Capture and Methanation of CO₂ Using Dual-Function Materials (DFMs) †

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Abstract: The conversion of CO₂ captured from flue gases, into synthetic natural gas (SNG) aims to create a closed carbon cycle, where excess H₂ produced from renewables is utilized to transform CO₂ released from existing conventional power plants into a reliable and high energy density carrier, that is CH₄. 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 CO₂ in the initial sorption step and then converting it into CH₄ upon H₂ inflow. The dispersion of the sorptive and catalytically active phases, the CO₂ affinity of the alkaline phase, the reducibility of the supported metals, and the selectivity towards CH₄ 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 CO₂.

Keywords: CO₂ hydrogenation; CO₂ 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 CO₂, into our atmosphere [1]. The problem of increasing anthropogenic CO₂ emissions can be partly countered by the storage of captured CO₂ into underground geological formations (carbon capture and storage, CCS) [2] or by the utilization of captured CO₂ for the production of useful chemicals, such as syngas, methanol, and methane (carbon capture and utilization, CCU) [3]. The conversion of CO₂ into chemicals often requires the use of hydrogen as a reducing agent. The full hydrogenation of CO₂ into CH₄ or CO₂ methanation aims to convert captured CO₂ and produced H₂ into a molecule with a higher energy density (CH₄) and allow for the utilization of the extensive natural gas grid for its transportation [4]. The CO₂ methanation reaction is also called the Sabatier reaction and is exothermic:

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}, \quad \Delta H^{\circ}_{298K} = -164 \text{kJ/mol}
\] (1)
CO₂ needs to be initially captured from industrial flue gases, either via absorption using liquids or adsorption using solids. Amongst the solid CO₂ adsorbents, CaO and CaO doped with various promoters are the most studied. Modified or unmodified CaO captures and releases CO₂ via a reversible carbonization/ decarbonization process [5]. The CO₂ can then be either stored or further processed to produce valuable chemicals.

The combination of the aforementioned processes, namely CO₂ capture and CO₂ 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 CO₂ sorption phase (such as CaO, MgO or Na₂CO₃) and a catalytically active methanation phase (metallic Ni or Ru nanoparticles) supported on a high surface area carrier (such as Al₂O₃ or ZrO₂) [6,7]. The Farrauto group have been the first to prepare a DFM that consisted of CaO and Ru phases supported on mesoporous Al₂O₃. CO₂ could be initially captured by the CaO sites and then spillover to adjacent Ru sites upon its hydrogenation during H₂ 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 CO₂ by using different material formulations [10,11].

The increasing interest of the research community in the fields of CO₂ capture and CO₂ 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 CO₂ Using Dual-Function Materials

The concept of dual-function materials (DFMs) for the the CO₂ capture and conversion to CH₄ 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 Al₂O₃. In a first step, a simulated flue-gas stream containing CO₂, O₂, N₂, and H₂O was introduced into the reactor containing the DFMs. CO₂ was retained by the CaO adsorbent phase and the high dispersion of CaO over the mesoporous Al₂O₃ support allowed for the reversible chemisorption and release of CO₂ at temperatures lower compared to those for bulk CaO. Later, H₂ was flown into the reactor and captured CO₂ was hydrogenated after its spillover towards Ru metal sites to eventually form CH₄. The optimized 5wt% Ru-10wt% CaO/Al₂O₃ composition produced around 0.5 mol CH₄ per kg DFM. The reversible CO₂ 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.](image-url)
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/Al2O3 DFM was shown to produce similar amounts of CH4 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 Na2CO3 and K2CO3 supported on Al2O3 was shown to be a more reliable approach to improve the performance of DFMs. The DFM with composition 5wt% Ru-10wt% Na2CO3/Al2O3 yielded 1.05 mol CH4 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 Na2CO3 or “Na2O”-type sorbent could achieve superior methanation kinetics by exhibiting faster hydrogenation rates. Furthermore, the RuOx oxides could rapidly reduce to metallic Ru at just 320 °C upon H2 inflow, after being previously oxidized during the CO2 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 CH4 could be produced upon hydrogenation at 320 °C, when CO2 capture was performed in the presence of O2.

The reaction mechanism for the combined CO2 capture and methanation over the 5% Ru, 10% Na2CO3 (or 6.1% “Na2O”)/Al2O3 DFM was studied by Proaño et al. [14] employing in-situ DRIFTS. Al-O-Na+ sites initially originated after the decomposition of Na2CO3 under a reducing atmosphere. CO2 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 CH4 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 CO2 process [15]. Through this process, CO2 captured from ambient air, where its concentration is as low as 400 ppm, can be successfully transformed into CH4 upon H2 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 % Na2O/Al2O3 DFM could improve the reducibility of Ni at 320 °C by 50% and 70%, respectively. An assumption was made that PtOx and RuOx 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% Na2O/Al2O3 DFM exhibited the highest CO2 adsorption capacity and CH4 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 CO2 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](image_url)
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 CH4 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 CO2 over Na2CO3 sites (Ru10Na2CO3) allowed for the methanation to proceed at lower temperatures. Regarding the reaction mechanism, adsorbed CO2 from the capture step was assumed to spillover to nearby Ru sites and then be hydrogenated into CH4 upon H2 inflow (Figure 3).

Bermejo-López et al. [19] also studied Ni-based DFMs with CaO and Na2CO3 as adsorbent phases. The presence of the adjacent CO2 adsorbent phase appeared to favour Ni reducibility, while the use of high Ni loadings was beneficial to increase the yield for CH4. Furthermore, the CO2 capture was performed under an O2-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.

Other material formulations have been also developed for DFM applications. Cimino et al. [20] impregnated γ-Al2O3 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/Al2O3, as well as facilitate faster methanation kinetics upon cyclic capture and methanation of CO2 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 CeO2 nanorods methanation catalyst. The increased population of sorption active sites led to the capture of a quite high amount of CO2, whereas high methanation activity was ensured by the highly active Ru/CeO2 catalyst, that could activate CO2 via oxygen vacancies in the CeO2 support, forming formate-type intermediates.

Regarding Ni-based DFMs, Hu et al. [21] used a ZrO2 support doped with K and La, and Ni as the active metal. K-addition in the support managed to greatly increase the CO2 adsorption capacity, with CO2 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-Al2O3 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 CO2 capture and methanation steps could be tuned so as to achieve an optimal utilization of reactant H2 gas (35 s for CO2 capture and 25s for CO2 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 CH₄ production under H₂ flow at temperatures lower than the ones needed for the decarbonization of CaCO₃. Further, 500 °C was chosen as the optimum temperature for the CO₂ capture and methanation process due to the high CO₂ capture capacity, CH₄ selectivity, and cyclic stability. Compared to the 5wt% Ru-10wt% CaO/Al₂O₃ DFM, operated at 320 °C [9], the prepared Ni/CaO material could capture at 500 °C around 13 times more CO₂ and convert it into CH₄ with a similar efficiency.

3. Conclusions

The emergence of novel dual-function materials that can perform the functions of capturing CO₂ from industrial flue-gases and converting it to CH₄ 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 CH₄ per kg of DFM). However, further efforts need to be undertaken in order to increase the CO₂ sorption capacity and CH₄ yield of these materials, as well as to explore the possibility of performing the CO₂ capture step from ambient air.

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