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# Capture and Methanation of $CO_2$ Using Dual-Function Materials (DFMs) †

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**Abstract:** The conversion of $CO_2$, captured from flue gases, into synthetic natural gas (SNG) aims to create a closed carbon cycle, where excess $H_2$ produced from renewables is utilized to transform $CO_2$ released from existing conventional power plants into a reliable and high energy density carrier, that is $CH_4$. In the last five years, extensive research effort has been dedicated to the synthesis and optimization of composite materials for the realization of this process. These materials, also known as dual-function materials or DFMs, typically consist of an alkaline metal oxide or carbonate phase, along with a Ru or Ni metallic phase supported on a high surface area carrier. The DFMs incorporate both sorptive and catalytic capabilities, capturing the $CO_2$ in the initial sorption step and then converting it into $CH_4$ upon $H_2$ inflow. The dispersion of the sorptive and catalytically active phases, the $CO_2$ affinity of the alkaline phase, the reducibility of the supported metals, and the selectivity towards $CH_4$ production are some of the parameters influencing their performance. Hereby, we aim to present the most recent works dedicated to the development and optimization of such dual-function materials to be used in the combined capture and methanation of $CO_2$.

**Keywords:** $CO_2$ hydrogenation; $CO_2$ capture and utilization; synthetic natural gas; dual-function materials

## 1. Introduction

The expanding global economy requires the utilization of readily available energy sources, such as fossil fuels, to keep up with the always increasing energy demands of our society. The use of fossil fuels as an energy source inevitably results to greenhouse gas emissions, such as $CO_2$, into our atmosphere [1]. The problem of increasing anthropogenic $CO_2$ emissions can be partly countered by the storage of captured $CO_2$ into underground geological formations (carbon capture and storage, CCS) [2] or by the utilization of captured $CO_2$ for the production of useful chemicals, such as syngas, methanol, and methane (carbon capture and utilization, CCU) [3]. The conversion of $CO_2$ into chemicals often requires the use of hydrogen as a reducing agent. The full hydrogenation of $CO_2$ into $CH_4$ or $CO_2$ methanation aims to convert captured $CO_2$ and produced $H_2$ into a molecule with a higher energy density ($CH_4$) and allow for the utilization of the extensive natural gas grid for its transportation [4]. The $CO_2$ methanation reaction is also called the Sabatier reaction and is exothermic:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O,\ \Delta H_{298K} = -164\ kJ/mol \quad (1)$$

$CO_2$ needs to be initially captured from industrial flue gases, either via absorption using liquids or adsorption using solids. Amongst the solid $CO_2$ adsorbents, CaO and CaO doped with various promoters are the most studied. Modified or unmodified CaO captures and releases $CO_2$ via a reversible carbonization/ decarbonization process [5]. The $CO_2$ can then be either stored or further processed to produce valuable chemicals.

The combination of the aforementioned processes, namely $CO_2$ capture and $CO_2$ methanation, can be realized via the utilization of composite materials that can perform both functions. These materials are known as dual-function materials (DFMs) and typically consist of a $CO_2$ sorption phase (such as CaO, MgO or $Na_2CO_3$) and a catalytically active methanation phase (metallic Ni or Ru nanoparticles) supported on a high surface area carrier (such as $Al_2O_3$ or $ZrO_2$) [6,7]. The Farrauto group have been the first to prepare a DFM that consisted of CaO and Ru phases supported on mesoporous $Al_2O_3$. $CO_2$ could be initially captured by the CaO sites and then spillover to adjacent Ru sites upon its hydrogenation during $H_2$ inflow [8]. Ru was chosen as the active metal due to its superior methanation activity and high reducibility, being able to be reduced back to its metallic state at just 320 °C [9]. Further works have shown that there are many possibilities to perform the combined capture and methanation of $CO_2$ by using different material formulations [10,11].

The increasing interest of the research community in the fields of $CO_2$ capture and $CO_2$ methanation has boosted the number of publications regarding DFMs during the last five years. Thus, the recent progress made in the development of such novel materials will be summarized.

## 2. Capture and Methanation of $CO_2$ Using Dual-Function Materials

The concept of dual-function materials (DFMs) for the the $CO_2$ capture and conversion to $CH_4$ was first introduced by Farrauto and co-workers [8] (Figure 1). The materials were prepared via the subsequent impregnation of Ca and Ru precursor salts on high surface area $Al_2O_3$. In a first step, a simulated flue-gas stream containing $CO_2$, $O_2$, $N_2$, and $H_2O$ was introduced into the reactor containing the DFMs. $CO_2$ was retained by the CaO adsorbent phase and the high dispersion of CaO over the mesoporous $Al_2O_3$ support allowed for the reversible chemisorption and release of $CO_2$ at temperatures lower compared to those for bulk CaO. Later, $H_2$ was flown into the reactor and captured $CO_2$ was hydrogenated after its spillover towards Ru metal sites to eventually form $CH_4$. The optimized 5wt% Ru-10wt% $CaO/Al_2O_3$ composition produced around 0.5 mol $CH_4$ per kg DFM. The reversible $CO_2$ chemisorption and release over highly dispersed CaO, along with methanation over highly active and reducible Ru sites allowed for the process to proceed isothermally at 320 °C.

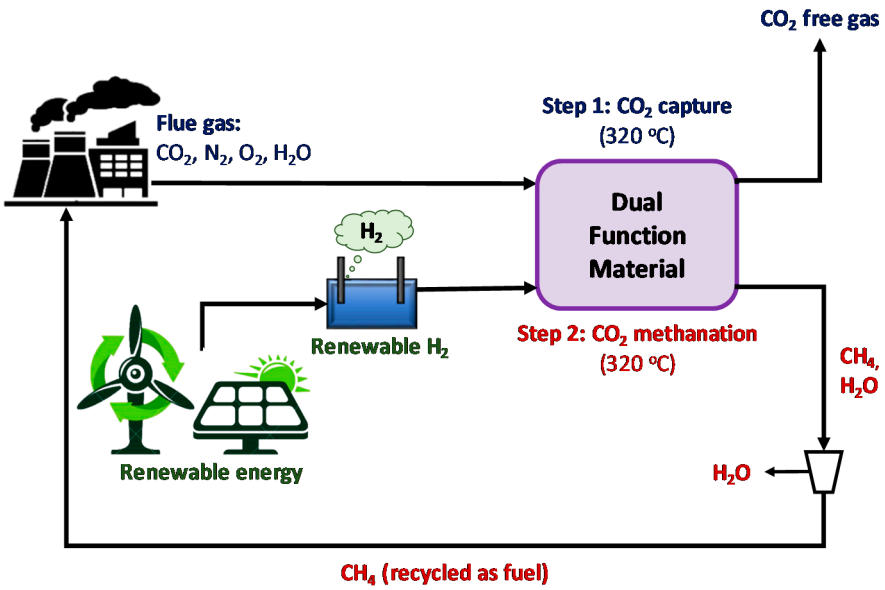



**Figure 1.** Schematic summarizing the dual-function materials (DFM) concept. Reproduced with permission from ref. [7]. Copyright 2020 MDPI.

Besides Ru, Rh could be also used as an active metal in DFMs [12]. The use of just 0.1 wt% Rh loading in a Rh-CaO/$Al_2O_3$ DFM was shown to produce similar amounts of $CH_4$ to the DFM with 5 wt% Ru. However, the very high price of Rh (being about 10 times more expensive than Ru) discourages its further implementation. Also, the use of other adsorbent phases such as $Na_2CO_3$ and $K_2CO_3$ supported on $Al_2O_3$ was shown to be a more reliable approach to improve the performance of DFMs. The DFM with composition 5wt% Ru-10wt% $Na_2CO_3/Al_2O_3$ yielded 1.05 mol $CH_4$ per kg DFM, roughly twice the amount of similar DFM compositions that use CaO as the adsorbent phase.

The role of Ru in DFM applications has been further studied by Wang et al. [13] and Duyar et al. [9]. Ru, when combined with a $Na_2CO_3$ or "$Na_2O$"-type sorbent could achieve superior methanation kinetics by exhibiting faster hydrogenation rates. Furthermore, the $RuO_x$ oxides could rapidly reduce to metallic Ru at just 320 °C upon $H_2$ inflow, after being previously oxidized during the $CO_2$ capture step from the simulated flue-gas stream. In contrast, oxidized Ni required a much larger hydrogenation temperature to revert to its metallic state and thus, no $CH_4$ could be produced upon hydrogenation at 320 °C, when $CO_2$ capture was performed in the presence of $O_2$.

The reaction mechanism for the combined $CO_2$ capture and methanation over the 5% Ru, 10% $Na_2CO_3$ (or 6.1% "$Na_2O$)/$Al_2O_3$ DFM was studied by Proaño et al. [14] employing in-situ DRIFTS. Al-O-$Na^+$ sites initially originated after the decomposition of $Na_2CO_3$ under a reducing atmosphere. $CO_2$ from the gas stream was then largely adsorbed and retained by these sites as chelated carbonato complexes. The adsorbed carbonates were subsequently spilled over to nearby Ru-sites via and were hydrogenated into $CH_4$ via formate-type intermediates. Furthermore, the use of such DFMs, but with an even lower amount of Ru (0.5%) was shown to be viable for the combined direct air capture and methanation of $CO_2$ process [15]. Through this process, $CO_2$ captured from ambient air, where its concentration is as low as 400 ppm, can be successfully transformed into $CH_4$ upon $H_2$ inflow.

As mentioned before, Ni, although being much cheaper than Ru or Rh, is not considered viable for use in DFMs under flue-gas applications due to its lower reducibility [9]. However, Arellano-Treviño et al. [16] showed that the addition of small amounts of noble metals, namely 1wt% Pt and 1wt% Ru on a 10wt% Ni-6.1wt % $Na_2O/Al_2O_3$ DFM could improve the reducibility of Ni at 320 °C by 50% and 70%, respectively. An assumption was made that $PtO_x$ and $RuO_x$ phases were initially rapidly reduced and they in turn worked to split and spillover atomic hydrogen into nearby NiO sites. The bimetallic 1wt% Ru-10wt% Ni-6.1wt% $Na_2O/Al_2O_3$ DFM exhibited the highest $CO_2$ adsorption capacity and $CH_4$ yield among the studied materials, due to the synergy between the Ni and Ru active metals. Proaño et al. [17] also revealed that Pt atoms served as additional $CO_2$ capture sites in the form of Pt-CO species, but that they were inactive for methanation. In contrast, Ru sites in RuNi-based DFM aided the methanation process and provided superior reducibility and catalytic activity (Figure 2).

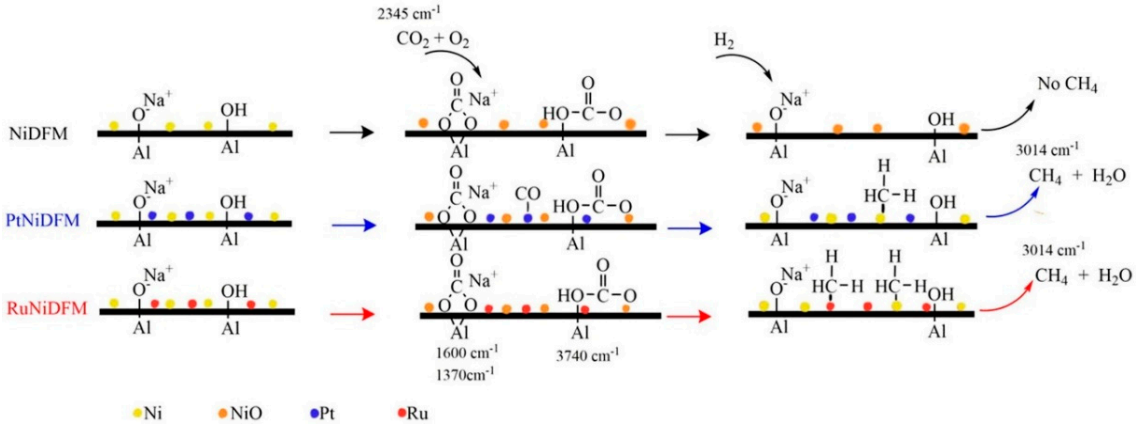



**Figure 2.** Mechanism of $CO_2$ capture and methanation over Ni-based DFMs and Ni-based DFMs impregnated with small amounts of Pt and Ru noble metals. Reproduced with permission from ref [17]. Copyright 2020 Elsevier.

Other research groups have also made meaningful contributions in the field of dual-function materials. Bermejo-López et al. [18] studied the reaction mechanism and the effect of adsorbent loading over Ru-based DFMs. They found that higher adsorbent loading increased the material's basicity and $CH_4$ yield. Furthermore, the type of sorbent also exerted a great influence, since strong basic sites over CaO (Ru10CaO) favoured methanation at higher temperatures, while weaker adsorption of $CO_2$ over $Na_2CO_3$ sites ($Ru10Na_2CO_3$) allowed for the methanation to proceed at lower temperatures. Regarding the reaction mechanism, adsorbed $CO_2$ from the capture step was assumed to spillover to nearby Ru sites and then be hydrogenated into $CH_4$ upon $H_2$ inflow (Figure 3).

Bermejo-López et al. [19] also studied Ni-based DFMs with CaO and $Na_2CO_3$ as adsorbent phases. The presence of the adjacent $CO_2$ adsorbent phase appeared to favour Ni reducibility, while the use of high Ni loadings was beneficial to increase the yield for $CH_4$. Furthermore, the $CO_2$ capture was performed under an $O_2$-free atmosphere in this case and the temperature required for the hydrogenation of adsorbed carbonates was quite higher compared to DFMs with Ru as the active metal.

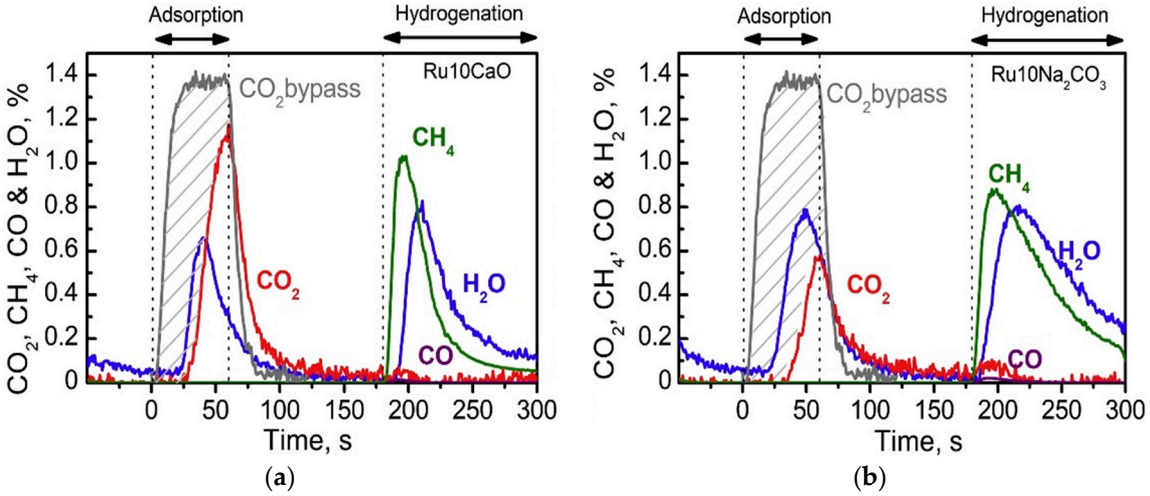



**Figure 3.** $CO_2$, $H_2O$, $CH_4$ and CO concentration profiles during one $CO_2$ adsorption and hydrogenation cycle at 370 °C with (**a**) Ru10CaO and (**b**) $Ru10Na_2CO_3$ samples. Reproduced with permission from ref. [18]. Copyright 2019 Elsevier.

Other material formulations have been also developed for DFM applications. Cimino et al. [20] impregnated γ-$Al_2O_3$ spheres with various alkalimetals (Li, Na, K and Cs) and used Ru as an active metal. Li was the only alkalimetal that could result in increased methanation activity compared to benchmark $Ru/Al_2O_3$, as well as facilitate faster methanation kinetics upon cyclic capture and methanation of $CO_2$ at a temperature as low as 230 °C. Also, Sun et al. [10] prepared a DFM via mechanical mixing of an alkali nitrate promoted MgO sorbent and a Ru supported on $CeO_2$ nanorods methanation catalyst. The increased population of sorption active sites led to the capture of a quite high amount of $CO_2$, whereas high methanation activity was ensured by the highly active $Ru/CeO_2$ catalyst, that could activate $CO_2$ via oxygen vacancies in the $CeO_2$ support, forming formate-type intermediates.

Regarding Ni-based DFMs, Hu et al. [21] used a $ZrO_2$ support doped with K and La, and Ni as the active metal. K-addition in the support managed to greatly increase the $CO_2$ adsorption capacity, with $CO_2$ being bonded as bidentate carbonates, whereas La-addition favoured the methanation kinetics due to the formation of easily reducible formate intermediates. Furthermore, Zhou et al. [11] employed a different material type, namely a 2D-layered $Ni/MgO\text{-}Al_2O_3$ composite derived from an initial hydrotalcite precursor as a DFM. Co-precipitation synthesis of the initial Ni- and Mg-containing hydrotalcites was followed by high temperature calcination and reduction to obtain the final 2D-layered composites, that contain a plethora of MgO basic sites. The authors showed that increased Ni contents could weaken the metal-support interaction, whereas the durations of the individual $CO_2$ capture and methanation steps could be tuned so as to achieve an optimal utilization of reactant $H_2$ gas (35 s for $CO_2$ capture and 25s for $CO_2$ methanation).

Finally, Jo et al. [22] used a simple Ni/CaO catalyst-sorbent, prepared by the citrate sol-gel method. The addition of the Ni phase over the CaO sorbent facilitated its regeneration and $CH_4$ production under $H_2$ flow at temperatures lower than the ones needed for the decarbonization of $CaCO_3$. Further, 500 °C was chosen as the optimum temperature for the $CO_2$ capture and methanation process due to the high $CO_2$ capture capacity, $CH_4$ selectivity, and cyclic stability. Compared to the 5wt% Ru-10wt% $CaO/Al_2O_3$ DFM, operated at 320 °C [9], the prepared Ni/CaO material could capture at 500 °C around 13 times more $CO_2$ and convert it into $CH_4$ with a similar efficiency.

## 3. Conclusions

The emergence of novel dual-function materials that can perform the functions of capturing $CO_2$ from industrial flue-gases and converting it to $CH_4$ using renewable hydrogen has opened a new pathway to recycle our emitted carbon resources. This new field has attracted numerous research efforts during the last five years and great progress has been made towards enhancing the materials performance (as usually expressed in mol of produced $CH_4$ per kg of DFM). However, further efforts need to be undertaken in order to increase the $CO_2$ sorption capacity and $CH_4$ yield of these materials, as well as to explore the possibility of performing the $CO_2$ capture step from ambient air.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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