Policies and Motivations for the CO_2 Valorization through the Sabatier Reaction Using Structured Catalysts. A Review of the Most Recent Advances

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Abstract: The current scenario where the effects of global warming are more and more evident, has motivated different initiatives for facing this, such as the creation of global policies with a clear environmental guideline. Within these policies, the control of Greenhouse Gase (GHG) emissions has been defined as mandatory, but for carrying out this, a smart strategy is proposed. This is the application of a circular economy model, which seeks to minimize the generation of waste and maximize the efficient use of resources. From this point of view, CO_2 recycling is an alternative to reduce emissions to the atmosphere, and we need to look for new business models which valorization this compound which now must be considered as a renewable carbon source. This has renewed the interest in known processes for the chemical transformation of CO_2 but that have not been applied at industrial level because they do not offer evident profitability. For example, the methane produced in the Sabatier reaction has a great potential for application, but this depends on the existence of a sustainable supply of hydrogen and a greater efficiency during the process that allows maximizing energy efficiency and thermal control to maximize the methane yield. Regarding energy efficiency and thermal control of the process, the use of structured reactors is an appropriate strategy. The evolution of new technologies, such as 3D printing, and the consolidation of knowledge in the structing of catalysts has enabled the use of these reactors to develop a wide range of possibilities in the field. In this sense, the present review presents a brief description of the main policies that have motivated the transition to a circular economy model and within this, to CO_2 recycling. This allows understanding, why efforts are being focused on the development of different reactions for CO_2 valorization. Special attention to the case of the Sabatier reaction and in the application of structured reactors for such process is paid.

Keywords: CO_2 methanation; Sabatier reaction; CO_2 hydrogenation; structured reactors; microchannel reactor; monoliths; foams; washcoating; 3D-printing; robocasting; exothermic reaction; Carbon Capture and Utilization (CCU); Carbon Capture and Storage (CCS); circular economy

1. Introduction

Nowadays, we are facing a scenario in which the effects of global warming are advancing rapidly, and the search for solutions goes beyond a simple technological challenge [1]. More integrated solutions are needed that connect different areas and, thus, generate a change in the model of life that allows guaranteeing the future of the planet and the permanence of the human beings in a sustainable way. One of the first steps to launch the search for solutions to stop global warming is the approach of laws, agreements, and treaties at the global, regional, and local level, which recognize the problem,

define the main topics and propose a strategy of action that incorporates the different sectors, including scientific and technological.

In this sense, the reduction of greenhouse gas (GHG) emissions is one of the objectives in the new strategies to curb climate change. However, such a challenge implies the modification of the current productive process and a deep re-evaluation of our lifestyle, which has social, economic, cultural, and political implications. This is why the circular economy model has been proposed as an alternative that seeks to make our relationship with the planet and its resources sustainable and guarantee a future for the new generations [2].

These new approaches have led, for example, to viewing CO_2 as no longer waste but rather a raw material with which you can obtain value-added products among which is a substitute for natural gas [3]. This explains the renewed interest in the reactions of the transformation of CO_2 that, until now, have only been involved in industrial processes in the treatment of relatively small amounts of this compound. There has been no large-scale production that allows industrial processes without CO_2 emissions. This is because the economic profitability of the CO_2 transformation reactions strongly depends on a sustainable and renewable H_2 supply in most cases, as well as on an efficient thermal and mass transport control, the implication of which is a considerable investment. Until now, such investment has not been a priority in any productive sector. However, this approach is changing because, in addition to being harmful to the environment, emitting CO_2 will be somewhat more expensive thanks to the laws that regulate the limits of pollution globally, as can be seen, for instance, in the evolution of the cost of emitting CO_2 in Europe (Figure 1).

Figure 1. Evolution of the allowance for the emission of CO_2 in Europe (Adapted from the European Emissions Allowances data reported in Reference [4]).

Therefore, technologies are being developed to overcome the disadvantages that slow down the massive use of CO_2 and one of the key points is the implementation of structured catalysts since these systems precisely favor the transport processes. In addition, with an adequate design, these allow to more effectively match the recovery of CO_2 in recycling strategies of said compound in the traditional processes that emit it, increasing the global energy efficiency. These strategies agree with the new circular economy model.

In this context, it has been considered important to present a summary of the trends in policies for the control of greenhouse gas emissions and specifically CO_2 (highlighting the case of Europe). How CO_2 recycling is integrated into the transition to the circular economy, and the need for an important technological development that allows such integration, which is reliant on the advances on structured reactors needs to be understood.

Furthermore, the review is focused on the hydrogenation of CO_2 to produce methane, known as CO_2 methanation reaction or Sabatier reaction [5], because it is one of the most promising strategies within the concept of power-to-gas (P2G) [6] to convert this source of carbon in an energy vector.

Although some general considerations regarding the more used catalyst for this reaction will be presented, only the application of structured systems will be outlined in detail. Surprisingly, there is a relatively small number of works devoted to the study of structured systems for CO_2 methanation. These researches have begun to emerge in the last 15 years showing that this is an emerging field.

2. European Policies for the Transition to a Low-Carbon Economy as a Case of Study of the Global Panorama

Although the journey of building a comprehensive worldwide climate policy started in the 1990s, it really took off around the year 2000 with the Kyoto Protocol [7]. Nevertheless, the proposed measurements have demonstrated to be insufficient considering the critical evidence of climate change as produced by global warming [8]. This has motivated the recently formulated Paris Agreement (2015) [9] that made history by being the first globally binding agreement committed to the slowdown of global warming while seeking to reduce poverty and inequality in the world. Nevertheless, these are not easy tasks since the reduction of CO_2 emissions may not be desirable in developed but principally in emerging nations. In fact, the literature presents points of view where a nexus between economic growth and CO_2 emissions is observed [10–12]. As Mardani et al. [10] pointed out the new perspectives suggest that energy conservation policies should be appropriate to cope with the reduction of CO_2 emissions without affecting economic growth.

This has motivated the formulation of the Global Goals for Sustainable Development in 2015 that the global leaders agreed to for a better world by 2030. These goals aim to fight poverty and inequality, as well as to stop climate change, thus, inspiring governments, business, civil society, and the general public to work for a better future for everyone [13]. Specifically, objective 13 (Climate Action) proposes taking urgent actions to combat climate change and its effects. This objective has launched action plans that can be an opportunity to modernize infrastructure worldwide [13]. This implies actions or targets, such as that of to integrate climate change measurements into policies and planning.

One of the clearest examples at present is that of China, which is currently positioned to become the leading economy worldwide if it continues on current projections. This implies the use of enormous resources. However, measures are being taken to prevent the effects of its great development. For instance, in 2013 it was launched the Air Pollution Action Plan [14], and probably this was China's most influential environmental policy of the past five years [15]. Therefore, the second phase of the plan has been proposed as a new 2018–2020 Three-year Action Plan "winning the blue sky war" [15], which shows the intention of the government to improve the environmental conditions generated by development.

Unfortunately, there is not the same course of action in American policy and, taking into account, that today they are the main economy worldwide, their rejection of the Paris Agreement means the loss of one of the countries that should be leading the fight against climate change. And though the United States Environmental Protection Agency (EPA) recently showed a decrease in the United States' Greenhouse Gas Emissions during President Trump's first year in Office [16], it is only a matter of time before it is demonstrated that the US should resume the policies of previous governments. The European Union (EU) has confirmed its commitment with such agreement and has designed a climate policy to reduce the increase in the global average temperature to below 2 °C. For this, by 2050, the emissions of greenhouse gases (GHG) should be to 80% below the 1990 levels, and intermediate milestones for the achievement of this aim are 40% emissions cuts by 2030 and 60% by 2040 (Figure 2), according to the Low Carbon Roadmap and the Energy Roadmap [17] formulated by the EU. Both roadmaps are based primarily on economic and cost-effectiveness considerations follow criteria such as: (i) the creation of a new carbon market-based in renewable sources; (ii) the legal support for the promotion of the use of renewable energies; (iii) the technology update for enhancing the energy efficiency; (iv) the promotion of a new generation of cars and vehicles for reducing the CO_2 emissions, and (v) the promotion of legal and economic support for the enhancement of technologies

for the capture and store CO_2 (following strategies of carbon capture and storage (CCS)), emitted by power stations and industrial buildings [18]).
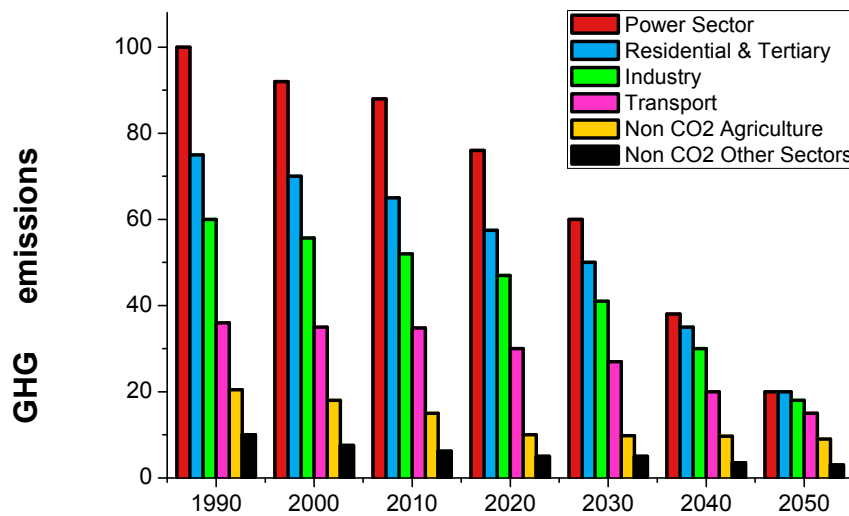

Figure 2. Transition to a low-carbon European Union (EU) economy in 2050 (Green House Gas (GHG) emissions by sector over time as % of 1990 levels). Adapted from [17].

However, although there is clarity in the CO_2 emission targets that are expected to be reached in 2050, the transition to a low-carbon economy in basic sectors such as power generation, industry, transport, agriculture, and construction will be slightly different since each sector has its own dynamics. For instance, for the power sector, a fast transition is projected due to the probable mix of comparatively low-cost low-carbon technologies (renewable energies or sources). Similarly, the construction sector will show a rapid transition, probably because of the new design of low-energy houses, the deep renovation of existing buildings, and the increased efficiency of heating and cooling systems.

Conversely, for the transport and industry sector it is expected a moderate transition until 2030, mostly achieved through efficiency improvements, but after 2030, innovative technologies would be needed (e.g., deployment of electric mobility and Carbon Capture Storage (CCS)). Regarding the agricultural sector, a transitional low-carbon model will be closely linked to meat consumption, and hence a reduction of CO_2 emissions would require behavioral changes of global population diet.

To make the transition to a low-carbon economy, it is estimated that EU should invest €270 billion, during the period 2010–2050. These investments will be in capital goods, which help the transition towards low-carbon generation technologies, such as solar, on and off-shore wind, and nuclear power, extended grid connections, new automotive and other transport technologies, low-energy houses, more efficient appliances, etc. However, despite this big economic effort, the transition to low-carbon economies will open new market opportunities, especially for the manufacturing industry once the main technological challenges are overcome. Thus, new opportunities for the achievement of a better life for the people will be created, through the generation of new jobs that will promote the economic growth of the region. In addition, the EU would become less dependent on expensive imports of oil and gas, as well as less vulnerable to the increases in oil prices. Thanks to that, the EU could save between €175–320 billion annually in fuel costs over the next 40 years [17]. Additionally, the cooperation between the member states of the EU will be strengthened through the creation of strategical alliances, such as that required for the interconnection in electricity networks. The interconnection aims to support the internal market for electricity to enable greater penetration of renewable energy and to improve the security of supply. In addition, the implementation of clean technologies and electricity-based mobility will reduce air pollution in European cities, resulting in the enhancement of the life-quality and health of the population.

3. Transition to a Circular Economy Model and Carbon Capture and Utilization (CCU) Approaches

In the last decade, the new concept and development model of the Circular Economy has been formulated as a suitable approach for facing the challenges of the current global scenario. Its aims to ensure the future of the planet by providing a better alternative to the dominant linear economic development model, the so-called "take, make and depose" [2,19] (Figure 3). In this sense, the Circular Economy model is based on three main "actions", also known the so-called 3R's principles: reduction, reuse, and recycle [2,20], whose aim is to address a smart use of the resources, ensuring long life cycles of products while the environmental impact of the productive processes caused by the generation of waste and pollution is reduced.
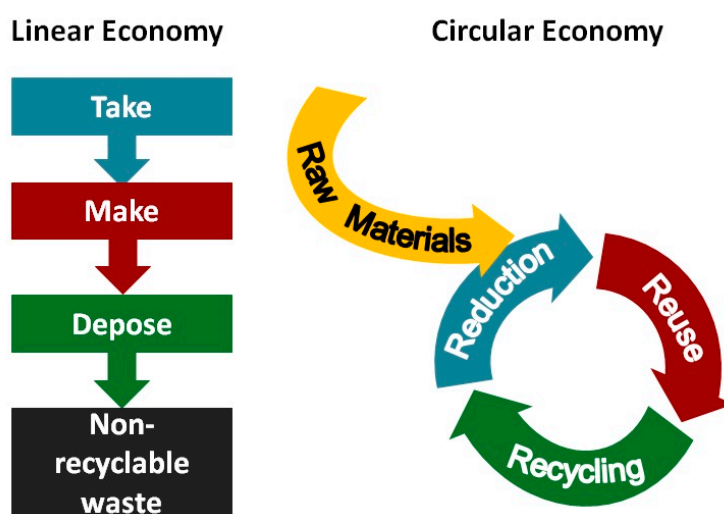

Figure 3. Difference between linear economy and circular economy.

To change the economic model from a linear to a circular approach will need a modification in the way in which things are made. For example, putting sustainability and closed-loop thinking at the heart of business models and industrial organization. This kind of philosophy will have considerable implications for society [21].

From a global point of view, a circular economy could help enable developing and developed countries to industrialize, without placing unsustainable pressure on natural resources and breaching environmental limits. For companies, this kind of model offers a sustainable growth fit for a world where the prices of raw materials are higher every day.

The economic potential for this model is huge, as was projected in the McKinsey analyses carried out by the Ellen MacArthur Foundation, where it was established that if a subset of the EU manufacturing sector adopted circular economy business models, it could realize net materials cost saving worth up to €538.49 billion per year by 2025 [22]. For this economy, the resource loop would be closed, so that big volumes of finite resources, like minerals or metals, are recovered and reused [23]. Other goods can be made from plant-based materials, which are biodegradable, and can be reused as fertilizer at the end of their life. To face this, it is necessary a change in the basic structures of the industrial system.

The EU, as was commented before, has agreed to a strategy for "a resource-efficient Europe" under its strategy for 2020, and introduced an initiative to address raw-materials security [24]. Some countries have their own strategies, for example, Germany has the National Resource Efficiency Programme [25], the Netherlands proposed "materials roundabout"—a hub for the high-grade recycling of materials and products [26], and the United Kingdom has produced a study focusing on economic instruments and raw-materials security [27].

Within this context, CO_2 is now one of the most abundant residues produced in linear economy models. In fact, sectors, such as chemicals, refineries, cement, iron and steel, aluminum, and paper producers, are responsible for the 68% of industry emissions [28], which represents a huge waste of raw material if CO_2 becomes considered a renewable carbon source rather than a residue. This has motivated strategies such as the Carbon Capture and Utilization (CCU) that goes beyond the aims of Carbon Capture and Storage (CCS).

CCU not only presents depleting the emissions of excessive amounts of carbon to the atmosphere by capturing and storing the CO_2 from the exhaust gas produced in industrial processes but also the use of such carbon dioxide as a carbon source for producing energy carriers, chemicals or materials. It is important to differentiate CCU from CCS technology, since, though both face the climate change mitigation, their impact on CO_2 emissions is not the same. The potential of CCU for reversing climate change is more complex and relies on the efficiency of the entire process, the renewable character of the required energy input (considering the corresponding emissions for the production of such energy too), the storage time of CO_2 in the products, and their final use [29]. In this sense, there are different sectors whose economic activity could be enhanced by the inclusion of the CO_2 valorisation within their productive process, such as the petrochemical industry, the power sector, the pharmaceutical, food, polymer, stainless steel, and cement industries, among others [30–35]. Therefore, a renewed interest has been awakened in all processes that allow the chemical transformation of CO_2 into value-added products.

4. CO_2 Valorisation through the Sabatier Reaction

CCU technologies imply that CO_2 has to be first captured [36] and then transformed into valuable products. However, although both processes deserve special attention, the present review is mainly focused on CO_2 utilization rather than the capture step. In this sense, some catalytic reactions can be highlighted as possible routes for obtaining valuable products from CO_2, such as olefins, methanol, formic acid, and dimethyl ether [37]. Additionally, although CO_2 recovery and use may be interesting for different sectors, they must pay attention in its origin, considering parameters such as purity and the recovery procedures, for ensuring the economic profitability of the entire process. In addition, the scheme presented in Figure 4, emphasizes that H_2 must be accessible to valorize CO_2.
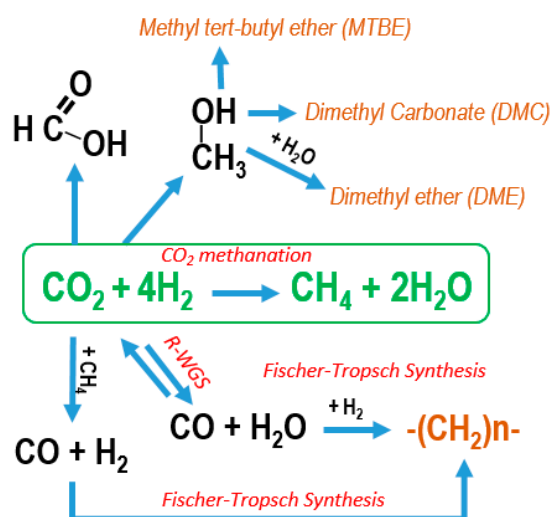

Figure 4. Possible catalytic reactions for the CO_2 valorization.

Within the presented alternatives, a preferable technology to remove and utilize the emitted CO_2 gas is the catalytic conversion in methane through the Sabatier reaction, allowing a procedure to treat large amounts of CO_2 in a short time [38,39]. The CO_2 methanation (Equation (1)) was firstly reported by Paul Sabatier and Jean-Baptiste Senderens in 1902 [40]. Sabatier gives six main applications of the
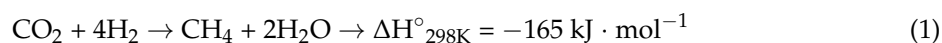
direct hydrogenation method [41], one of them is the CO hydrogenation used to produce methane or gaseous mixtures rich in methane, on a large scale. The catalytic hydrogenation of CO_2 to CH_4 is an old process that was mainly used for the purification of hydrogen by removing small amounts of CO_2 before ammonia synthesis [42,43], and for the production of substitute natural gas (SNG) [44–46]. Nowadays it has received renewed interest, due to the increased global energy demand and the reduction/utilization of GHG [47,48], and particularly CO_2 methanation is one of the most promising strategies within the P2G technology since the produced CH_4 is a substitute for natural gas, which has an existing and well-consolidated distribution grid. Such existing distribution infrastructure would allow this resource to be exploited immediately, minimizing the investment required to massively apply this technology.

Regarding the price of natural gas, this can be cheap for some industries depending on their geographic location within in the distribution radius of a consolidated network. However, as demonstrated in Figure 1, the tendency for CO_2 emissions indicates a clear growth that will force, sooner or later, industries to look for an alternative and this can be the production of methane.
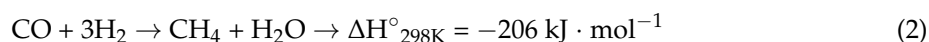
However, CO_2 methanation is far from being industrially implemented despite being thermodynamically favored because of the high cost of hydrogen [49,50]. Thus, the profitability of the Sabatier reaction strongly depends on the supply of cheap and renewable hydrogen.

The direct low-cost transformation of carbon dioxide into methane is highly exothermic, although less than the indirect valorization through CO methanation industrially developed [51] (Equation (2)).
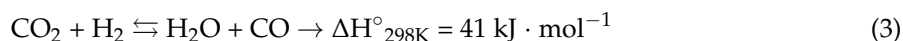
CO_2 methanation

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \rightarrow \Delta H^\circ_{298K} = -165 \text{ kJ} \cdot \text{mol}^{-1} \tag{1}$$

CO methanation

$$CO + 3H_2 \rightarrow CH_4 + H_2O \rightarrow \Delta H^\circ_{298K} = -206 \text{ kJ} \cdot \text{mol}^{-1} \tag{2}$$

Reverse water-gas shift (R-WGS)

$$CO_2 + H_2 \leftrightarrows H_2O + CO \rightarrow \Delta H^\circ_{298K} = 41 \text{ kJ} \cdot \text{mol}^{-1} \tag{3}$$

The most widely accepted mechanism of this reaction is the combination of an exothermic CO methanation, and the endothermic reverse water-gas shift (R-WGS) (Equations (2) and (3) respectively) [52]. This explains the product distribution in the thermodynamic equilibrium, simulated for a stoichiometric feed-stream of CO_2 (15 Vol.%) and H_2 (60 Vol.%) with N_2 for balance (Figure 5), where it is observable that the CO evolution is promoted with temperature resulting in the decrease of the selectivity to CH_4 formation.
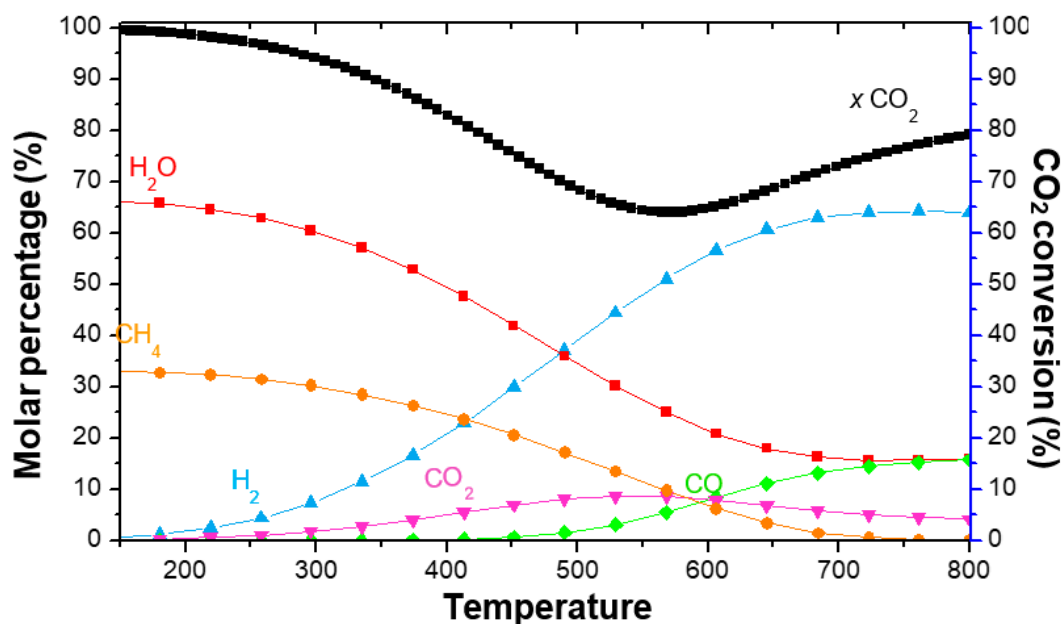
Figure 5. Thermodynamic equilibrium analysis of CO_2 methanation (H_2/CO_2 = 4/1 molar; P = 1 atm).

The main problem associated with CO_2 valorization is its high chemical stability. The C=O double bond breaking is disfavored considering both entropy and enthalpy [53], and at 2000 °C only 2% dissociation into CO and O_2 is estimated to occur [54].

There are recent reviews on the catalytic hydrogenation of carbon dioxide [48,55]. Supported Ru-, Rh-, or Co-based catalysts on different support oxides (TiO_2, SiO_2, Al_2O_3, CeO_2, ZrO_2) have been extensively studied for the hydrogenation of CO_2 [56,57]. However, Ni-based catalysts remain the most widely studied materials mainly due to their low cost [58] despite the highest turnover numbers of Ru-based catalysts [59]. The process efficiency is controlled by the configuration of the catalytic reactor since its high exothermicity, but also by the catalyst activity throughout its lifetime [60]. In his comprehensive review, Jalama [59] addresses all the aspects that affect the kinetics of CO_2 hydrogenation including the active phase, the support, promoters, and even pore size and particle shapes. However, this excellent study is devoted only to the hydrogenation of pure CO_2.

The nature of the support plays a crucial role for high activity of CO_2 methanation. This has resulted in a considerable amount of work that considers the effect of supports and promoters on the catalyst efficiency. The addition of alkaline or alkaline-earth cations promote dissociation and helps gasifying carbon deposits. The high oxygen storage capacity of reducible oxides, such as CeO_2, the easiness of the reducibility of the active phase, the metal dispersion or the support basicity are key factors in the catalyst activity [56].

The CO_2 methanation is sensitive to the structure of the catalysts, and this strongly depends on their chemical composition and the preparation method. Therefore, to improve the activity of the catalyst, efforts must be devoted to optimizing the synthesis conditions, the selection of high surface area supports with tailored pore sizes and optimized basicity and a careful selection of the active phase including bimetallic or multi-metallic active phases. In general, most of the studies are carried out in quite simple systems, and as a consequence, there is a strong need to develop a fundamental understanding of this reaction.

After reviewing of several works, an efficiency order of the different active phases tested for CO_2 methanation can be proposed, following the sequence, Ru > Ni > Co > Fe > Mo which increases the productivity by increasing the metal content [61–69]. Suitable supports have been compared, result in an inferred efficiency order CeO_2 > Al_2O_3 > TiO_2 > MgO [55,68,70–73].

In the case of Ni-based catalysts, the main cause of deactivation seems to be the sintering of the metallic particles that is favored through the formation of the volatile $Ni(CO)_4$ molecules [74].

The second cause of deactivation is the formation of carbon deposits that reduce the number of surface sites for the adsorption of CO and H_2 dissociation. Resistance to sintering through a better metal-support interaction [75] and the addition of water to prevent carbon deposits [76] are common strategies, although this also influences the sintering behavior of the catalyst. Ru and other noble metals-based catalysts are stable under operating conditions and more active than Ni-based catalysts [77].

The excellent review by Jalama [59] analyzes the different aspects that influence the kinetics of the methanation reaction suggesting the general routes for CO_2 hydrogenation. Two main paths are proposed for the reaction. The first one involves CO as an intermediary and a second one that does not involve CO and may have formate-like intermediates. Recent in operando spectroscopic studies mainly for Ni-based catalysts, have shown the nature of the support influences the CO_2 hydrogenation mechanism [78]. Adsorbed CO and formate species are nowadays accepted to form on Ni- and Ru-based catalysts acting as active intermediate species in the hydrogenation of CO_2. In some cases, CO may be formed through formate decomposition. The relative proportion of the active intermediate species is determined by the physicochemical properties of the catalyst support and, therefore, active supports do participate in the reaction mechanism.

If traces of CO_2 are attempted to be converted into methane, as in the case of ammonia plants, the elevated exothermicity of the reaction does not seem to be a problem. However, in the case of the synthesis of Synthetic Natural Gas (SNG), limited heat transfer causes hot spots, affects the lifetime of construction materials and catalysts and, finally, thermal runaway of the reactor may occur. Moreover, the chemical equilibrium shifts away from optimum conditions. To avoid this, several reactor concepts have been proposed among them, cascades of fixed bed reactors with limited conversion, wall-cooled fixed bed reactors, fluidized bed reactors or slurry bubble reactors are used or currently being investigated [61]. However, very few studies are reported in process intensification for this reaction using microchannel reactors, which is an alternate concept allowing the effective reaction heat removal due to their advantageous surface-to-volume ratio [61,79]. By structuring the catalyst, the temperature hot spot is reduced to moderate values and the lifetime of the catalyst is extended by decreasing the activity loss with time.

Most of the studies are performed using pure CO_2 and do not represent real industrial conditions, neither do they pay attention to the presence of contaminants. Industrial feedstocks typically contain trace amounts of sulfur compounds that in H_2 atmospheres may result in H_2S in the feed stream. The effect of this contaminant on the methanation of CO_2 has been analyzed by Szailer et al. [80], and an unexpected result on adding small amounts of H_2S (~22 ppm) to the CO_2 feedstock was observed. H_2S can promote the reaction on TiO_2- and CeO_2-supported metals clusters of Ru, Rh, and Pd. On the contrary, for ZrO_2- and MgO-based supports or when the H_2S content is high (~116 ppm), the catalyst results were poisoned [79]. There are, however, few studies devoted to studying the effect of these contaminants and most of them relate to CO_2 extracted from biogas sources. Even fewer studies are dedicated to the analysis of flue gas methanation.

Mitsubishi disclosed a procedure for transforming the CO_2 contained in power plant flue gas into methane. In their procedure, they decoupled the heat of the waste stream to be further used in the catalytic methanator loaded with Rh catalyst [81].

Müller et al. [82] tested the performances of a 60%Ni/SiO_2 catalyst in the CO_2 methanation reaction of conventional power plants flue gas effluents at 350 °C and stoichiometric H_2-to-CO_2 ratios. They report a stable catalyst with selectivity close to 100% and CO_2 conversions and CH_4 yields greater than 80%. However, in the presence of O_2, SO_2, and NO_2, both CO_2 conversion and CH_4 yield are affected. Nitrogen oxides hardly contribute to the modification of the methanation process, and O_2 up to 8% in concentration has no significant influence apart from decreasing the process efficiency due to the hydrogen combustion reaction. However, ~80 ppm SO_2 concentrations result in a continuous decrease in CO_2 conversion since SO_2 is reduced to H_2S during the reaction that poisons the nickel catalyst.

Recently, academic studies on the integration of the methanation reaction with oxycombustion system within the P2G strategy have appeared claiming the feasibility of the process [83–85]. Moreover, Meylan et al. [86] analyzed several scenarios for the use of CO_2 emissions in the light of EU directives. They conclude that to valorize the CO_2 issued from fossil resources by methanation could make sense, since it allows significant emissions savings exemplifying a possible process for the cement industries where valorization of the unavoidable CO_2 emissions can help decrease industrial emissions of GHG.

Pilot plants within the P2G concept are already in operation [87]. In most cases, H_2 is produced by water electrolysis, being the electrolysers powdered by renewable energy sources and almost pure CO_2 after separating it from biogas using amine scrubbers. This approach with small modifications is already patented, and a scheme of the patented process is shown in Figure 6 [88].
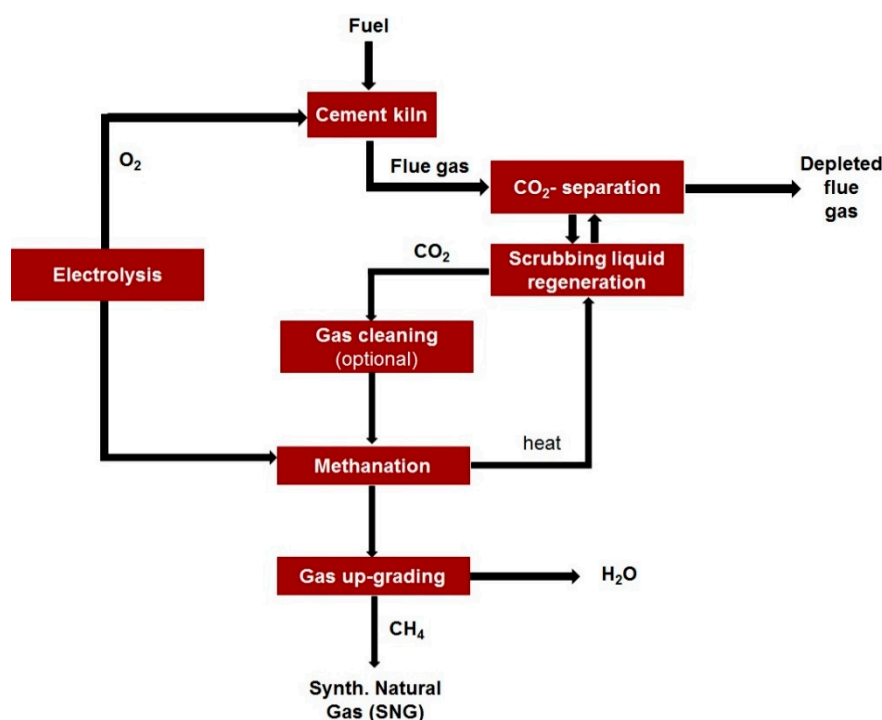

Figure 6. An overview of the synergetic effects of combining diverse industrial processes. Adapted from Reference [88].

Among them, the Audi e-gas plant, located in Werlte (Germany), has been in operation since 2013. It is based on the catalytic methanation of pure H_2 and CO_2 in a single isothermal fixed-bed reactor; the HELMETH project that involves Sunfire GmbH aiming to integrate high-temperature electrolysis and CO_2 methanation. The Desert Research Institute (DRI) in the USA presented a system built in a trailer that consists in a PEM electrolyser powdered by solar panels and wind turbines coupled to a methanator loaded with ring-shaped PK-7R Haldor Topsoe catalyst which is able to operate up to 430 °C. Methanation of flue gases is almost exclusively attempted by research groups at the Brandenburg University of Technology who tested their approach for three months at Schwarze Pumpe power plant, in Germany [89].

A final approach that combines CO_2 capture and methanation has recently been proposed. Farrauto's group, with the support of BASF, is developing a process based on Dual Functional Materials (DFM) [90–92]. Their methods take the profit of the CO_2 spillover from the CaO support to the metallic sites of the Ru/Al_2O_3 methanation catalyst [93]. However, this approach cannot be utilized using flue gases since the redox cycles imply the oxidation of metallic Ru by CO_2 that is further reduced by H_2. In the presence of O_2, this cycle cannot take place, and the catalyst becomes inefficient [94].

5. The Use of Structured Reactors for the Sabatier Reaction

The activity and selectivity of the catalysts for these reactions are dramatically influenced by heat and mass transfer in the reactor. Heat management is a key issue in all processes involving highly exothermic or endothermic reactions, particularly when elevated conversion levels are expected, and structured catalysts may provide an optimal heat control during these processes since the high surface-to-volume ratios improve thermal management. This allows shorter space-time yields, especially in miniaturized reactors, such as those with microchannels, where the reduction of geometric dimensions allows to decrease the transport limitations. Thus, the benefits of the use of structured reactors strongly depend on their design, considering variables such as the shape, size, and density of the channels, among others related to their geometry [95–120]. Additionally, as expected, the selection of the material to manufacture the structured reactors is a determining factor [95]. Metals are highly attractive due to their high heat transfer coefficient and several cases, including alloys, have tested up to now. Most of the metallic monolithic structures developed so far are built out of Al-alloyed ferritic stainless steels foils [120–125]. However, the almost universal utilization of this alloy within the catalytic community is their use at temperatures well below the optimum service temperature and under hydrogen and carbon-rich atmospheres, resulting in migration of alloy elements to the catalytic layer, brattling its joining to the wall of the structured reactor [122,126]. Consequently, further studies about the evolution of the structured systems submitted to reactive atmospheres are required to avoid their degradation, as well as the contribution of uncontrolled processes during the reactions. What is curious is the fact that this is a subject not addressed very often and there are only a few studies in the literature that provide alternative strategies for enhancing the stability of the structured during the reactions or that present the monitoring of the degradation of the structured systems under reactive atmospheres [125–129]. Although this is not within the main scope of the present review, it has to be remarked that the evolution and wear of the structured during the operation have to be taken into account not only for the CO_2 methanation but also for any reaction.

Even though the Sabatier reaction has been widely studied, this has been mainly carried out in fixed-bed reactors [130], and the use of structured systems has not been considered until the last decade. One of the scenarios where the advantages of the structured reactors have been attractive is the design of in-situ propellant production for Mars exploration. In particular, the Sabatier reaction is one of those considered for the design of applications able to use local resources to "live off the land", commonly referred to as in-situ resource utilization (ISRU), which aims to expand robotic and human extraterrestrial exploration and to establish a long-term human presence beyond low earth orbit, as noted by Hu et al. [131]. These authors, in a cooperation between the US Pacific Northwest Laboratory and the NASA, proposed the conversion of Martian atmospheric CO_2 into useful materials such as methane that can be used as fuel for the return journey using water electrolysis as the pathway for the production of the required hydrogen and O_2 that may be used for life support. For this purpose, the use of microchannel reactors was considered since, that under this scenario, the efficiency of the process should be maximized in the so-called NASA's ISRU. It essentially integrates a CO_2 methanation unit and an R-WGS (Figure 7) but also involves complementary processes that make the process sustainable.
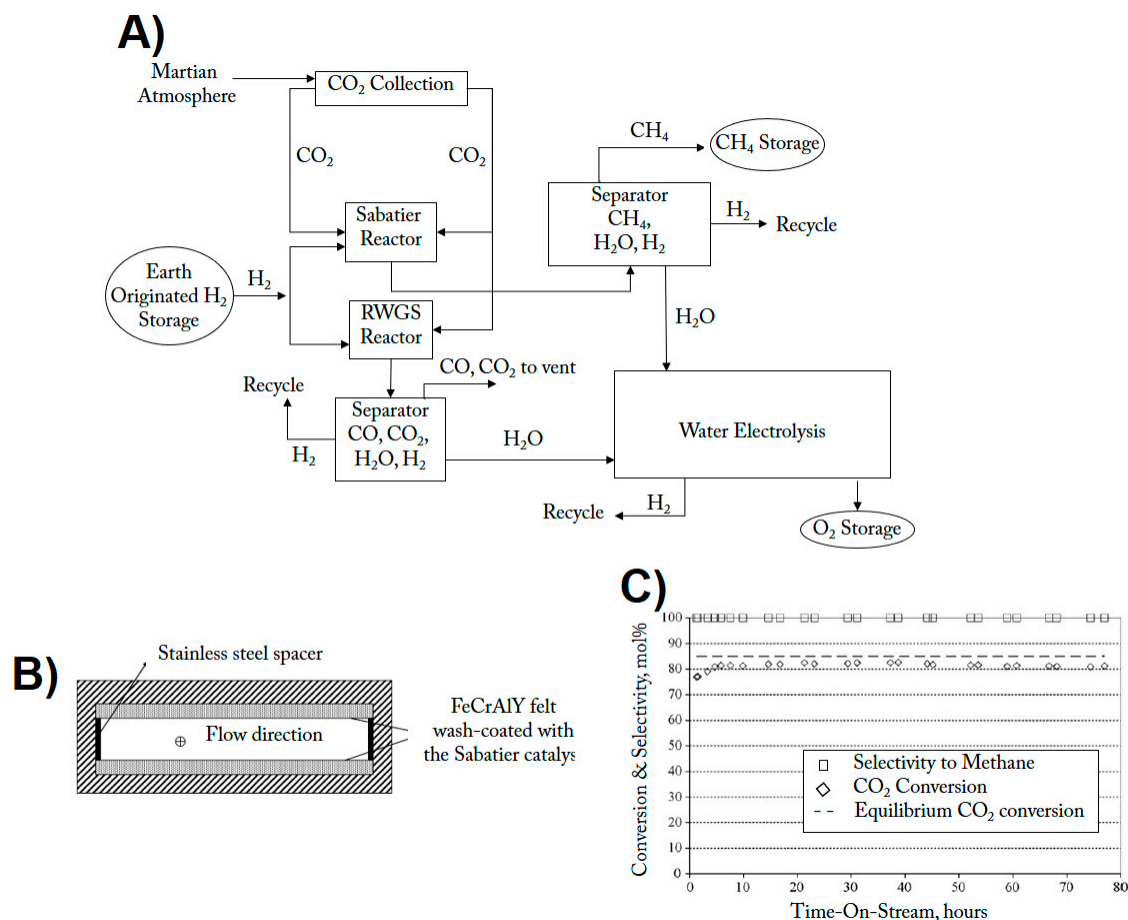
Figure 7. The NASA's in-situ resource utilization (ISRU): (**A**,**B**) Top view of the reactor channel installed with structured catalyst; (**C**) Catalyst stability testing under repeated shutting down and restart conditions (3% Ru/TiO_2 as structured catalysts). Adapted from Hu et al. [131].

In this manuscript, for the Sabatier reaction, a Ru/TiO_2 catalyst was used, and the structured systems were prepared using porous FeCrAlY intermetallic alloy to achieve low-pressure drop and improve heat transfer. Through single channel tests (Figure 6B), it was observed that the operation of the reactor was very steady. In general, the microreactors allowed operating under well-controlled isothermal conditions and through this work, the authors demonstrated a successful transfer of the intrinsic kinetic performance obtained at the powder catalyst level to structured systems.

More recently, within the context of the CO_2 recycling strategies, Roger et al. [132] presented preliminary results of the study of structured cellular foam-based catalysts in a platelet milli-reactor. To improve the heat transfer, foams coated with different catalysts were manufactured with β-SiC. This material is chemically inert and has mechanical and thermal resistance, although it presents a low specific surface area (20 cm^2/g). Nevertheless, by growing nanofibers on the foam's surface, the specific area can be increased up to (20 cm^2/g), so the effects of the nanofibers were evaluated. Later, these authors presented the performance of the open cell foams with a special focus on the exothermicity of the process, followed using infrared thermography with the experimental setup proposed presented in Figure 8 [133]. In this case, foams made with different materials were studied (alumina, aluminium, and SiC).
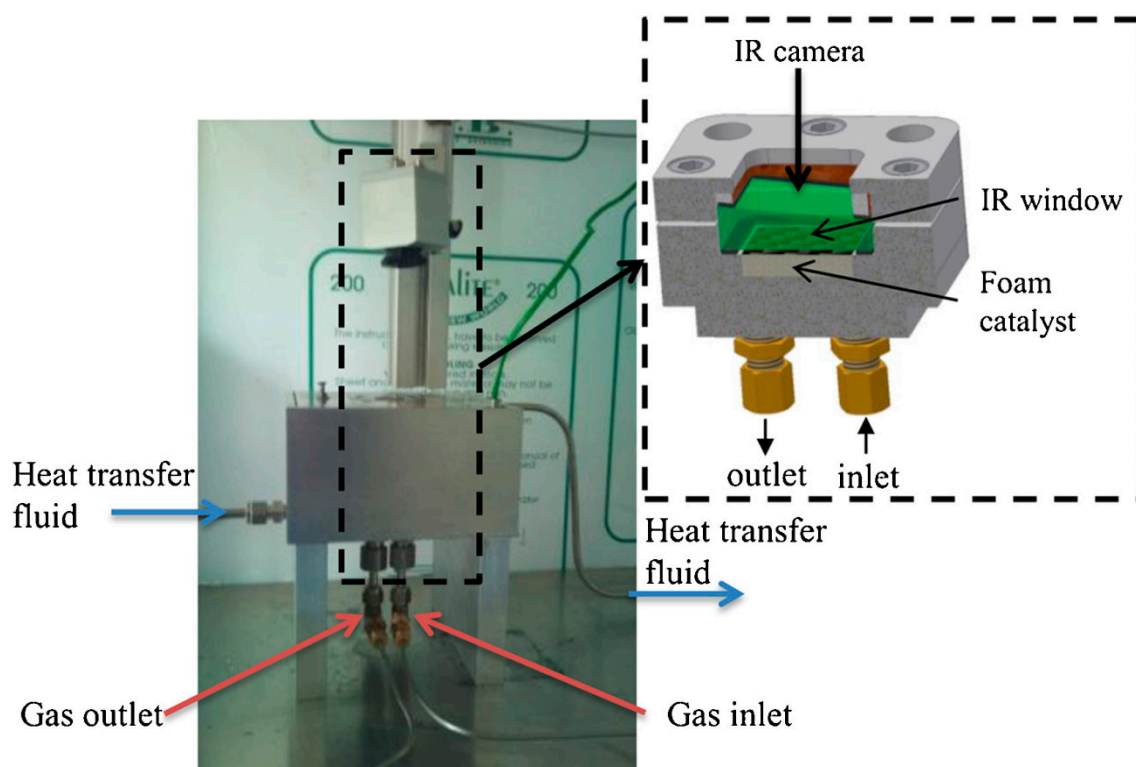
Figure 8. Experimental setup of the study of the performance of the platelet milli-reactor Adapted from Frey et al. [133].

Through this study, it may be confirmed how important the selection of the material is. For instance, it was observable that the coating of the catalyst over every substrate requires specific treatments of the surface. Additionally, the kind of material influences the thermal profile during the reaction as well as the catalytic activity due to the differences in surface area of the substrates. The thermographs obtained during the experiments represented the temperature in the structured system and the setup allowed to establish that at the beginning of the reaction, a fast temperature increase is produced. Then the temperature increased all over the system of reaction following the flow direction. As expected, the thermal conductivity of the substrates increased in the following order: alumina < aluminium < SiC, although some hot-spots were also observed in the last case. Although it is clear that further advances are required for this experimental setup, this is an interesting approach not only for the advancement of structured catalysts but also for the integration of in-situ experiments that allow obtaining information under more realistic operational conditions.

In another work, Tada et al. [134] studied the use of sponge Ni catalysts, where the material of the structured system played the role of the active phase. The authors suggested advantages regarding the facile manufacturing of these sort of reactors. Moreover, they attributed the high activity of the devices to the great number of crystal defects of fcc-Ni in the sponge. Nevertheless, the thermal stability of the surface Ni species is the main drawback of this system since the active defects of the structured may disappear under high-temperature treatments.

Fukuhara et al. [135] reported the use of a nickel-based structured catalyst for CO_2 methanation. They developed a honeycomb-type structured system with a high methanation performance. First, they tested different oxides (Al_2O_3, TiO_2, ZrO_2, Y_2O_3, MgO, CeO_2, and zeolites) as support for the active phase (10 wt%-Ni), and the best results were obtained with Ni/CeO_2, so, from this catalyst, they prepared the structured system by the wash-coating method on an aluminium-fin substrate (Figure 9). The powder catalysts exhibited a difference in the activity at 250 °C, due to the accumulation of energy as a result of the exothermicity, while the structured catalyst was able to transfer that energy excess.
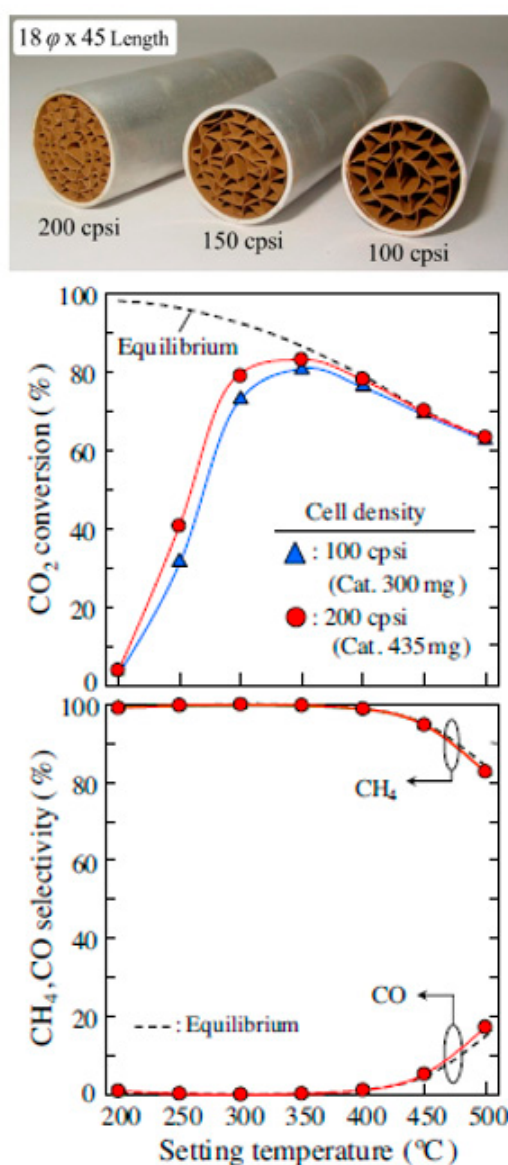
Figure 9. Image of the honeycomb-type Ni-based catalysts and catalytic performance of the honeycomb-type Ni/CeO$_2$ catalyst with different cell densities. Adapted from Fukuhara et al. [135].

Another aspect remarked by the authors is the fact that the cell density of the structured systems clearly influenced the performance. Therefore, the structured catalyst with the stacked-type-fin enhanced the performance to improve the properties of the mass transfer in the reaction field. Additionally, the stability of the structured systems was successfully probed during almost 125 h. Later in another paper derived from this work, Fukuhara and coworkers presented a more comprehensive study of the use of metallic monoliths coated with Ni/CeO$_2$ catalyst [136]. In this case, various configurations of metallic honeycomb-type reactors, which were plain, stacked, segment, and multi-stacked (Figure 10) were constructed and evaluated under different reaction conditions (i.e., inlet temperature, feed flow rate and CO$_2$ partial pressure), aiming to establish a suitable configuration for enhancing the heat transfer during the process.
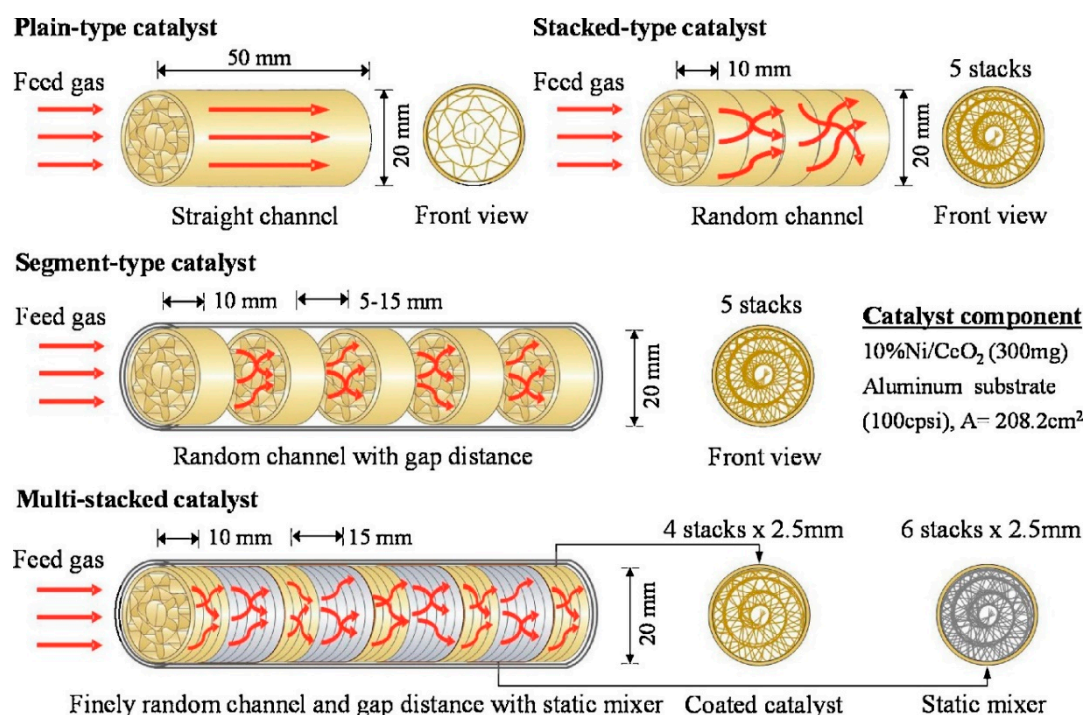
Figure 10. Configuration of the honeycomb-type catalysts. Reproduced with permission from Reference [136]. Copyright S. Ratchahat, M. Sudoh, Y. Suzuki, W. Kawasaki, R. Watanabe, C. Fukuhara, 2018.

The evaluation of the different configurations of the structured reactors revealed that multi-stacked catalysts could maintain the high methanation performance even under high feed flow rate condition of 3000 mL/min at pure feed gas component, with a moderate hot-spot formation. This resulted in the boosting of the CO_2 conversion (>90%) and the CH_4 selectivity (>99.5%). Furthermore, the catalytic activity was maintained at 300 °C and 3000 mL/min over 76 h. Therefore, it was confirmed that the multi-stacked configuration is a suitable approach for the enhancement of the catalytic performance during the CO_2 methanation and this was associated to the enhancement of the transport phenomena according to the studies of heat and mass balances (using an overall heat transfer coefficient (U) and the reaction rate constant (K)) (Figure 11).
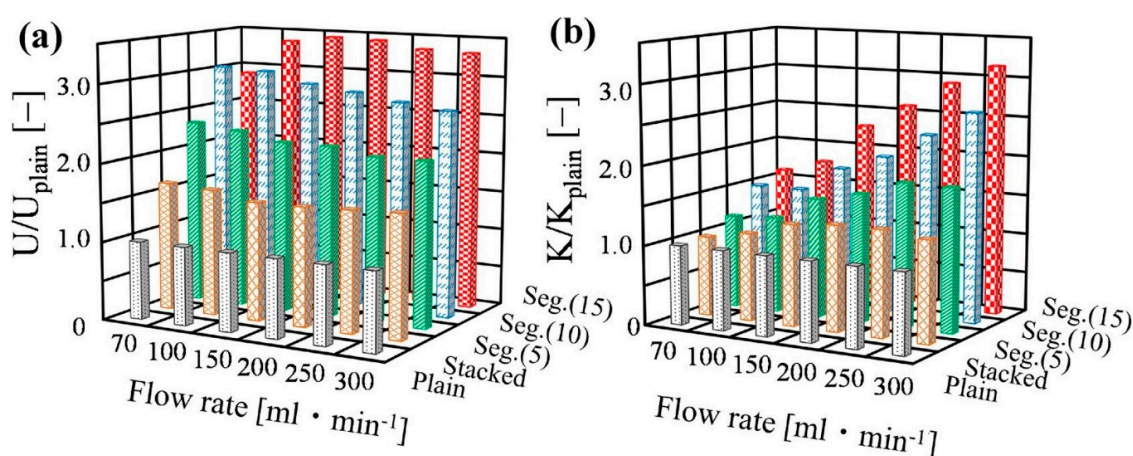

Figure 11. (**A**) Enhancement of the heat and mass transport phenomena with the stacked and segment-type configurations: (**A**) U values; (**B**) K values. Reproduced with permission from Reference [136]. Copyright S. Ratchahat, M. Sudoh, Y. Suzuki, W. Kawasaki, R. Watanabe, C. Fukuhara, 2018.

Probably the most comprehensive study about the heat transfer analysis during CO_2 methanation using metallic structured reactors was recently presented by Schollenberger et al. [6]. In this work, stainless steel and aluminum honeycomb-type monoliths coated with Ni/Al_2O_3 commercial catalyst were tested and the obtained results at laboratory scale that allowed to carry out the scale-up demo-scale by means of numerical modeling. Therefore, it is important to remark that the experiments carried out in the laboratory including kinetic studies and heat transport analysis allowed to establish the basis for the technical feasibility evaluation in a bench-scale plant added to a biomass gasification plant considering the geometry and boundary conditions as presented in Figure 12.
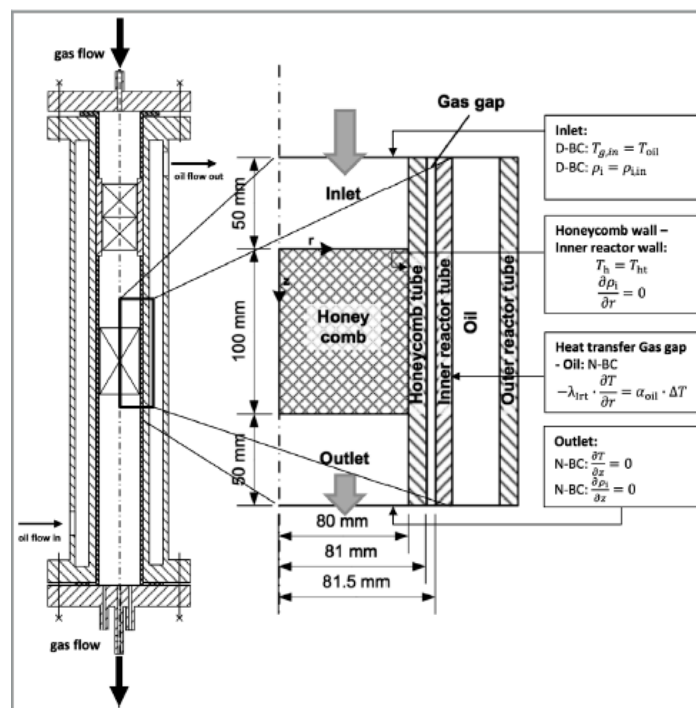

Figure 12. Reactor geometry and boundary conditions for numerical modeling. Reproduced with permission from Reference [6]. Copyright D. Schollenberger, S. Bajohr, M. Gruber, R. Reimert, T. Kolb, 2018.

For the heat transfer analysis, it was established the radial thermal conductivity for a honeycomb structure, strongly depends on the dimensions and the thermal conductivity of the material of construction, as well as on the gas flowing through the structure and is flow velocity. The experimental setup and the data evaluation procedure for measuring the temperature profiles in the monoliths without reaction (as reference) are presented in Figure 13, and the evaluation of the experimental results was based on the energy balance around the honeycomb represented by Equation (4). One of the most relevant results of this communication is that it was demonstrated how the thermal efficiency has to be a critical criterion for the design of a catalytic application for the CO_2 methanation adaptable to a scaled-up process.

$$\rho_g c_{P,g} u_{0,g} \frac{\delta T}{\delta z} = \lambda_{r,\ eff} \left(\frac{\delta^2 T}{\delta r^2} + \frac{1}{r} \frac{\delta T}{\delta r} \right) + \lambda_{z,\ eff} \frac{\delta^2 T}{\delta z^2} \tag{4}$$
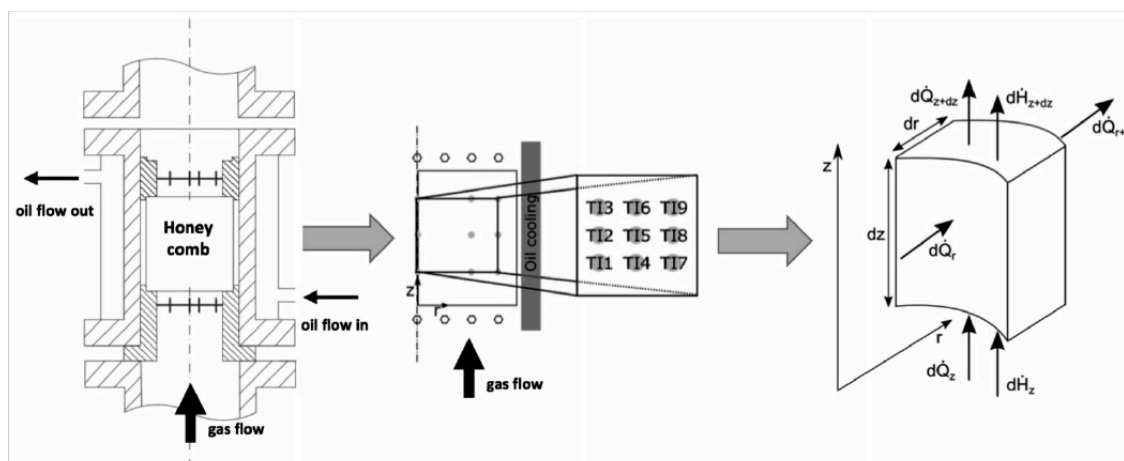
Figure 13. Experimental setup for the study of honeycomb-type monoliths: position of the monolith in the measuring section (**left**), the positioning of the thermocouples (**middle**), and a schematic volume element for balancing (**right**). Reproduced with permission from Reference [6]. Copyright D. Schollenberger, S. Bajohr, M. Gruber, R. Reimert, T. Kolb, 2018.

To solve the differential equation, the following boundary conditions were set:

- $T = T_{in}(r)$ at z = 0 (Dirichlet boundary condition (D-BC)),
- $\frac{\delta T}{\delta z} = 0$ at z = L (Neumann boundary condition (N-BC)),
- $\frac{\delta T}{\delta r} = 0$ at r = 0 (Neumann boundary condition (N-BC)),
- $T = T_{wall}(z)$ at r = R (Dirichlet boundary condition (D-BC)).

An alternative to the use of metals for manufacturing the substrates of structured reactors is the synthesis of three-dimensional network materials, controlled using synthesis. For instance, Liu et al. [137] reported the production of NiO/SBA-15 monoliths with a mesoporous framework that creates the pathways for the pass of the reactants and allows their contact with nickel species. However, heat transport is hardly achievable, despite the interesting results in this sort of structured system and considering that mass transport phenomena may be improved.

The use of ceramic monoliths in the Sabatier reaction have also been explored within the study of Ni/GDC (Ni/gadolinium-doped-ceria) structured on cordierite substrates. These devices allowed a superior heat releasing than the fixed-bed catalyst. However, the discussion was principally focused on the advantages of the use of monoliths for the enhancement of the mass transport during the reaction. Although the authors pointed out that with low-loaded monoliths (0.2 g/cm^3), poor catalytic activities were observed due to the short contact time between the reactants and the catalytic layer.

Finally, the appearance of modern additive technologies for the manufacture of 3D objects, among which are the techniques of 3D printing and three-dimensional fiber deposition (3DFD) (robocasting technique), has opened a new field of exploration of design and manufacturing of multiple objects, including structured reactors. The 3DFD technique enables the production of periodic porous ceramic and metallic structures, thus, there are interesting advantages on using these techniques for obtaining structured reactors, such as the fact that more complex geometries can be produced, or that the manufacturing processes may be carried out more easily with a superior reproducibility and reducing of the production costs.

One of the few works combining these novel methodologies for the Sabatier reaction is that presented by Danaci et al. [138]. These authors proposed the manufacturing of Ni/Al$_2$O$_3$ coated macro-porous structures using the robocasting technique that allowed obtaining different structures made with stainless steel (316 L) (Figure 14). In general, it was confirmed the superior performance of the structured catalysts compared with that of the powder catalyst, and useful information regarding the anchoring of the catalyst to the walls of the monoliths was also presented. However, the most

remarkable result is the evidence of the direct influence of the geometry design over the catalytic activity. In this case, the structured catalyst of "zig-zag" configuration showed better results and the probable improvement of the heat and mass transport phenomena must be the reason.
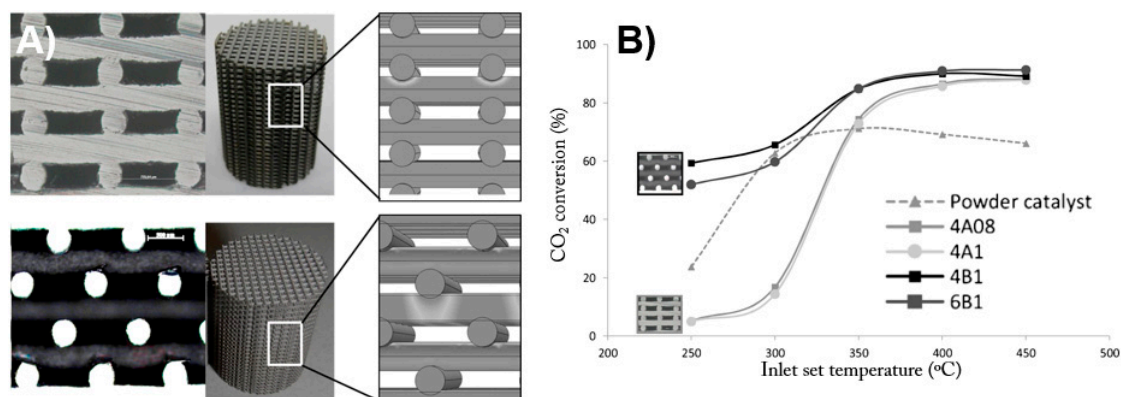

Figure 14. Monoliths obtained using robocasting for the Sabatier reaction. (**A**) Cross-sectional images of the different configuration of the structured monoliths obtained using three-dimensional fiber deposition (3DFD); (**B**) Catalytic performance of the structured reactors vs. the powder catalyst. Adapted from Danaci et al. [138].

More recently, the same research team applied the 3DFD technique for obtaining the structured reactors using copper as raw material [139]. In all cases, the systems were coated with a Ni/Al_2O_3 catalyst. However, the remarkable fact of this work is that it confirms the tendency to explore different materials such as copper to optimize the obtaining of structures through 3D printing (Figure 15). This implies the optimization of different variables during the printing process as well as the during the washcoating with the selected catalyst.
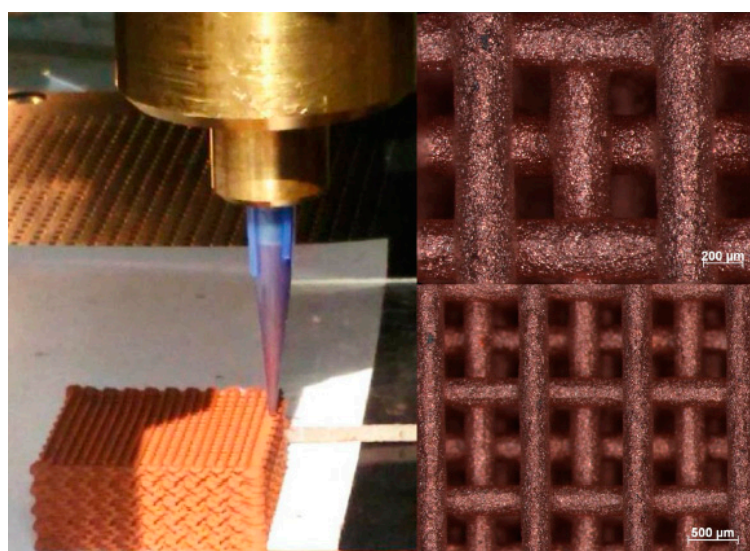

Figure 15. 3D printed structured reactors made with copper. Reproduced with permission from Reference [139]. Copyright S. Danaci, L. Protasova, F. Snijkers, W. Bouwen, A. Bengaouer, P. Marty, 2018.

6. Concluding Remarks

The current policies regarding the control of GHG emissions and the need of advances for the CO_2 recycling, which is a strategy in agreement with the required transition to a circular economy model, make the application of structured reactors for CO_2 methanation a topic of growing interest. In the works published up to now, it has been confirmed that the structured systems favor the mass transport

during the reaction, but mainly a better transfer of heat, which is decisive for such exothermic reaction whose CH_4 yields depends on a good thermal control.

Regarding the catalysts, the more active systems (mainly Ni-based catalysts), are the most widely used for manufacturing the structured catalysts. As for the manufacturing of the substrates where the catalysts are deposited, different materials have been studied. However, metals such as aluminum, copper, and stainless steels are preferred due to their high heat conduction respect to that of ceramic materials.

Despite all these positive aspects of the use of structured reactors in the Sabatier reaction, the studies presented so far do not represent a significant advance with respect to the knowledge that already exists of this type of systems in other reactions. However, the emergence of 3D printing technology has opened a wide range of possibilities in terms of the type of materials that can be used and, especially the design of the substrates, which can present geometries able to potentiate even more the benefits observed so far. These types of technologies are also allowing the development of increasingly robust simulation systems, based on reliable 3D modeling, which allows us to think that the optimization of new devices will be increasingly intelligent. Therefore, it is evident that this is a promising field in which growth in the number of works is foreseen in the near future.

Among the challenges that future works dedicated to this topic must face, is the use of materials with better conductive properties than metals. Similarly, develop designs of reactors with an optimized geometry to maximize catalytic performance and make production both cheaper and profitable. Finally, and perhaps the most difficult of all, is to study structured reactors in real applications of CO_2 recycling in industrial processes that, in addition to this compound, generate another type of pollutant that can have an important impact on catalytic performance. For this, much more complex strategies are required in which the purification of CO_2 before methanation will play an important role.

Conflicts of Interest: The authors declare no conflicts of interest.

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