<sub>2</sub> outer layer. In comparison with non-encapsulated materials, this catalyst remained stable for longer reactions time during DRM. As mentioned above, this is explained by the prevention of sintering due to the yolk@shell structure, but also because of the reduction of coke formation even though further research is needed to fully understand the exceptional behaviour of these encapsulated catalysts. Interestingly, after a long period of reaction, carbon nanotubes are formed in the catalyst due to non-encapsulated Ni particles, indicating the main drawback of this strategy: the necessity of a reliable method to obtain a homogeneous encapsulation of active phase particles over the catalyst's surface.

#### ■ Stabilization of nickel in an inorganic matrix

To prevent particles from sintering, a complex inorganic matrix can be used to stabilise active sites inside their structures. Different materials such as perovskites, spinel or fluorites have been used for this purpose in DRM reaction [24,25]. These structures not only prevent metal particles from sintering but also maintain them active and

Table 2

## Design strategies approach for optimization of Ni DRM catalysts.

Strategies	Advantages	Drawbacks
<p><i>Fine-tuning the electronic environment of Ni to prevent coking and sintering</i></p> 	<ul style="list-style-type: none"> <li>■ Ni–O–K sites: enhanced electronic properties (inhibit CO dissociation)</li> <li>■ Mg–O–K sites: gasification of carbonaceous deposits</li> </ul>	<ul style="list-style-type: none"> <li>■ Ni–O–K sites can be decomposed into NiO and K<sub>2</sub>O in presence of steam for a long time</li> </ul>
<p><i>Encapsulation of Ni in core@yolk shell structure</i></p> 	<ul style="list-style-type: none"> <li>■ Confinement effect</li> <li>■ Prevention of sintering</li> <li>■ Diffusional control</li> <li>■ Coke mitigation</li> <li>■ High stability</li> <li>■ Enhanced redox properties</li> <li>■ High metal dispersion: strong metal-support interaction</li> <li>■ High stability</li> </ul>	<ul style="list-style-type: none"> <li>■ Uncontrolled encapsulation: presence of non-encapsulated particles</li> <li>■ Nickel is only fully reduced and exsolved at high temperature</li> </ul>
<p><i>Nickel stabilised on inorganic matrixes</i></p> 	<ul style="list-style-type: none"> <li>■ High stability</li> <li>■ Similar catalytic properties to Pt-group metals</li> <li>■ Good redox properties</li> <li>■ Strong-metal support interaction</li> </ul>	<ul style="list-style-type: none"> <li>■ It can be easily oxidized by air or CO<sub>2</sub>. It must be passivated</li> </ul>
<p><i>Transition metal carbides (TMCs)</i></p> 	<ul style="list-style-type: none"> <li>■ Similar catalytic properties to Pt-group metals</li> <li>■ Good redox properties</li> <li>■ Strong-metal support interaction</li> </ul>	<ul style="list-style-type: none"> <li>■ It can be easily oxidized by air or CO<sub>2</sub>. It must be passivated</li> </ul>

accessible for reactants. Le Saché *et al.* [26] studied a series of Ni-based catalysts stabilised on inorganic matrixes consisting of lanthanum zirconate pyrochlore with different Ni loadings (0, 2, 5 and 10 wt. %). The results showed that 10 wt.% Ni catalysts presented high activity towards DRM and remain stable during a long-term stability test of 360 h. The characterization of 10 wt.% Ni pyrochlore catalyst after the stability test showed that the inorganic structure was intact, and Ni particles were

exsolved to the catalysts surface forming small Ni clusters, responsible for the high activity.

#### ■ *Transition metal carbides catalytic systems*

Our team has recently reviewed the state of the art on transition metal carbides (TMCs) for CO<sub>2</sub> conversion

reactions [27]. Since TMCs have properties similar to platinum group metals, these materials have received considerable attention as promising catalysts for DRM reactions. For instance, Dias-Barbosa et al. [28] evaluated Ni–Mo<sub>2</sub>C and Ni–WC catalysts in DRM employing different CH<sub>4</sub>/CO<sub>2</sub> ratios. They found that Ni–Mo<sub>2</sub>C is active under excess of CH<sub>4</sub> but it is deactivated in excess of CO<sub>2</sub>. Contrarily, Ni–WC remains active in excess of CO<sub>2</sub> but it is unstable in excess of CH<sub>4</sub>.

Certainly, the unique and tuneable properties of TMCs make them ideal substitutes for precious metals resulting in promising catalysts for DRM reaction. However, although TMCs are desirable materials for DRM reactions some of their inherent properties still hindered the maximization of their performance. For example, the surfaces of most TMCs materials are very reactive to air or CO<sub>2</sub> and thus must be passivated, although the oxidation degree is not always easy to control.

#### CO<sub>2</sub> methanation: sabatier reaction

CO<sub>2</sub> methanation (Eq. (2)), also called the Sabatier reaction, produces methane from CO<sub>2</sub> and hydrogen generated by water electrolysis. This is an exothermic reaction that typically operates between 200 and 400 °C depending on the catalyst and experimental conditions [29]. Although the Sabatier reaction is thermodynamically favourable at low temperatures, kinetic limitations become important due to the high energy barrier that implies the complex eight-electron mechanism of reduction [30]. Therefore, it requires an optimal catalyst to achieve desirable methane production rates and high selectivity [31,32].

#### Enhancing Ni-based catalysts for CO<sub>2</sub> methanation

It is commonly known that group-VIII metals such as Ni, Fe, Co, Ru, Pd and Rh present high catalytic activity and selectivity into methane at low temperatures for CO<sub>2</sub> methanation [33]. Particularly, the major interest is focused on nickel for large-scale production, since it has an optimal combination of activity, selectivity, abundance and low price [34]. Nevertheless, Ni-based catalysts require high reaction temperatures above 400 °C to activate the chemically inert CO<sub>2</sub> molecules and often Ni-catalysts suffer metal sintering [34,35]. Remarkable efforts have been addressed to develop Ni catalysts supported by novel materials able to preserve the high catalytic performance of CO<sub>2</sub> methanation at lower temperatures. For instance, Ni-based metal-organic frameworks as a precursor of Ni NPs confined in carbon nanospheres shell have been tested as an efficient catalyst for CO<sub>2</sub> methanation at low temperatures [36]. In general, metal-organic framework-derived catalysts present enhanced reducibility and remain stable for a longer period than conventional ones. The use of core@yolk-shell structures in CO<sub>2</sub> methanation is also an interesting strategy for designing optimized Ni catalysts due to the

confinement effect, which supposes an enhancement of the catalytic performance and protection against sintering of the active phase.

In this scenario, Ni-based catalysts can be optimized by controlling different parameters that include active phase dispersion, structure, morphology, metal-support interaction, surface chemistry, and so on. All these aspects merit further attention but all of these aspects have already been peer-reviewed by different authors [30,34,37–39], so to avoid redundant information and follow the spirit of the journal we will focus the discussion on the most recent strategies to nanoengineer highly efficient Ni-based catalysts for CO<sub>2</sub> methanation. The take-home message of this section is a screenshot of recent effective reaction engineering approaches to enhance CO<sub>2</sub> methanation.

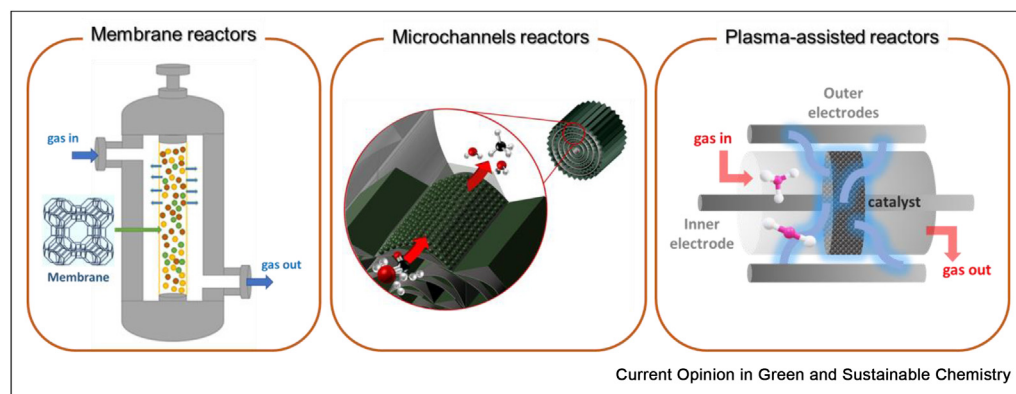
#### Reaction engineering approaches to boost methanation performance

No matter the selected structure or morphology, novel Ni-based catalysts are the system of choice for CO<sub>2</sub> methanation is very remarkable. Hence, assuming the catalysts formulation is somehow established chances to improve the reaction might come from reaction engineering and reactor design. Herein we discuss the most relevant advances in the development of new reaction engineering approaches to boost the CO<sub>2</sub> methanation at LT using Ni-based materials (Figure 2).

#### ■ Catalytic membrane reactors

During CO<sub>2</sub> methanation, water is produced as a by-product. According to Le Chatelier's Principle, water can be removed shifting the equilibrium towards methane production and increasing the process conversion. Moreover, water knocking out is also crucial to mitigate the deactivation of the catalyst since water favours the growth of the catalyst particles and induces nickel oxidation. In this scenario, integrating a water-removal membrane with the catalyst to form a catalytic membrane reactor remarkable increases the overall process efficiency. Zeolites are presented as the main promising materials for the application of water-permeable membranes due to their thermal stability, their topology and microporous structure as well as their adjustable hydrophilicity by varying Si/Al ratio. This is explained by the fact that the presence of Al sites allows the insertion of cations into the zeolite, resulting in a higher affinity to water molecules. However, decreasing Si/Al ratio destabilizes the zeolite structure, so a balance of these two parameters is needed [40]. Zeolite quality is essential for the correct separation in membrane reactions, so the preparation method of these materials plays a crucial role. Recent theoretical studies have demonstrated the achievement of higher CO<sub>2</sub>

Figure 2

CO<sub>2</sub> methanation reaction engineering approaches.

conversions and optimal CH<sub>4</sub> yield with the use of these zeolite-based membranes [41]. Nevertheless, the harsh conditions of the CO<sub>2</sub> methanation imply the decomposition of the zeolitic materials and the reduction in H<sub>2</sub>O affinity, so thermal stable membranes are also needed.

- *Application of microchannel reactors technology for CO<sub>2</sub> methanation.*

Commercial methanators typically used for Sabatier reaction are based on conventional fixed-bed reactors. However, the reaction is highly exothermic and requires efficient heat removal to avoid hotspot formation and catalyst thermal deactivation. In this context, the utilization of microreactors offers a unique opportunity for heat management thus enhancing catalytic performance. Microreactors present multiple advantages such as size reduction, resulting in a decrease in linear dimensions, an increase in the surface-to-volume ratio, volume reduction and production flexibility. Among the benefits of microchannel reactor technology, it must be emphasized the faster start-up of production at lower costs and simple scaling up leading to cost reduction in terms of materials, transport and energy, and the higher flexibility to market demands.

In the last few years, our research group has developed different approaches for designing structured catalysts and microchannel reactors aiming at improving heat and mass transport. The benefits attained in microstructured catalysts and the influence of channels geometry on the CO<sub>2</sub> methanation performance have been recently demonstrated. The boosted catalytic performance showed by substrates based on pseudo-gyroid geometries compared to the traditional honeycomb monoliths was associated with the enhanced mass and heat transport phenomena [42–44]. In other successful

work, García-Moncada et al. [45] tested several Ni/CeO<sub>2</sub> catalysts with different morphology of ceria deposited onto multichannel micro-monoliths. In comparison to powdered catalysts, the structured catalysts achieved high reaction rates of methanation at 300 °C showing negligible deactivation even after 90 h.

- *Plasma-assisted CO<sub>2</sub> methanation*

The activation of CO<sub>2</sub> with plasma has gained enormous popularity in the last years to drive CO<sub>2</sub> methanation with optimal performance at lower energy inputs. Plasma is a state of matter composed of superheated gas where electrons have sufficient energy to escape from the atoms forming an ionized gas. The most common plasma used in catalytic reactors is based on dielectric barrier discharge plasma [46]. The application of non-thermal plasma is able to reduce reaction energy barriers and make possible CO<sub>2</sub> methanation even at temperatures as low as ambient conditions overcoming the kinetic limitations. Recently, Da Costa et al. [47] reported an interesting review which discussed the advantages of plasma-activated CO<sub>2</sub> methanation compared to the traditional thermochemical approach using Ni-based catalysts. Although plasma-activation of CO<sub>2</sub> could be driven even in the absence of a catalyst, it is well known that the combination of plasma with the adequate catalytic material increases the conversion into methane and reduces the energy consumption [48].

#### CO<sub>2</sub> methanation for power generation

CO<sub>2</sub> methanation represents a viable option for the economical optimization of heavy carbon industries such as steel and cement where methane is used to generate energy. Assuming a renewable H<sub>2</sub> source, CO<sub>2</sub> methanation could be integrated into the operation reducing CO<sub>2</sub> emissions and recycling back the produced

Figure 3

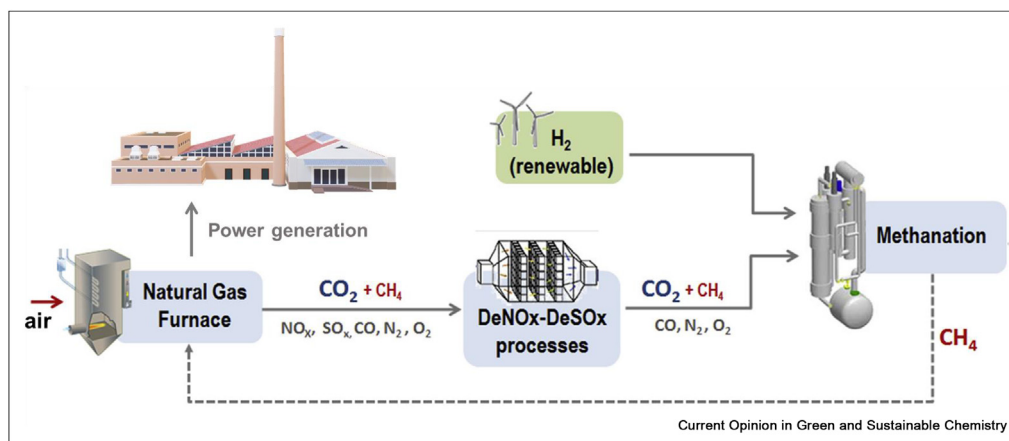


Diagram of the unification of the methanation process with a natural gas furnace used in heavy carbon industries. Adapted from reference [49].

synthetic methane thus increasing the economical proceeds (Figure 3). The optimization of this process reflects the presence of methane traces related to incomplete combustion on the methanator which can affect the performance of the methanation reaction. Pastor-Pérez et al. [49] studied how these methane traces affect the reaction over Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst promoted with Mn and Co, concluding that catalytic activity was improved in the presence of methane. Therefore, this study opens a field of investigation for the optimization of methanation units with recycling loops of methane, increasing activity and reducing the overall cost.

### Concluding remarks and perspectives

Gas-phase CO<sub>2</sub> conversion processes are meant to play a central role to decarbonise the heavy carbon industry. A major advantage of gas-phase CO<sub>2</sub> conversion reactions is the fact that they can be easily adapted to the current industrial infrastructure of major CO<sub>2</sub> emitters (*i.e.* cement manufactures, steel-making plants or refineries) minimising the investment and facilitating a fast response to curve emissions. Among these processes, rWGS, CO<sub>2</sub> methanation and DRM represent direct CO<sub>2</sub> upgrading routes whose success heavily depends on the design of optimal catalysts. This work showcases the recent trends and challenges the catalysis community is facing towards the design of advanced catalysts formulations and reactors in this field. We envisage intense investigation in LT rWGS catalysts where alkali-promoted systems will play a crucial role. The DRM reaction will benefit from smartly designed Ni-based formulations where the active sites are protected somehow in inorganic matrixes of encapsulated core@yolk-shell structures. Also, new zero-band gap phases such as Ni-O-K

will expand the DRM catalysts horizons. As for the CO<sub>2</sub> methanation, new reactor configurations such as micro-reactors and membrane technology as well as non-thermal plasma seem to open a new route to overcome Sabatier's reaction limitations while offering a direct route for synthetic natural gas production and beyond.

All in all, the future of gas-phase CO<sub>2</sub> conversion technologies shares a common destiny with progress in catalysts design which is a cornerstone to enable the transition towards a low-carbon future.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgments

Financial support for this work has been obtained from the Spanish Ministerio de Ciencia, Innovación y Universidades (Grant: RTI2018-096294-B-C33) and Junta de Andalucía projects with references US-1263288 and P20-00667, both programs being co-funded by the European Union FEDER. This work is also sponsored by the Spanish Ministry of Science and Innovation through the projects PID2019-108502RJ-I00 and grant IJC2019-040560-I both funded by MCIN/AEI/10.13039/501100011033 as well as RYC2018-024387-I funded by MCIN/AEI/10.13039/501100011033 and by ESF Investing in your future. Financial support from the European Commission through the H2020-MSCA-RISE-2020 BIOALL project (Grant Agreement: 101008058) is also acknowledged.



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