

## Review

# A Review of Advances in Carbon Dioxide Capture with the Aim of Reusing Them as Fuel

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**Abstract:** Currently, converting CO<sub>2</sub> from industrial exhaust into fuel is a challenging issue that many researchers are working on. As it is obvious, adsorption and conversion are two distinct processes, and there is a need for special materials and conditions to occur in each of them. Lately, there have been efforts to combine these two steps by using dual functional materials (DFMs) and making adsorbents and catalysts simultaneously. DFMs comprise two components. The first component of DFMs is the adsorbent, which researchers can get from oxides, carbonates, or both. The second component is the catalyst, which is typically made of metallic elements, such as Nickel or Ruthenium. Capturing systems of CO<sub>2</sub> by DFMs, innovative developments, and suggested ways to boost the efficiency of CO<sub>2</sub> capture are discussed in this review. DFMs made with changed adsorbents perform better in CO<sub>2</sub> adsorption and conversion, according to sources.

**Keywords:** capturing & conversion of CO<sub>2</sub>; dual functional materials (DFMs); adsorbents; catalyst; fuel

## 1. Introduction

Due to global warming, rising greenhouse gases and air pollution, there have been efforts to develop cleaner and more reliable energy sources. Hydrogen is a significant source of energy. Combining it with oxygen produces energy and steam, which is why people are interested in this system. The second eco-friendly method is using solar cells to produce electricity from sunlight. Capturing CO<sub>2</sub> gas and converting it to fuel is another desirable technology that is being discussed here [1–6].

It causes consumption and climate change to the increase in population and the need for more energy to ensure human well-being in today's world. In the energy supply cycle, CO<sub>2</sub> gas plays two different roles. Fossil fuel combustion causes it to enter the environment and air pollution which may trigger many respiratory diseases. CO<sub>2</sub> gas results in global warming, climate changes and rising seawater levels so mass increase of CO<sub>2</sub> can even cause drowning of coastal cities in the near future. Mentioned reasons are among the most vital reasons of CO<sub>2</sub> emission. To minimize the damage caused by CO<sub>2</sub> gas, a second role for it through strategies outlined in the international treaty has been discussed which allows to capture of the gas and reuse it as a fuel [6–9].

Despite progress in capturing and converting CO<sub>2</sub>, obstacles remain in its reuse. The materials used for CO<sub>2</sub> capture are one of the most significant challenges. Many researchers have conducted studies in this field. DFMs are used to tackle some of these challenges practically. DFMs can detect CO<sub>2</sub> in diluted exhaust gas from industrial plants and aid in CO<sub>2</sub> transportation and storage using carbon capture and storage (CCS) technology. Researchers

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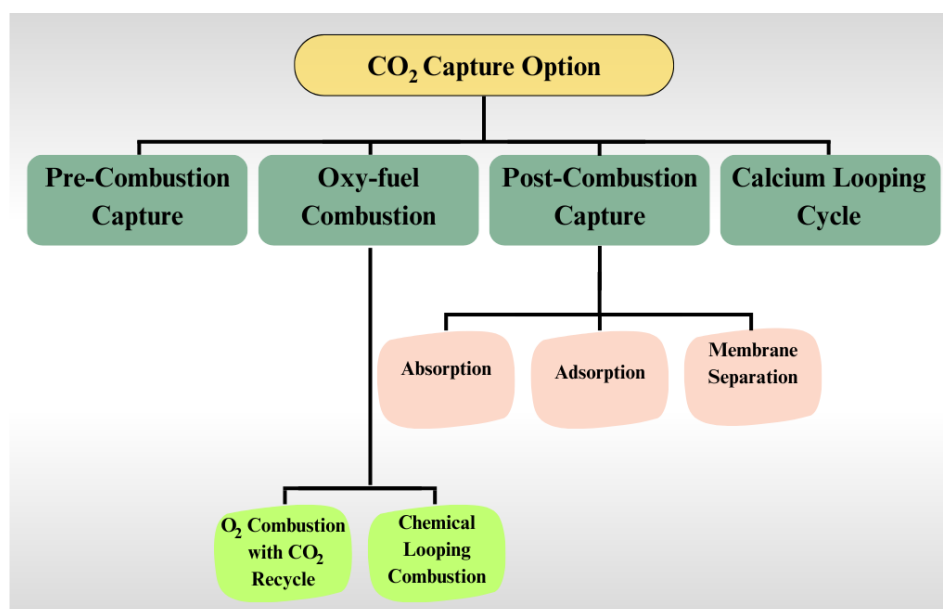
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make these materials by combining a sorbent component with a catalytic component. commonly used alkali metal oxides or carbonates are commonly used as sorbent components to prepare active points for direct CO<sub>2</sub> capturing [10–14].

CCS technology relies on special materials with a high capacity for sorbing CO<sub>2</sub>. These materials need to stay stable in super-hot or quite cold conditions. Scientists are researching various materials to find the best ones for different purposes [15–17]. CCS has three main types: pre-combustion, oxy-fuel combustion, and post-combustion. These methods are sensitive to temperature changes, which affect how much CO<sub>2</sub> they can capture [16–18]. This review explains CCS technology briefly and focuses on the materials used to sorbing CO<sub>2</sub> in DFMs. It also talks about the progress made in recent years and what other advances might happen in the future.

## 2. Different Methods of CO<sub>2</sub> Capturing

Figure 1 summarizes CO<sub>2</sub> capture methods. The pre-combustion sorption approach involves partially burning fossil fuels and producing CO<sub>2</sub> gas. Next, the system directs the carbon monoxide (CO) into a chamber with a catalyst, resulting in a reaction that produces CO<sub>2</sub> and hydrogen. Processes by the team capture and make CO<sub>2</sub> available for reuse through adsorption and absorption processes. Oxy-fuel combustion is another technique that captures CO<sub>2</sub> by reacting to fuel with oxygen in a condensation process. Oxygen can be generated by burning recycled CO<sub>2</sub> or using a solid material in a process called chemical looping combustion (CLC). The calcium looping cycle is a versatile method that can be used both before and after combustion. By utilizing calcium oxide (CaO), this method captures CO<sub>2</sub> from exhaust gases and forms the calcium carbonate (CaCO<sub>3</sub>) [18, 19].



**Figure 1.** CO<sub>2</sub> capture options (redrawn by authors from Zhao et al. [19])

Capturing CO<sub>2</sub> using post-combustion methods involves three steps: sorption, membrane separation, and surface adsorption. In the sorption stage, CO<sub>2</sub> is removed from exhaust gases by reacting it with a chemical solvent, usually amine-based solutions, like monoamines, diamines, triamines in water, and diisopropanolamine. [20, 21]. While amine scrubbing systems have been extensively developed for CO<sub>2</sub> capture from exhaust gases, they still face several significant challenges. Problems with amine solutions involve high energy costs, low CO<sub>2</sub> sorption capacity, and thermal instability of amines. To address these challenges associated with amine-based solutions, solid amine sorbents have been developed. These solid materials functionalized with amines offer several advantages, including lower energy requirements compared to amine-based solutions. A key reason for their reduced energy demand is their lower heat capacity when compared to amine-based solutions [22].

In a recent study conducted by Zhang et al. [23], a comprehensive parametric analysis was undertaken to assess the heat requirements for the regeneration of solid amine-based materials. The heat demand for Polyethyleneimine (PEI)/SiO<sub>2</sub> is 2.46 GJ per metric ton of CO<sub>2</sub>, while Monoethanolamine (MEA) requires 3.9 GJ and optimized MEA requires 3.3 GJ. Furthermore, it was observed that amine-functionalized solid materials

exhibit superior CO<sub>2</sub> adsorb capacities and heightened resistance to exhaust gas contaminants. The widespread use of solid materials in industries is on hold until technology improves.

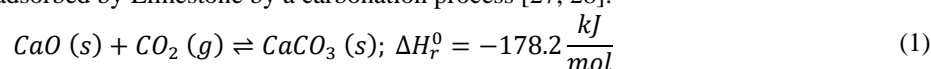
Among post-combustion CO<sub>2</sub> capture techniques, membrane separation technology stands out. More research is needed to improve membrane stability, gas purity, and recovery rates. Adsorption techniques for CO<sub>2</sub> capture are promising because they require low energy, are easy to handle, and are not affected by corrosion. Scientists are researching the combination of adsorbents and catalysts to make DFMs [21, 23].

### 3. Different CO<sub>2</sub> Sorbents

Having characteristics such as high sorption capacity, low production cost, low regeneration needs, fast kinetics, and long-term stability are the most important features that can be controlled to selectively CO<sub>2</sub> capturing from exhaust gases. Zeolites and activated carbon selectively capture materials, but their effectiveness decreases with high temperatures. While Hydrotalcites have shown promise in CO<sub>2</sub> capture, their sorption capability is limited for large-scale industries. Research has shown that mesoporous materials perform well and have a high absorption capacity at low temperatures [24, 25]. In general, sorbents used for CO<sub>2</sub> sorption are grouped into three different categories: oxide-based, carbon-based, and other sorbents which are discussed below.

#### 3.1 Oxide-based sorbents

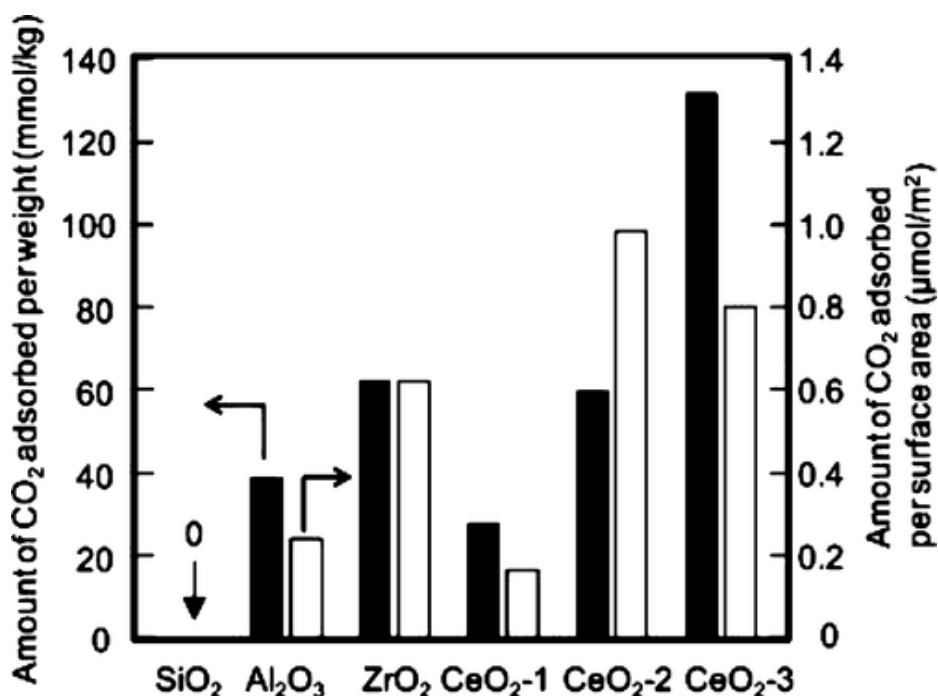
In many sources, CaO (Lime) has been introduced as an excellent sorbent due to its characteristics such as low cost and high tendency to react with CO<sub>2</sub>, CaO is the basis of the calcium looping cycle technology [24, 26, 27]. CaO can be obtained from Limestone/Dolomite by calcining at a temperature about 900°C. As shown in equation 1, CO<sub>2</sub> can be adsorbed by Limestone by a carbonation process [27, 28].



Despite the good properties and performance of CaO as a sorbent for CO<sub>2</sub> Capture, it also has its disadvantages. A drawback is increased mechanical failure because of excessive sintering during high-energy regeneration. Also, the carbonation rate slows down and drops after the formation of the first layers of CaCO<sub>3</sub>. By using powdered CaO and increasing the amount of surface, this problem can be solved approximately, but other challenges such as high-pressure drop, entrainment of the flow, and attrition of materials have been observed [27]. In order to investigate these disadvantages more closely and their elimination, different research have been conducted to investigate CaO. For example, Florin et al. [29] have investigated the sorption ability of CaO obtained from CaCO<sub>3</sub> nanoparticles. Changing the structure of CaO didn't matter because there was enough time for sorption during the test cycles. Additionally, other results showed a 20% increase in CO<sub>2</sub> sorption and desorption capacity after 100 cycles of 20 minutes, compared to bulk CaO [29]. Li et al. [30] investigated the hydration of CaO by using a mixture of ethanol-water to improve the sorbing reaction. The results showed that by doubling the initially prepared mixture, the sorption capacity of the catalyst is improved. Also, Pichardo et al. [31] showed that the adsorption capacity of CaO can be increased by modifying the synthesis method. They created CaO by combining two methods: rapid solution combustion and high-energy milling. They then studied how quickly it adsorbs under standard conditions. they also found that the new CaO when subjected to a CO<sub>2</sub> flow at 25 °C and 1 atm, it is easily converted into CaCO<sub>3</sub>. The high conversion of CaO was attributed to the improvement of structural and textural properties such as nano adsorbent fluffy structure, specific surface area (Brunauer-Emmett-teller (BET)), and large pore volume.

Belova et al. [33] tried to improve the sorption capacity of calcium oxide (CaO) and prevent sintering by dispersing it on an inert alumina (Al<sub>2</sub>O<sub>3</sub>) substrate. Initially, the carbonation reaction exhibited rapid kinetics. However, once a carbonate layer had been established, the reaction rate became predominantly limited by the rate of CO<sub>2</sub> release within that formed layer. Increasing the surface area of CaO particles improved diffusion and sintering challenges. This issue has been investigated in another study by Gruene et al. [27] The reported results showed that the stability of the sorbent was obtained by dispersing CaO on Al<sub>2</sub>O<sub>3</sub>. In this research, the kinetics and CO<sub>2</sub> sorption capacity have been investigated by thermogravimetric analysis. It has been observed that during 84 cycles of CO<sub>2</sub> sorption and desorption, carbon at 650 °C has maintained 90% of its sorption efficiency, while the sorption capacity of bulk CaO after 20 cycles at 300 °C was decreased over 50%. Reports in the sources indicate that adding secondary particles to CaO improves CO<sub>2</sub> adsorption. For example, Anatzara et al. [32] have increased the stability of CaO by adding zirconium oxide (ZrO<sub>2</sub>) and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) compounds to CaO using the sol-gel method. In another research, Al-Mamoni et al. [33] added two metal elements; iron and gallium, as dopants to CaO, using the hydrothermal synthesis method. The results of CO<sub>2</sub> adsorption tests showed that by

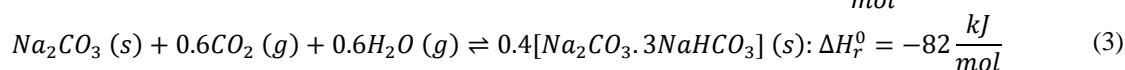
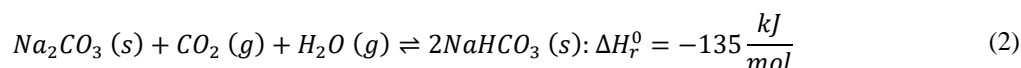
doping 10 W% of iron and gallium, the adsorption capacity has increased to  $13.7 \frac{mmol}{gr}$  for iron and  $14.2 \frac{mmol}{gr}$  for gallium, which is almost twice the value reported for undoped CaO. Yoshikawa et al. [36] examined how CO<sub>2</sub> adsorbs and desorbs on various metal oxides such as ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and CeO<sub>2</sub>. As the results are shown in Figure 2, silicon has shown no adsorption, while CeO<sub>2</sub> nanoparticles (2) and CeO<sub>2</sub> mesoporous material (1) have shown high adsorption due to their high specific surface area.



**Figure 2.** Amount of adsorbed CO<sub>2</sub> per weight (left axis), and amount of adsorbed CO<sub>2</sub> per surface area (right axis). Black and white bars show the value of each weight and surface area, respectively [34]

### 3.2 Carbonate-base sorbents

Carbonate base adsorbents offer the advantages of being cost-effective, energy-efficient, and corrosion-resistant. In their research, Liang et al. [38] determined that sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) can capture 90% of the CO<sub>2</sub> gas.



Yu et al. [35] improved Na<sub>2</sub>CO<sub>3</sub> sorption capacity to  $2.51 \frac{mmol}{gr}$  by using amine modification on Na<sub>2</sub>CO<sub>3</sub> using the sol-gel method. In this modification, amine-modified materials, Aminopropyltriethoxysilane (APTES) and Tetraethyl Orthosilicate (TEOS) were used. The results of the experiments showed that the amine-modified Na<sub>2</sub>CO<sub>3</sub> can be revived and is stable during 10 cyclic operations. Another carbonate substance that researchers have used is potassium carbonate (K<sub>2</sub>CO<sub>3</sub>). By examining the crystalline structure of K<sub>2</sub>CO<sub>3</sub>, Zhao et al. [36] found that the crystalline structure of materials has a significant effect on the amount of CO<sub>2</sub> capture. Their experiments showed that the CO<sub>2</sub> adsorption of hexagonal structure is higher than monoclinic structure.

It has been found that water and sulfur dioxide gas decrease the CO<sub>2</sub> absorption of K<sub>2</sub>CO<sub>3</sub> by forming K<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>CO<sub>3</sub>. The mechanism of how CaO, Ca(OH)<sub>2</sub>, and CaCO<sub>3</sub> could prevent the decrease in CO<sub>2</sub> sorption was investigated and The results showed that the sorption capacity after surface modification of K<sub>2</sub>CO<sub>3</sub> by Ca(OH)<sub>2</sub> would be  $70.7 \frac{KJ}{mol}$  Modified Ca(OH)<sub>2</sub> materials in K<sub>2</sub>CO<sub>3</sub>/γ Al<sub>2</sub>O<sub>3</sub> sorbent had higher CO<sub>2</sub> sorption capacity. They performed better than K<sub>2</sub>CO<sub>3</sub>/γ Al<sub>2</sub>O<sub>3</sub> sorbents in the presence of SO<sub>2</sub> in the exhaust gas [37, 38].

Li et al. [39] studied the thermal stability of K<sub>2</sub>CO<sub>3</sub> sorbent placed on ZrO<sub>2</sub> and titania (TiO<sub>2</sub>) for a fixed bed reactor in a 60–150 °C temperature range. The results showed a decrease in CO<sub>2</sub> sorption capacity when K<sub>2</sub>CO<sub>3</sub>/TiO<sub>2</sub> is calcined at a temperature of higher than 500 °C subjected to air or nitrogen. The reason for this reduction is attributed to the production of inactive species K<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> during calcination. However, the K<sub>2</sub>CO<sub>3</sub>/ZrO<sub>2</sub> despite being calcined at a temperature of 500 - 700 °C shows a high CO<sub>2</sub> sorption capacity of

about  $83\text{--}93 \frac{\text{mgCO}_2}{\text{g}}$ . Also, Zhao et al. [40] investigated the effect of  $\text{K}_2\text{CO}_3$  smeared by  $\text{Al}_2\text{O}_3$  on the amount of  $\text{CO}_2$  capture. This material was tested in a bubbling fluidized bed reactor and a sorption capacity of over 90% over 10 cycles was reported, which was improved compared to the untreated sample.

### 3.3 Other sorbents

Except oxide-based and carbonate-based materials, some other emerging materials are used for  $\text{CO}_2$  sorbing. Metal organic frameworks (MOFs) and covalent organic frameworks (COFs) are among the newest materials for  $\text{CO}_2$  capture. These materials, because of their special crystalline structure, porosity and high specific surface area are good candidates of being used for gas adsorption, separation, catalytic reactions, energy conversion and storage [41–44].

MOFs referring to their unique crystalline structure formed by metal ions and ligands might be a new alternative material for  $\text{CO}_2$  capture [45]. Liao et al. [46] synthesized a Ca-based  $\text{CO}_2$  sorbent and identified the structure-performance relationships affected by synthesis parameter. The practical maximum sorption capacities of Ca-based sorbents have been reported as 0.710, 0.673 and 0.650  $\text{g}_{\text{CO}_2}\text{g}_{\text{sorbent}}^{-1}$  for different specimens.

COFs are built by strong organic covalent bonds in a periodic arrangement from light elements of Hydrogen, Boron, Carbon, Nitrogen and Oxygen. COFs are grouped in different categories of Boron-based COFs, triazine-based COFs, imine-based COFs, and Boron/imine-based COFs which is related to the  $\text{CO}_2$  Capture ratio [47]. Liu et al. [48] synthesized a 2D azine-linked COF through solvothermal method which showed high crystalline and good thermal stability. The synthesized 2D COF recorded  $\text{CO}_2$  uptake of  $110 \text{ cm}^3\text{g}^{-1}$  at 273 K and 1 bar.

As it has been told oxide-based sorbents, carbonate-based sorbents, MOFs and COFs are different sorbents that can be used for  $\text{CO}_2$  capture. However, it must be said that oxide-based and carbonate-based sorbent have been used in a more widespread way. In the other hand, MOFs and COFs are newer, emerging, still growing, and most of studies in this fields are theoretical [41, 49].

## 4. Dual Function Materials (DFMs)

As it was mentioned before, DFMs comprise two components, sorbent and catalyst, usually oxides and carbonates are used as sorbents in these materials. As shown in Figure 3, two stages of  $\text{CO}_2$  gas capture and conversion are carried out in a temperature range of  $300 \text{ }^\circ\text{C}$  using hydrogen gas obtained from renewable energy sources, the captured  $\text{CO}_2$  gas from the industry exhaust turns into methane ( $\text{CH}_4$ ) gas, which can be used as fuel in the same industries. Using metal elements in the catalyst speeds up the conversion of captured  $\text{CO}_2$  into fuel, like methane. The capture capacity in DFM design is influenced by factors such as weight loading, ratio, temperature, and gas composition. Because of that the materials used as sorbents were examined in part 3, in the following, different DFMs have been examined based on the type of catalyst used in them.

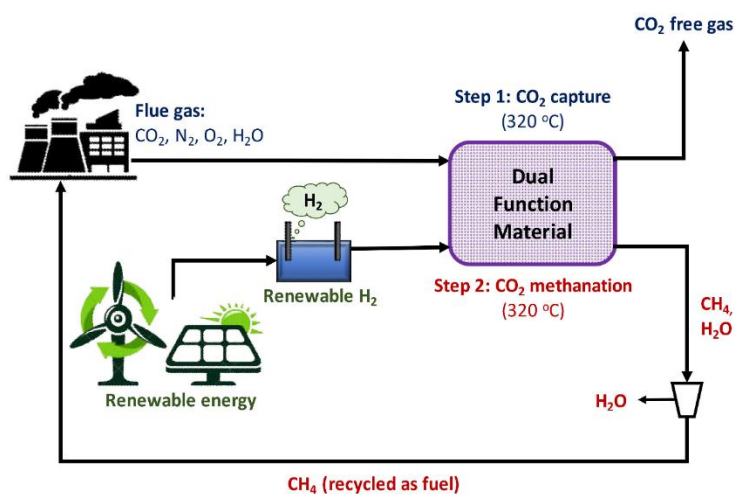


Figure 3. A summary of the performance of DFMs [50]

### 4.1 Other sorbents

Nickel is one of the metal elements which is mainly used as a catalyst in diverse industries. In the newly set and growing CO<sub>2</sub> capture industry, nickel is one of the most important candidates for use as a catalyst in DFMs. Nickel is used for CO<sub>2</sub> conversion reactions for instance Methanation [51–53], reverse water-gas shift (RWGS) [54–57], and reforming methane and other light alkanes [58–61]. The RWGS reaction mechanism over DFMs is shown in figure 4.

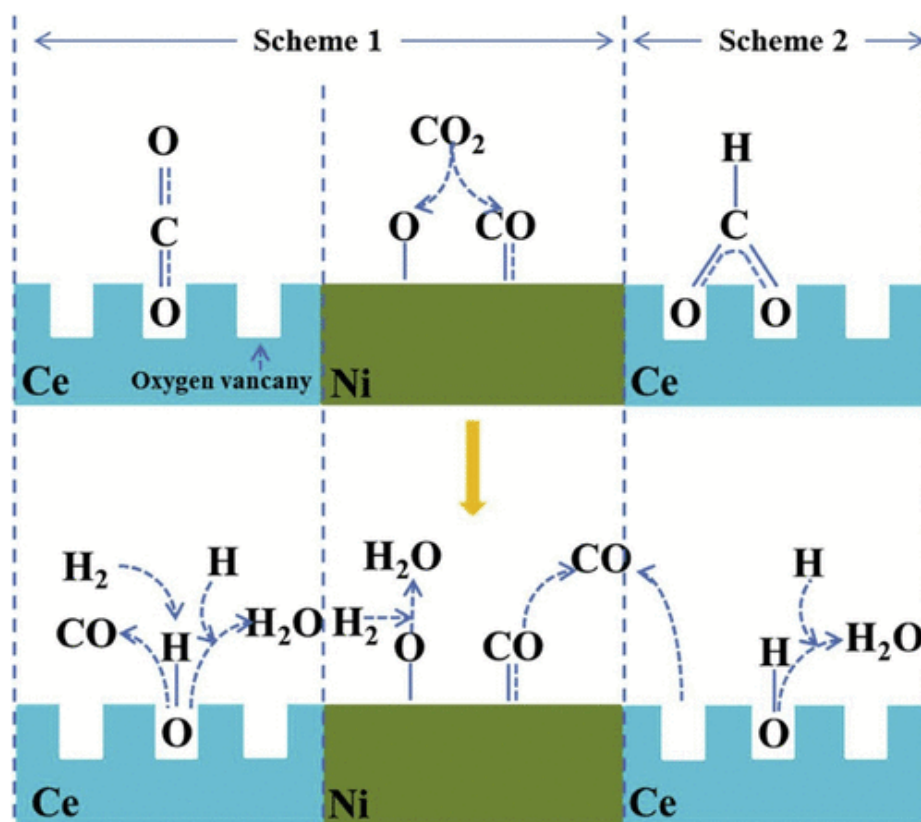
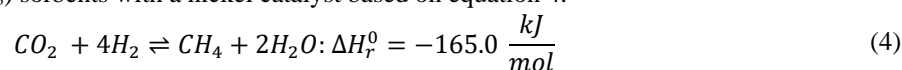


Figure 4. RWGS reaction mechanism over DFMs [34]

Tian et al. [57] achieved lower energy consumption (22% less) by reforming methane using sol-gel prepared CaO-Nickel DFMs through a calcium looping cycle. In another study, Kim et al. [62] used magnesium oxide (MgO) for methane reformation using a Nickel/MgO-Al<sub>2</sub>O<sub>3</sub> catalyst containing CaO sorbent. The results showed a 20 % volume reduction of CO<sub>2</sub> in nitrogen. The concentration of unreacted CO<sub>2</sub> in the exhaust gas is below 0.008%, showing a near-complete conversion of captured CO<sub>2</sub> in a single step. Sun et al. [62] by applying surface modification on CaO using cerium, investigated the sorption performance of CaO-Nickel DFMs. Nickel in CaO as a catalyst resulted in a doubled CO<sub>2</sub> conversion rate, going from 23.4% to 46%. In a different study, Lopez et al [60] examined the in-situ CO<sub>2</sub> capture and methane conversion rate. They used a combination of CaO and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) sorbents with a nickel catalyst based on equation 4.



Kinetic studies showed that methane production increases by nickel loading up to 142  $\frac{\mu mole}{g}$  in the sample of 15% nickel, and 15% CaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 520 °C. However, better results were obtained with samples containing Na<sub>2</sub>CO<sub>3</sub>, this value becomes 186  $\frac{\mu mole}{g}$  when using a 10 % Ni, 10% Na<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> sample even at low temperatures (400 °C) [63].

In another study, researchers examined how Platinum, Palladium, and Ruthenium changed the nickel catalyst. The obtained results showed that by adding only 1 % W of these precious metals, CO<sub>2</sub> capture capacity is improved; for instance, by adding 0.11 % W ruthenium, the sorption capacity would be 0.52  $\frac{mmole}{g}$  and methane conversion rate is increased to 0.38  $\frac{mmole}{g}$  at 320°C, which is much higher than the sample without ruthenium, 0.11  $\frac{mmole}{g}$  at 650 °C. Platinum and palladium-modified samples had lower rates compared to the unmodified samples. This led to the development of ruthenium-modified catalysts, discussed in Section 2.4 [61].

## 4.2 Ruthenium catalyst DFMs

Ruthenium is a precious metal which is known for its catalytic properties; ruthenium is widely used commercially in homogeneous and heterogeneous catalytic reactions. Ruthenium is attracting a lot of attention due to its fast reversible redox behavior between metallic and oxide states. Therefore, much researches have been carried out on ruthenium's applications in the process of converting captured CO<sub>2</sub> into methane. From the results it is obtained that this substance can be an excellent substitute for nickel catalyst in DFMs, however, ruthenium production is a high-cost process [64]. Table 1 shows some examples of conducted studies in this field. The results show that the conversion rate is boosted when the amount of catalyst is reduced.

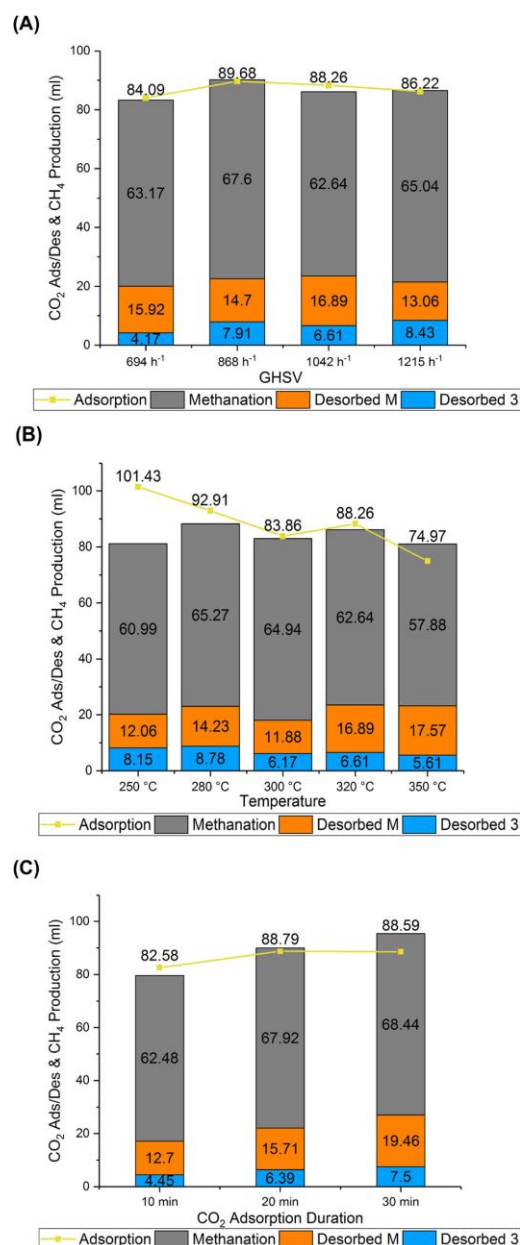
**Table 1.** The conversion rate of CO<sub>2</sub> into methane by ruthenium catalysts

Adsorbent	Conversion rate ( $\frac{mmol}{g}$ )	Temperature	Reference
5% Ru, 10% K <sub>2</sub> CO <sub>3</sub>	0.91	320	[65]
5% Ru, 10% Na <sub>2</sub> CO <sub>3</sub>	1.05	320	[65]
4% Ru, 5% CaO	0.33	280–400	[66]
4% Ru, 10% CaO	0.32	280–400	[66]
4% Ru, 15% CaO	0.26	280–400	[66]
4% Ru, 5% Na <sub>2</sub> CO <sub>3</sub>	0.29	280–400	[66]
4% Ru, 10% Na <sub>2</sub> CO <sub>3</sub>	0.38	280–400	[66]
4% Ru, 15% Na <sub>2</sub> CO <sub>3</sub>	0.41	280–400	[66]
10% Ru, 10% CaO	0.5	320	[8]
5% Ru, 6.1% Na <sub>2</sub> O	0.32	250–350	[67]

Bermejo-López et al. [66] investigated the mechanism of CO<sub>2</sub> storage and methanation by Ru-CaO/Al<sub>2</sub>O<sub>3</sub> and Ru-Na<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> DFMs. Adding more sorbent improves the catalyst's performance by creating stable carbonates. The impact of CaO on storage and methanation is more noticeable compared to Na<sub>2</sub>CO<sub>3</sub>. This is because CO<sub>2</sub> storage involves water release and hydroxide formation (NaOH or Ca(OH)<sub>2</sub>). The initial storage occurs on the surface of basic oxides (CaO or Na<sub>2</sub>O) and then continues on the hydroxide surface after the oxides are fully occupied. The hydrogenation step leads to the release of methane, water, and small amounts of CO, which indicates the high selectivity of these DFMs for methanation.

Zheng et al. [66] studied CO<sub>2</sub> adsorption and conversion rate using a DFM made of Ru-10% CaO/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a 5% composition. They analyzed the impact of the synthesis method, Al<sub>2</sub>O<sub>3</sub> substrate properties, and CO<sub>2</sub> adsorption conditions. Unlike nitrate salts, the chloride compounds RuCl<sub>3</sub> and CaCl<sub>2</sub> spread uniformly into the Al<sub>2</sub>O<sub>3</sub> particles. Active ruthenium species lower the adsorption and conversion rate of DFMs when water and oxygen are present. Due to having great anti-corrosion properties; Radium is an excellent candidate for applications that require a better oxidation resistance. It seems that ruthenium is still preferred for the development of DFMs based on its stability and relatively low price compared to radium [65]. For CO<sub>2</sub> capture and hydrogenation, Wang et al. [64] conducted cyclic aging studies using a 5% Ru-10% Na<sub>2</sub>CO<sub>3</sub>//  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sorbent. A 10-cycle aging test was performed using nitrogen-CO<sub>2</sub> gas under a free oxygen condition for storage and methanation, while a 12-cycle test was performed under simulated exhaust gas conditions which contained oxygen, all tests were done at 320 °C. The presence of oxygen leads to the formation of ruthenium oxide (RuO<sub>2</sub>), which causes the loss of catalytic activity. After the 10<sup>th</sup> cycle, the catalyst was regenerated by exposure to a large amount of hydrogen, resulting in CO<sub>2</sub> adsorption and methanation.

The parameter studies conducted by Wang et al. [67] with 5% Ru-1.6% Na<sub>2</sub>O/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sorbents showed that the gas flow feed rate, oxygen exposure time during the capture stage, and reaction temperature influence the performance of the catalyst. As shown in Figure 5-A, the amount of gas flow feed rate has a negligible effect on the amount of adsorbed CO<sub>2</sub> and formed methane. Based on the thermodynamics of the processes, an increase in temperature is expected to slightly adjourn both CO<sub>2</sub> adsorption and methanation steps (Figure 5-B). From Figure 5-C, it was concluded that by increasing exposure time the exhaust gas containing oxygen leads to the initial improvement of CO<sub>2</sub> adsorption, but it reaches the maximum point after 20 minutes when the increase in CO<sub>2</sub> concentration leads to an increase in methanation. Although increasing the exposure time to the expulsion gas increased ruthenium oxidation, a feed gas containing 15% H<sub>2</sub>/N<sub>2</sub> suffices to return the catalyst into the metallic state and initiate the methanation process, so no significant loss of activity was observed.



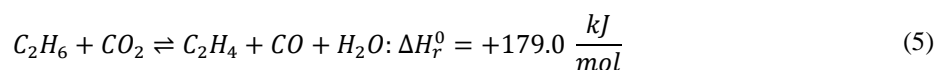
**Figure 5.** Parametric studies of 5% Ru-1.6% Na<sub>2</sub>O/γAl<sub>2</sub>O<sub>3</sub> adsorbent in the simulated exhaust gas conditions: (A) gas flow feed rate at 320°C. (B) temperature effect in  $\frac{1042}{h}$ . (C) Duration of adsorption (exposure to oxygen), temperature 320 °C,  $\frac{868}{h}$ . desorbed M = CO<sub>2</sub> desorbed during methanation, 3 desorbed = CO<sub>2</sub> desorbed during nitrogen expulsion [34]

In this regard, the studies conducted by Proaño et al. [68] on the Ru-Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> sorbent showed that CO<sub>2</sub> is captured in the active sites of ruthenium, alumina hydroxide groups and debranched carbonates in the Ru-Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> sorbent. Cimino et al. [69] studied the effect of alkaline promoters (lithium, sodium, and potassium) on the performance of Ru/Al<sub>2</sub>O<sub>3</sub>. These materials were synthesized through successive saturation of ruthenium and alkaline precursor, and alkaline nitrate and carbonate salts were used to evaluate the effect of promoting precursor. The lithium-ruthenium catalyst prepared using lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) shows the highest methanation activity. The Na-Ru/Al<sub>2</sub>O<sub>3</sub> and K-Ru/Al<sub>2</sub>O<sub>3</sub> sorbents did not work for methane production because the carbonates did not fully decompose and the active ruthenium sites were covered by amorphous substances. In general, doped alkaline catalysts are 4–5 times better than basic catalysts for the CO<sub>2</sub> capture process, with the order of lithium > sodium ≥ potassium.

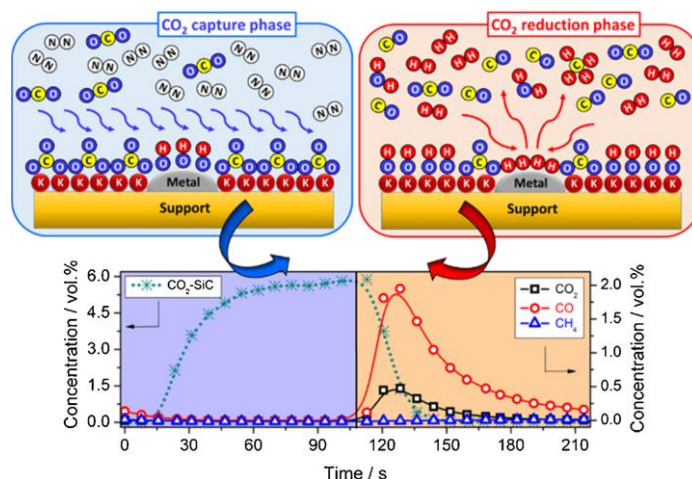
### 4.3 Other DFMs Used for Capture Process

CaO-based sorbents for ethane oxidative dehydrogenation with CO<sub>2</sub> were investigated by Al-Mamoori et al. [69], who used a chromium catalyst and H-ZSM-5 substrate.





Compared to the baseline study which was conducted with a mixture of CaO and catalyst, the authors observed a higher CO<sub>2</sub> capture when using double salts. While the material (K-Ca)/Cr/H-ZSM-5 shows a CO<sub>2</sub> capture capacity of  $5.2 \frac{mmole}{g}$ , the CO<sub>2</sub> capture capacity of (Na Ca)/Cr/HZSM-5 and CaO/Cr /H-ZSM-5 were  $3.2 \frac{mmole}{g}$  and  $0.8 \frac{mmole}{g}$ , respectively. This improved capture of double salts was attributed to the formation of double carbonates such as potassium calcium carbonate and sodium calcium carbonate. With the increase of chromium content, the conversion rate of CO<sub>2</sub> and ethane increased with a maximum rate of 10% by chromium weight and subsequently was reduced by the increase of chromium content to 15% by weight. This activity decreases when using 15% by weight of chromium and is attributed to poor dispersion and the formation of a chromium alpha-carbonate phase, which limits the selectivity towards ethane [70,71]. Bobadilla et al. [72] investigated the use of base metals for CO<sub>2</sub> capture and conversion. They used a FeCrCu-K catalyst and hydrotalcite sorbent which was synthesized through sequential impregnation. First, hydrotalcites were calcined at 600 °C to obtain homogeneously mixed oxides of MgO and Al<sub>2</sub>O<sub>3</sub>, and then the IW (incipient wetness) method was used to deposit metallic elements like iron, chromium, and copper by using nitrate precursors. The catalyst captures CO<sub>2</sub> by using nitrogen-CO<sub>2</sub> gas and by using pure hydrogen between 450 and 550 °C was subjected to the hydrogenation stage. The concentration profiles of CO<sub>2</sub> and CO during the capture and reduction stages are shown in Figure 6. As can be seen, CO<sub>2</sub> is effectively captured on potassium alkali metal which forms surface carbonates, and after changing to hydrogen, most of the CO<sub>2</sub> which is captured by hydrogen reacts in catalytic sites (iron, chromium and copper) and releases CO and some unconverted CO<sub>2</sub>.



**Figure 6.** Visual representation of the performance and mechanism of CO<sub>2</sub> capture and reduction on the catalyst material. For comparison, the carbon dioxide concentration profile measured using an inert silicon carbide (SiC) material is also shown [34]

Hyakutake et al. [73] have studied the promotion effect of copper/Al<sub>2</sub>O<sub>3</sub> catalysts with potassium and barium for use in CO<sub>2</sub> capture and conversion to acquire the chemical processes and active sites involved in them. CO<sub>2</sub> capture and reduction were conducted at 350 °C using different combinations of copper/Al<sub>2</sub>O<sub>3</sub>, copper-potassium/Al<sub>2</sub>O<sub>3</sub>, and copper-barium/Al<sub>2</sub>O<sub>3</sub>. The copper-potassium/Al<sub>2</sub>O<sub>3</sub> material in Figure 7 efficiently captures CO<sub>2</sub> and converts it to CO when hydrogen is present. The presence of CO dominant species was a result of copper surface oxidation in the copper/Al<sub>2</sub>O<sub>3</sub> catalyst, leading to a different mechanism. The use of copper-barium/Al<sub>2</sub>O<sub>3</sub> sample shows significant formation of CO in both capture and reduction stages. Although the copper-barium/Al<sub>2</sub>O<sub>3</sub> catalyst can capture CO<sub>2</sub> to some extent, some uncaptured CO<sub>2</sub>, however, was observed in the effluent stream. The presence of copper oxide was not found in the potassium-promoted catalyst, as shown by X-ray absorption fine structure (XAFS) studies, confirming its high dispersion and small particle size.

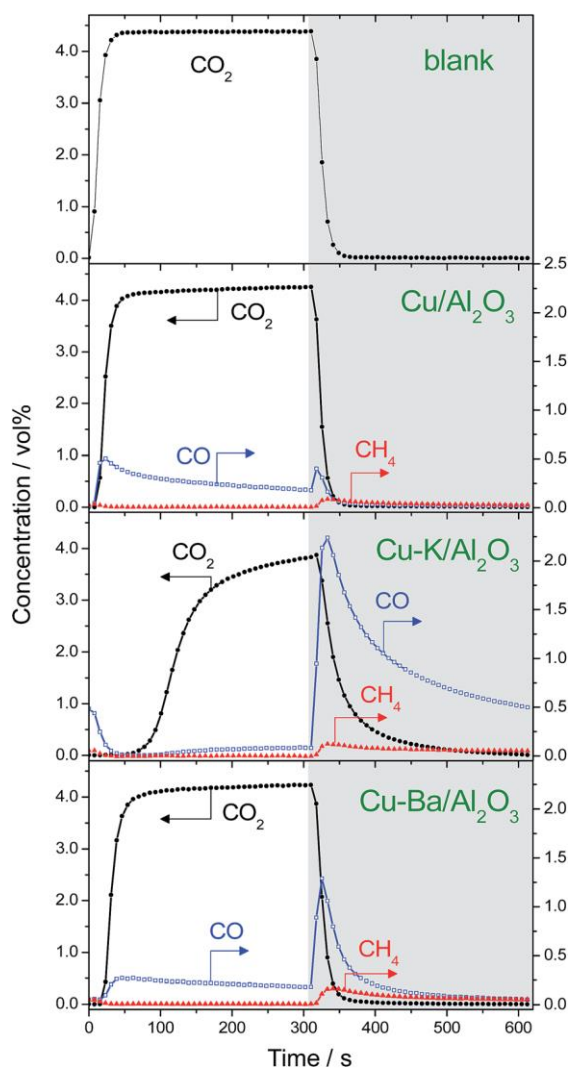


Figure 7. Concentration profile of CO<sub>2</sub> and reduction products (CO and CH<sub>4</sub>) after stabilization by several cycles [34]

In Figure 8 A schematic view of the working mechanism of DFMs is illustrated. The first step is adsorption in which the adsorbent is saturated with CO<sub>2</sub>. cause of the presence of oxygen, the metal nanoparticles may be partially oxidized. In the second step (methanation) hydrogen is fed. Metallic nanoparticles are back to the metallic state and will be active for the methanation process. The adsorbed CO<sub>2</sub> molecules on the adsorbent desorb the metal nanoparticles and are hydrogenated to methane. Steps are repeated cyclically.

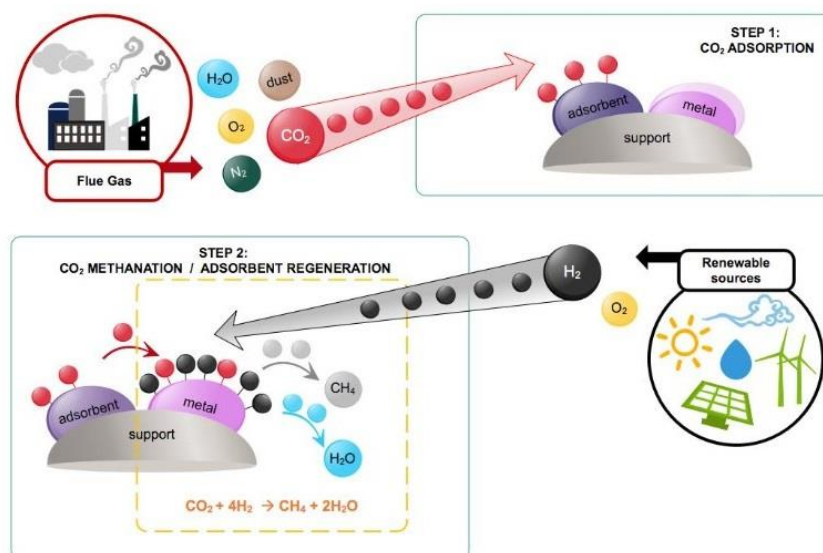


Figure 8. Schematic view of the working mechanism of DFMs [17]

## 5. Conclusions

In this review, the use of DFMs for CO<sub>2</sub> capture and conversion into Fuel is summarized. In order to discuss the structure of these materials, first, different sorbents have been discussed. Oxides, carbonates are excellent sorbents for CO<sub>2</sub> capture because of being cheap, abundant, and also highly reactive towards CO<sub>2</sub>. However, some new materials like MOFs and COFs are being used as sorbent too. The reactivity of these sorbents can decrease after repeated cycles of sorption and desorption. These challenges have been overcome by dispersing sorbents on a substrate, by modifying the synthesis method, and by introducing impurity species. Nickel-based DFMs show a good CO<sub>2</sub> capture capacity and also sufficient reactivity, these materials have been reported for a wide range of applications, including methane production, dry reforming of methane (DRM), and dry reforming of ethane (DRE). Although nickel is an affordable and abundant metal and shows a good activity for these reactions, it has some disadvantages which limit its use. Ni-based sorbents require a high reduction temperature that is typically over 600 °C, which means high energy consumption. In addition, these materials are easily deactivated under simulated exhaust gas conditions (containing oxygen and water) due to the formation of nickel oxide species that are not easily reduced under reaction conditions. Ruthenium-based structures are effective in reactions carried out at lower temperatures (~320 °C). Also, these structures can act isothermally for both capture and conversion processes and make them more efficient. In addition, due to the ease of ruthenium oxide species reduction, they show good stability in oxidizing feed conditions. The superior performance of ruthenium-based structures justifies their higher cost over nickel ones. However, the use of ruthenium-based structures is mainly limited to methanation reactions, and further studies are needed to investigate their activity towards CO<sub>2</sub> synthesis. Recent reports have demonstrated the use of copper-based systems to capture and convert CO<sub>2</sub> to produce syngas. Copper is a promising option for developing structures that can capture and convert CO<sub>2</sub> in exhaust gas. Due to being in the early stages of development, DFMs have primarily been studied for combining sorbents and catalysts using impregnation techniques. However, we believe that the future of this field will be improved in the design of nanostructures with catalytic components. Since copper-based catalysts are commonly used for methanol production, the use of copper-based DFMs could be a starting point in these efforts.

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