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CHAPTER

4

Sorption enhanced catalysis for CO_2 hydrogenation towards fuels and chemicals with focus on methanation

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4.1 Introduction

The combustion of fossil fuels is the major source of carbon emissions to the environment (Modak et al., 2020). To achieve the goal of reducing carbon emissions according to the Paris agreement, the use of fossil fuels should be radically diminished as a source of energy and chemicals (Rogelj et al., 2016; UNFCCC, 2015). This results in CO_2 and H_2 becoming increasingly important feedstock for the fuels and chemical industry, with hydrogen being produced by renewable electricity, e.g., solar or wind power (Lee et al., 2020; Rönsch et al., 2016).

Shifting from fossil to renewable resources means that a new industrial platform has to be developed to provide carbon-based fuels and large-scale base chemicals to replace the current petrochemical routes. The global demand cannot be met to a sufficient extent solely by the indirect use of carbon dioxide via biomass, necessitating the direct use from point sources or direct air capture. This increases the value of CO_2 from waste to a commodity chemical. The production of chemicals by hydrogenation of CO_2 (Fig. 4.1) is a promising way of CO_2 mitigation (Artz et al., 2018; Bailera et al., 2017; Rahman et al., 2017; Thomas & Harris, 2016), and also a possible solution for large-scale

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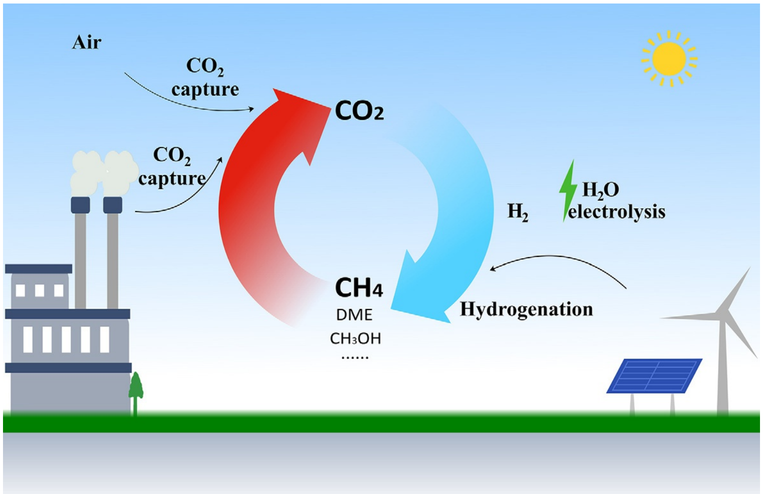

FIG. 4.1 A schematic of carbon cycle with CO_2 utilization by hydrogenation, producing methane.

energy storage to cope with the intermittent nature of wind and solar sources as well as the energy demand fluctuations (Bailera et al., 2017).

Several routes have been developed for CO_2 utilization through hydrogenation. Typical products include base and intermediary chemicals such as methane, methanol, formic acid, and dimethyl ether (Alvarez et al., 2017; Modak et al., 2020; Saeidi, Amin, & Rahimpour, 2014).

Methanol is an important and widely used liquid fuel and base chemical, around 95 million tons of methanol was produced in the world in 2019 (Bazaluk et al., 2020). The methanol synthesis from CO_2 hydrogenation is thermodynamically limited and more favorable at high pressure (Dang et al., 2019; Din et al., 2019; Xie et al., 2020). Around 700,000–800,000 tons of formic acid are produced per year in the world, CO_2 hydrogenation to synthesize formic acid is an important route for formic acid production (Bulushev & Ross, 2018). Dimethyl ether is an excellent fuel substituent for diesel and Liquefied Petroleum Gas (Roy, Cherevotan, & Peter, 2018) and the dimethyl ether global market was around 20 million tons in 2020 (Nakyai & Saebea, 2019). What is more, 3929.2 billion cubic metres methane (natural gas) was consumed in 2019 worldwide (BP p.l.c, 2020).

The CO_2 methanation reaction (Sabatier reaction (4.1)) was discovered in 1902 by Sabatier and Senderens (Sabatier & Senderens, 1902). CO_2 hydrogenation to produce methane (4.1) has great potential as an energy carrier (Thomas & Harris, 2016). This stems from the benefits of combining renewable hydrogen produced with wind or solar power, for instance, with CO_2 from traditional stack emissions such as power plants, biomass conversion processes (Li et al., 2017), or even air capture combined with the ease of distribution of the renewable methane in existing infrastructure. Moreover, CO_2 methanation has a higher energetic efficiency compared to producing, e.g., methanol from CO_2 for energy storage, the exergy efficiency of methanation and methanol synthesis being 30.1% to 18.2%, respectively (Uebbing, Rihko-Struckmann, & Sundmacher, 2019). Today, the methane, methanol, formic acid, and dimethyl ether are important chemicals used as fuels or raw materials in the industry (Alvarez et al., 2017).

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O;\ \Delta H^0_{298} = -165\,\text{kJ/mol} \tag{4.1}$$

Methanation is typically hampered by the thermodynamic conversion being far from 100% under currently viable reaction conditions (Fig. 4.2) (Alvarez et al., 2017; Ashok et al., 2020; Rönsch et al., 2016). According to Le Chatelier's principle (Carvill et al., 1996), the equilibrium can, however, be shifted by removing one of the reaction side products, which in many reactions between CO_2 and H_2 is water. This can be efficiently achieved by sorbents like zeolites (Borgschulte et al., 2013; Delmelle et al., 2016; Haije & Geerlings, 2011; Terreni et al., 2019; Van Berkel et al., 2020). This process is called a sorption enhanced reaction (Carvill et al., 1996). In addition to a high-purity reaction product, the sorption-enhanced CO_2 hydrogenation is also beneficial for high energy efficiency, lower temperature and pressure operation, and process simplification/intensification as less process steps and reactors are required (Carvill et al., 1996). Sorption enhanced CO_2 hydrogenation processes include sorption-enhanced CO_2 methanation (Borgschulte et al., 2013), methanol synthesis (Terreni et al., 2019) and dimethyl ether synthesis (Guffanti et al., 2021; van Kampen et al., 2020) to mention only a few. The current review mainly focuses on sorption enhanced CO_2 methanation as a case exemplifying the typical challenges encountered in CO_2 hydrogenation as well as some solutions for tackling them.

Sorption-enhanced CO_2 methanation (Fig. 4.3) was developed to obtain close to 100% conversion and yield in the otherwise thermodynamically limited conditions (Borgschulte et al., 2013; Walspurger et al., 2014). The water adsorbing capacity in the processes' operating window and catalytic performance are the critical material challenges in sorption enhanced CO_2 methanation. Even though novel catalysts, which are active at lower temperature than traditional catalysts are being developed, the water adsorbent still has to work at a relatively high

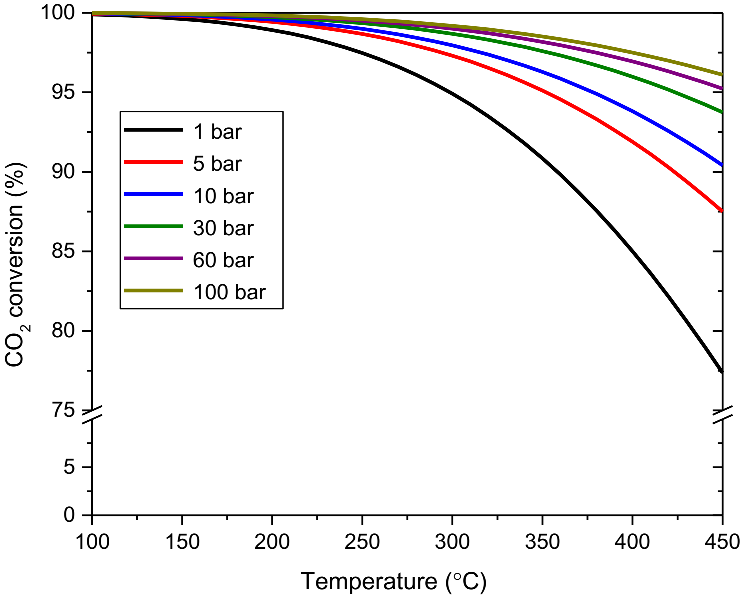

FIG. 4.2 Thermodynamic equilibrium conversion for the stoichiometric feed gas composition of CO_2 methanation.

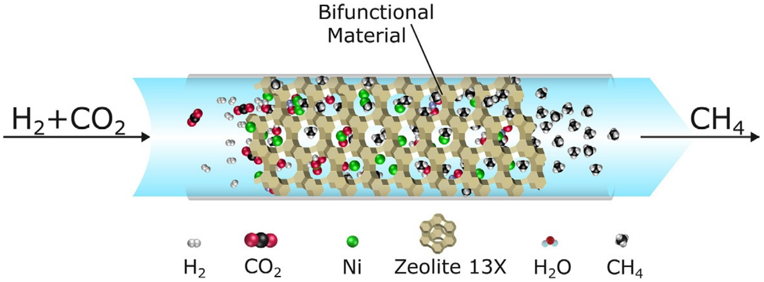

FIG. 4.3 Schematic of sorption enhanced CO_2 methanation.

temperature when thinking purely of adsorption, in order for reasonable reaction rates to be maintained. High temperature is not beneficial for water adsorption as high temperature rather enhances desorption. This emphasizes the importance of a proper material as the water adsorbent, which also acts as an efficient catalyst support (bifunctional material) in addition to developing low-temperature activity.

Despite the importance of the topic for developing efficient large-scale methanation processes, review publications on bifunctional materials synthesis and application for sorption enhanced CO_2 methanation are scarce. The current work presents the background and the state of the art in synthesis and application of these bifunctional materials and provides an outlook on future developments in sorption enhanced CO_2 methanation in particular and of sorption enhanced reactions in general.

4.2 Sorption enhanced catalysis for CO_2 methanation

Water sorbent

Sorbent choice

The requirement for a sorbent to be viable in sorption enhanced reactions is that the equilibrium vapor partial pressure is lower than that of the hydrogenation reaction. In the sorption enhanced CO_2 methanation, the water sorbent must be able to operate efficiently at a high temperature (>200°C) since the minimum working temperature of a conventional Ni-based catalysts, for example, is well over 300°C. Silica-gel cannot be used as its extremely low water capacity at the methanation reaction temperature (Goldsworthy, 2014; Wang & LeVan, 2009). The most promising sorbent class for CO_2 methanation is zeolites (van Kampen et al., 2019), which provides high water absorption capacity and are stable under the reactor and regeneration conditions.

During the last decades, around 70 scientific papers have been published on CO_2 methanation with the help of a zeolite, and the number of publications has increased significantly during the last 10 years (Fig. 4.4). The FAU (X and Y type) and LTA framework zeolites are the most studied ones. The FAU and LTA zeolite frameworks can be found in Fig. 4.5, more zeolite structure information can be found from reference (Newsam, 1986). Over 50% of the existing publications focused on utilizing FAU zeolite for CO_2 methanation. However, most publications mainly focus on the metal-zeolite catalysts preparation, characterization, and the catalytic performance in CO_2 methanation, where the zeolite is merely a support disregarding the sorption effect.

To investigate the sorption effect of Ni/5A zeolite catalysts in CO_2 methanation, Borgschulte et al. loaded Ni on 5A zeolite using the ion-exchange method. Their results show that

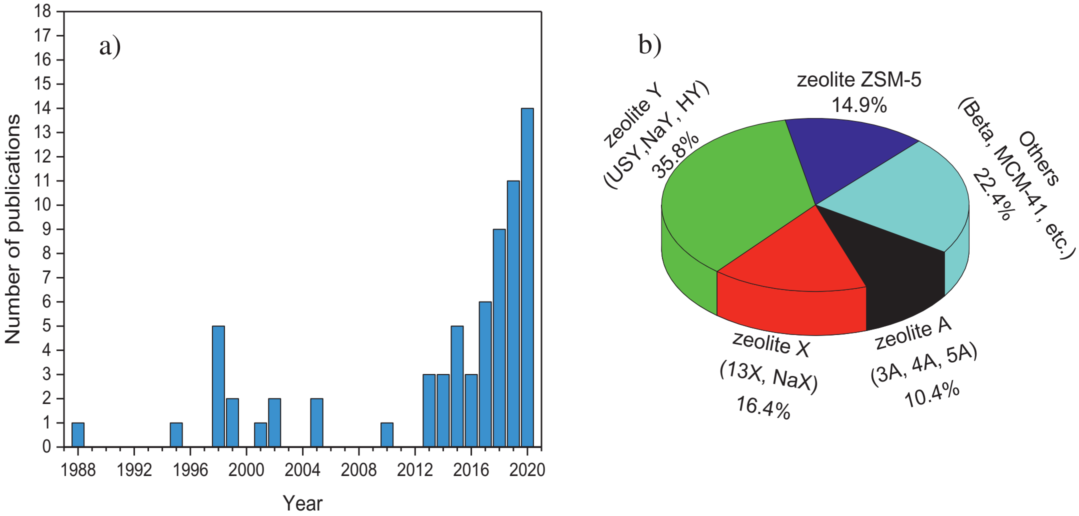

FIG. 4.4 Publications analysis (A) indexed topic as CO_2 methanation and zeolite/molecular sieve, (B) percentage of zeolite/molecular sieve used in CO_2 methanation. *Source: Web of Science, range 1900–2020, 3rd September.*

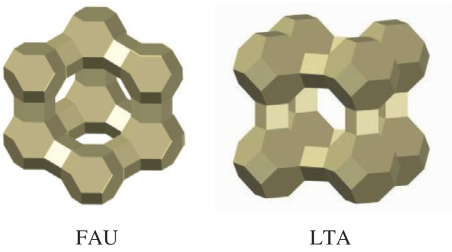

FIG. 4.5 The figurative construction of FAU and LTA zeolite frameworks that contain sodalite cages.

Ni/zeolite 5A can be used as an efficient bifunctional catalyst (Borgschulte et al., 2013). Similar to 5A zeolite, 4A zeolite has a high water sorption capacity. In 2014, Walspurger et al. reported results using 4A zeolite (physically mixed with commercial Ni/Al_2O_3 catalyst): around 100% CO_2 conversion could be obtained in the temperature range 250–350°C (Walspurger et al., 2014). However, by comparing the kinetics of Ni/5A and Ni/3A bifunctional material, Borgschulte et al. found that the CH_4 selectivity was greatly enhanced when the zeolite's pore size is larger than 5 Å (Borgschulte et al., 2015), 5 Å is large enough to allow the reactants (H_2 and CO_2) and the product (CH_4, CO) to enter and leave the zeolite.

A sorbent with a larger pore size should be beneficial for the rate diffusion of the reactants and products. Compared to LTA type zeolite (3A, 4A, and 5A), zeolite 13X (FAU) not only has a bigger pore size but it also presents a higher water sorption capacity (Ghodhbene et al., 2017; Tatlier, Munz, & Henninger, 2018). It was reported that 5%Ni/13X (5% is the weight percentage of Ni on the catalyst) displayed nearly threefold operation time compared to

5%Ni/5A in sorption enhanced CO_2 methanation, likely due to 13X having a higher water sorption capacity (Delmelle et al., 2016). Even though the CO_2 conversion levels with both 5A and 13X zeolite catalyst were similar (Delmelle et al., 2016). As can be seen from Fig. 4.4B, zeolite Y (FAU type) is also widely used as the catalyst support for CO_2 methanation. However, the water sorption effect of Y zeolite has not been discussed in the literature on CO_2 methanation (Graça et al., 2014; Quindimil et al., 2018; Westermann et al., 2015, 2017).

Regeneration of sorbents

The sorbent regeneration, i.e., the desorption of water is an essential step in the continuous operation of sorption enhanced CO_2 methanation. Sorbents have typically been regenerated under N_2, Air, or H_2 atmosphere at 300–500°C (Coppola et al., 2020; Delmelle et al., 2016; Walspurger et al., 2014). According to the Clausius-Clapeyron Eq. (4.2), the water sorption capacity decreases significantly when sorption temperature increases from 200 to 300°C as displayed in Fig. 4.6, while the regeneration temperature does not have a large effect on the subsequent water uptake for 4A and 3A zeolite (Coppola et al., 2020; Walspurger et al., 2014). Compared to H_2, air is a better carrier gas for the regeneration of the sorbent, since N_2 and O_2 have higher efficiency in carrying out water from the zeolite 5A and 13X due to oxygen and nitrogen molecules having sizes and weights that are comparable to the water molecule (Delmelle et al., 2016), but getting rid of the inert air constituents should be taken into consideration for the next cycle in practice operation.

$$\ln\frac{p}{p_0} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{4.2}$$

where p is the vapor partial pressure, p_0 is the reference pressure, T is adsorption temperature, R is the universal gas constant, ΔH^0 and ΔS^0 are the standard enthalpy and entropy change of the adsorption process, respectively (Bevers et al., 2007).

Walspurger et al. reported the zeolite 4A water sorption capacity at 200, 250, and 300°C under a water partial pressure of 0.039 bar. The

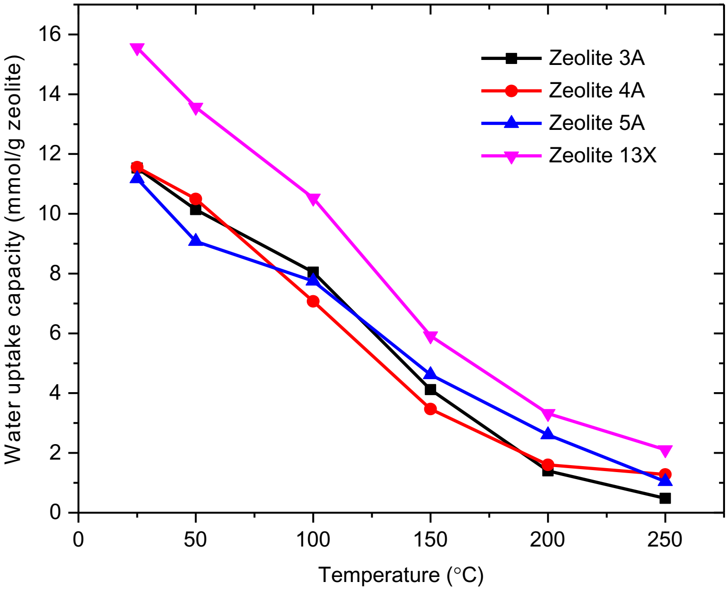

FIG. 4.6 Water mass uptake capacity under at 20°C saturated N_2 flow at different temperatures at 100 kPa total pressure for bead-shaped zeolites LTA-(3A, 4A, and 5A) and FAU-13X. *Data from Ghodhbene, M., et al. (2017). Hydrophilic zeolite sorbents for in-situ water removal in high temperature processes.* The Canadian Journal of Chemical Engineering, *95(10), 1842–1849.*

water capacity ranged from 0.98–2.00 mmol/g, clearly dependent on the sorption temperature as described by a Clausius-Clapeyron equation (Walspurger et al., 2014). Zeolite 3A showed similar water uptake capacity as zeolite 4A at sorption temperatures ranging 200–300°C (Coppola et al., 2020). The mass transfer rate during adsorption on zeolite 3A can be described by a linear driving force approximation, as the mass transfer resistance is predominantly determined by micropore resistance, due to the cage aperture (van Kampen, Boon, & van Sint Annaland, 2020). Zeolite 13X has a higher water uptake capacity compared to zeolite 3A, 4A, and 5A in the temperature range 20–250°C (Fig. 4.6) (Ghodhbene et al., 2017).

Other potential sorbents

Zeolites have been shown to be the most promising materials for in situ water removal in CO_2 methanation. The scientific articles published on CO_2 methanation with zeolites have mainly focused on FAU and LTA types zeolites, even though some other zeolites such as EMT and AFR could also be promising to be used for water removal (Ng & Mintova, 2008). Most work regarding the water sorption capacity for many typical zeolites has been performed at low temperature (<100°C) (Fig. 4.7) (Tatlier et al., 2018), however, the research on the water capacity of zeolites at high temperature (above 200°C) under different water partial pressures (>16.4 kPa) is scarce (Simo et al., 2009). Hardly any broad temperature and pressure range isosteres have been reported, even though the actual operational temperature in chemical processes is typically significantly above 100°C. Further work needs to be performed regarding the zeolites that could be used in sorption enhanced CO_2 hydrogenation.

Some new materials like MOF-74 and MOF-801 may also have the potential for water

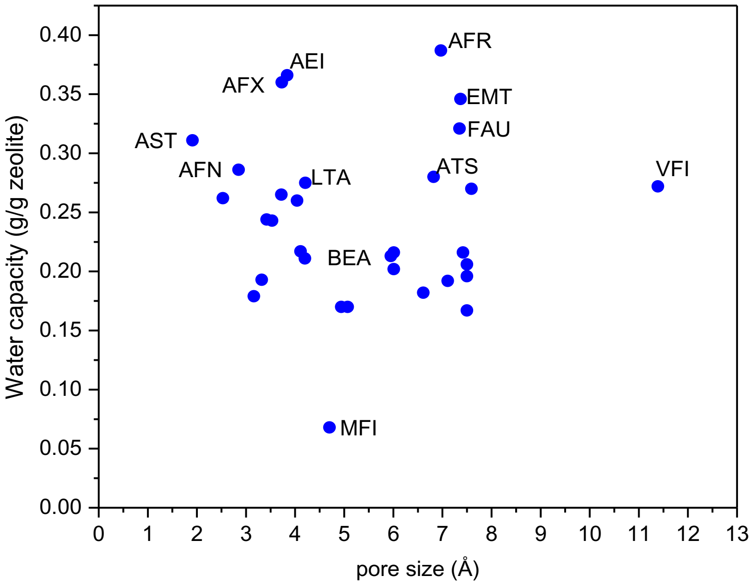

FIG. 4.7 Water adsorption capacity of zeolite with respect to its pore size. *Water capacity data from Tatlier, M., Munz, G., & Henninger S.K., (2018). Relation of water adsorption capacities of zeolites with their structural properties.* Microporous and Mesoporous Materials, 264, *70–75, pore size data from IZA-SC. Copyright © 2017 Structure Commission of the International Zeolite Association.*

removal since they have a large water uptake capacity at room temperature (Furukawa et al., 2014), however, their thermal stability at higher temperatures, >200°C, is questionable. Furthermore, one drawback is that their ecological footprint is substantial due to the organic precursors used in their manufacturing. Further study is needed for those materials.

Catalytic metals and promoters

Active metals such as Ni, Co, Ru, Rh, etc., have been studied for CO_2 methanation (Ashok et al., 2020; Lee et al., 2020; Nie et al., 2019; Sreedhar et al., 2019), and in some studies metals like W, La, and Ce, were used as promoters to enhance the catalytic metal dispersion increase, coke resistance, and anti-CO-poisoning ability (Sreedhar et al., 2019; Yan et al., 2016). The relevant active metals and promoters are displayed in Fig. 4.8.

The observed order of activity and selectivity for the respective metal catalysts on CO_2 methanation is shown below (Lee et al., 2020; Rönsch et al., 2016). However, this order is only a generalized trend and sometimes differs depending on, e.g., different metal-support interactions (Lee et al., 2020).

$$\text{Activity}: \text{Ru} > \text{Fe} > \text{Ni} > \text{Co} > \text{Rh} > \text{Pd} > \text{Pt} > \text{Ir}$$

$$\text{Selectivity}: \text{Pd} > \text{Pt} > \text{Ir} > \text{Ni} > \text{Rh} > \text{Co} > \text{Fe} > \text{Ru}$$

Catalytically active metals

Nickel (Ni) is the most widely used active metal for conventional (Aziz et al., 2015; Li et al., 2016; Rönsch et al., 2016; Walspurger, Haije, & Louis, 2014) and sorption enhanced CO_2 methanation (Bacariza et al., 2019a; Borgschulte et al., 2013; Delmelle et al., 2016; Walspurger et al., 2014), due to its rather high activity, CH_4 selectivity, and low cost, which makes Ni an interesting active metal from a commercial perspective (Fechete & Vedrine, 2015). 5%Ni/SiO_2 catalyst has an approximate apparent activation energy of 84 kJ/mol in CO_2 methanation (Aziz et al., 2014).

Cobalt (Co) catalysts exhibit a similar methanation activity and CH_4 selectivity comparable

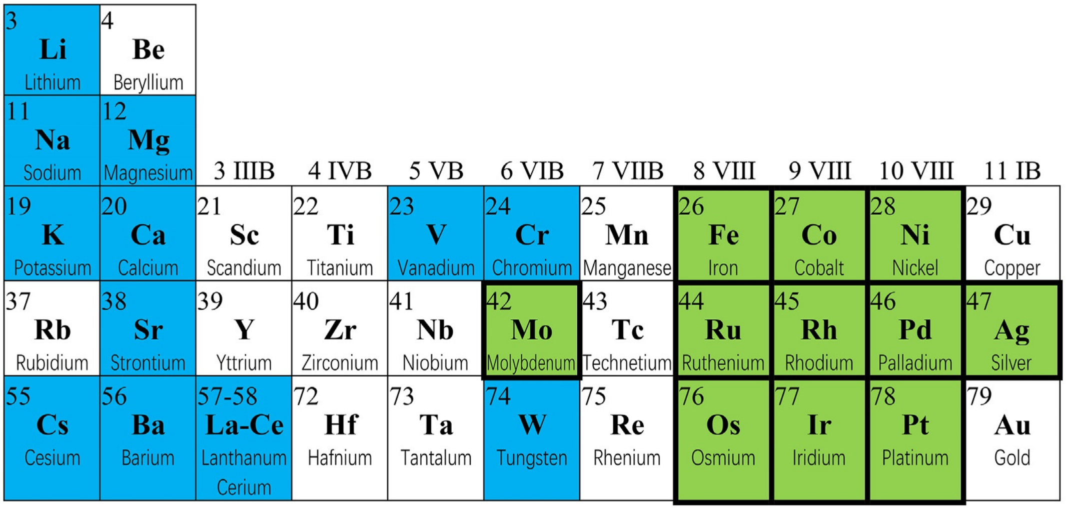

FIG. 4.8 Active metals *(marked in green; dark gray in print version, with thick borders)* and promotional metals *(marked in light blue; dark gray in print version)* for CO_2 methanation, excerpt from the periodic table of elements (Rönsch et al., 2016).

to Ni, the apparent activation energy of Co/MCF-17 in CO_2 methanation has been determined to be around 80 kJ/mol (Beaumont et al., 2014a). However, cobalt is not as widely used for commercial application since it is more expensive (Li et al., 2018; Sreedhar et al., 2019). Ashok et al. described that morphologies, surface orientations, catalyst supports, and cluster size of metals are the key factors in Co catalyst performance in CO_2 methanation (Ashok et al., 2020), like with other catalysts.

Iron (Fe) catalysts have been used for CO_2 reduction with H_2, and they exhibit a high activity, while showing low CH_4 selectivity, around 85% of the product gas is CO when using 5wt%Fe/13X at 350°C (Franken & Heel, 2020; Merkache et al., 2015; Wang et al., 2016), which hindered its use even though Fe is cheaper and less toxic than Ni and Co, and much cheaper than noble metals (Rh, Ru, Pd, Pt). 15%Fe/SiO_2 displayed a 134 kJ/mol of apparent activation energy for CO_2 methanation at 253 to 299°C (Weatherbee, 1984).

Molybdenum (Mo) has a low activity in CO_2 methanation and the number of publications on Mo catalysts for CO_2 methanation is low. A special feature of Mo is that it has the highest sulfur species tolerance (Rönsch et al., 2016). The reported apparent activation energy of Mo-based graphene catalysts for CO_2 methanation ranges between 62 and 115 kJ/mol (Primo et al., 2019).

As discussed above, the water adsorption capacity is higher at lower temperatures due to thermodynamics, therefore low-temperature catalytic activity of the bifunctional materials in CO_2 methanation would be highly beneficial for the sorption enhanced CO_2 methanation.

Ruthenium (Ru) is known as one of the most active metals for CO_2 methanation even at lower temperatures (Rönsch et al., 2016), and thus it is an attractive alternative (Ashok et al., 2020). An apparent activation energy of 41 kJ/mol was obtained by researchers for Ru/MgO catalyst in CO_2 methanation which was measured at 80 to 180°C (Mori et al., 1996). Ru on NaY and 5A zeolite catalysts have been observed to yield high CH_4 selectivity (Hastings et al., 2002), whereas 100% yield of CH_4 has been reported to be obtained at 160°C using Ru/TiO_2 catalyst (Abe et al., 2009). The dispersion of Ru on zeolite (13X and 5A) is important for the catalyst performance in CO_2 methanation (Wei et al., 2020) and high dispersion of Ru has been obtained on FAU zeolite with the ion-exchange method (Bando, Arakawa, & Ichikuni, 1999; Lee et al., 2019a).

Rhodium (Rh) has been reported to be an active metal for CO_2 methanation at low temperatures (Swalus et al., 2012), and its activation energy has been reported to be as low as 17.0 kJ/mol (3%Rh/TiO_2), and a turnover frequency of 0.524×10^2 (s^{-1}) in CO_2 methanation at 120°C (Karelovic & Ruiz, 2013a). Rh could thus be a promising active metal for sorption enhanced CO_2 methanation when loaded into zeolite, as the water uptake capacity of zeolites is increased dramatically at temperatures lower than 200°C (Fig. 4.6).

Platinum (Pt)-modified ZSM-5 zeolite catalyst has displayed high catalytic activity and CH_4 selectivity even with 0.5% loading of Pt (Sápi et al., 2019). Pt can promote the activity of Co for CO_2 methanation (Beaumont et al., 2014b). The apparent activation energy has been reported to be 94 kJ/mol for Pt/Al_2O_3 in CO_2 methanation (Kikkawa et al., 2019).

Luo et al. prepared a highly dispersed palladium (Pd)/Fe catalyst, and the results showed that Pd promoted and stabilized the catalyst significantly (Luo et al., 2020). 23.5 kJ/mol of apparent activation energy was measured at 250 to 350°C for Pd/γ-Al_2O_3 in CO_2 methanation (Karelovic & Ruiz, 2013b).

A summary of CO_2 methanation catalysts using different active metals can be found in Table 4.1.

Promoters

Promoters are used to improve the catalyst performance and their introduction may influence the catalyst properties such as the acidity,

TABLE 4.1 Summary of CO_2 methanation catalysts using different active metals.

Catalyst	m_{cat}[a] g	GHSV[b] mL/g/h	H_2: CO_2 –	p[c] (bar)	T[d] (°C)	X_{CO_2} (%)	S_{CH_4} (%)	E_a[e] (kJ/mol)	Reference
5%Ni/SiO_2	0.200	50,000	4:1	1	300	42.4	96.6	84	Aziz et al. (2014)
5.9%Ni/Al_2O_3	0.100	30,000	4:1	1	250	2	98.1	92	Kikkawa et al. (2019)
4.9%Co/MCF-17	0.050	60,000	3:1	6	250	5.1	58.8	80	Beaumont et al. (2014a)
15%Fe/SiO_2	0.39	1470[f]	4:1	1	253	7.7	12.9	134	Weatherbee (1984)
MoO_3-3/ graphene	0.020	12,000	3:1	10	400	21	100	79	Primo et al. (2019)
MoS_2-3/graphene	0.020	60,000	3:1	10	400	20	90	62	Primo et al. (2019)
0.5%Ru/γ-Al_2O_3	0.375	5000	4:1	1	350	82	99.5	68.1	Falbo et al. (2018)
3%Rh/TiO_2	0.200	6000	4:1	1	120	0.65	100	17	Karelovic and Ruiz (2013a)
2%Rh/γ-Al_2O_3	0.200	6000	4:1	1	200	6.2	100	16.4	Karelovic and Ruiz (2013b)
19.5%Pt/Al_2O_3	0.100	30,000	4:1	1	250	2	2	94	Beaumont et al. (2014a)
1.1%Pt/MCF-17	0.050	60,000	3:1	6	250	1	98	–	Kikkawa et al. (2019)
5%Pd/γ-Al_2O_3	0.200	6000	4:1	1	300	4.3	100	23.5	Karelovic and Ruiz (2013b)

[a] m_{cat}, *catalyst mass used in experiments.*
[b] GHSV, *gas hourly space velocity, mL/g_cat/h.*
[c] p, *reaction pressure.*
[d] T, *reaction temperature;* X_{CO2}, *CO_2 conversion;* S_{CH4}, *CH_4 selectivity*
[e] E_a, *apparent activation energy;* f, *unit is/h*

basicity, dispersion of the active metal, etc., and as a result affect the activity, selectivity, and the resistance to coke deposition.

In addition to promoting the catalyst activity and stability, adding W in the Ni-MgO_x catalyst can promote its anti-CO-poisoning ability and resistance against coke formation (Yan et al., 2016).

Na has been observed to have a negative effect on Na/Ni/CeO_2 catalysts performance on CO_2 methanation, even at low concentrations (0.1 wt%). The adding of Na was reported to decrease the amount of chemisorbed CO_2 on Na/Ni/CeO_2 catalysts, and the CO_2 methanation activity of Na/Ni/CeO_2 decreased with Na content. While a positive effect of Na was observed for CO_2 methanation over Na/Ni/SiO_2 catalysts in which the amount of chemisorbed CO_2 increases with Na content (Le et al., 2018). This was speculated to be related to the position on and interaction of Na with the support. The Na content in 13X zeolite is around 10 wt%, but Ni/13X catalyst has shown high activity in CO_2 methanation (Wei et al., 2021). The effect of alkali promoters (Li, Na, K, Cs) seems to depend also on the active metal, support, dispersion, and loading (Petala & Panagiotopoulou, 2018).

The addition of lanthanum (La) in Ni/BETA zeolite catalyst can promote CO_2 conversion since La enhances the formation of surface hydroxyl groups greatly, which can interact with CO_2 and thus promote CO_2 conversion (Chen et al., 2019). The increasing amount of CO_2 adsorbed by the catalyst as a result of the La_2O_3 was reported to lead to a higher CO_2 methanation activity and CH_4 selectivity (Quindimil et al., 2018). Quindimil et al. reported that the Ni particle growth was influenced by La during catalyst calcination (Quindimil et al., 2018). Cerium (Ce) is a typical metal used as a promoter. It has been reported that Ce can further improve the catalyst activity and selectivity, due to the ability to promote CO_2 dissociation (Graça et al., 2014; Westermann et al., 2017).

Preparation of the bifunctional material

In general, the catalyst activity and selectivity will be influenced by different preparation methods and different supports, since the active metal dispersion, particle size, and location (Graça et al., 2014), the acidity, and interaction with the Si-Al framework will be different. In order to remove the water produced during the CO_2 methanation, a zeolite should be used in preparing the bifunctional material, which sets certain requirements for the preparation. There are two types of routes for the preparation of materials combining both catalytic and high water uptake capabilities: (a) mixing and shaping (physical mixture) route; (b) catalytic metal loading (chemical) route as displayed in Fig. 4.9.

Mixing and shaping route

In the mixing and shaping route, the catalyst preparation process is separated from the synthesis of the sorbent. In this way, the bifunctional material preparation will not be limited by the sorbent structure and other properties, such as the pore size, the acid and basic sites, etc. It is an easier way to prepare the bifunctional material compared to loading the metals directly on the sorbent, as all possible catalyst preparation methods can be utilized, such as impregnation, ion-exchange, deposition precipitation, chemical vapor deposition, atomic layer deposition, and co-precipitation (Pierson, 1999; Schlögl, 2008). As long as a highly active catalyst can be obtained (even purchased from commercial companies), mixing the catalyst and sorbent can be performed. One of the few examples is from Walspurger et al.. They physically mixed

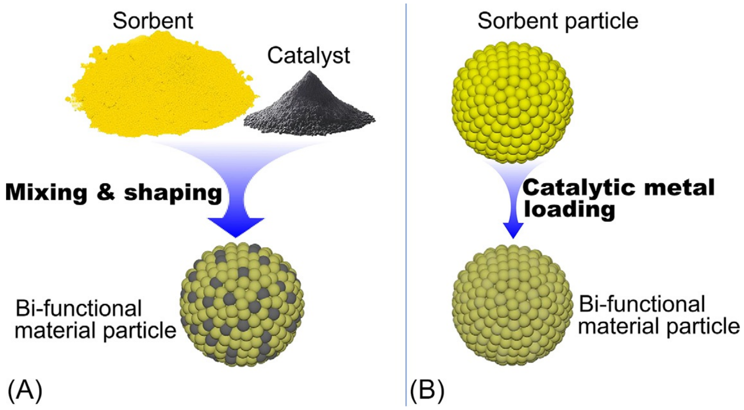

FIG. 4.9 A schematic representation of bifunctional material preparation routes. (A) Mixing and shaping route; (B) Catalytic metal loading route.

a commercial Ni catalyst with 4A zeolite and pelletized the mixture for sorption enhanced CO_2 methanation and, around 100% CO_2 conversion was obtained at 250–350°C (Walspurger et al., 2014). However, the pelletizing is not always straightforward as mechanical stability may pose an issue. Moreover, pore blockage during pelletizing can significantly decrease the surface area of the material. This again results in significantly lower performance both in the catalysis as well as in the absorptive capacity and kinetics.

Catalytic metal loading route

Although the mixing and shaping route is very flexible, the distance between the sorbing and catalytic site would be in a micro-meter scale in these bifunctional materials. Terreni et al. reported that nano-structuring sorption enhanced catalysts to shorten the diffusion pathway is superior over physical mixtures of macroscopic sorbents and other catalysts which result in longer diffusion path lengths (Terreni et al., 2018). In other words, in sorption enhanced CO_2 methanation, close proximity of sorption and catalytic sites is a prerequisite to conversion enhancement and process intensification. Materials prepared by loading the active metals directly into the zeolite would therefore be preferable.

Ion exchange is a typical method for catalyst preparation; the active metal, Ni for instance, can be loaded in the zeolite by exchanging it with the Na^+, K^+, Ca^{2+} from the zeolite framework (Schlögl, 2008). Recent publications have used ion exchange to prepare bifunctional materials with sorption enhancement (Borgschulte et al., 2013, 2015, 2016). In an ion-exchange process, a certain amount of metal salt (Ni precursor, e.g., nickel nitrate) is dissolved in distilled water. The sorbent, also acting as the catalyst support, is added into the solution and the mixture solution is stirred before filtering and washing with distilled water, after which the obtained solid sample is dried before calcination (Borgschulte et al., 2013; Schlögl, 2008). The metal loading is limited by the amount of exchangeable ions in the zeolite, however, the method results in highly dispersed catalyst when successful.

Impregnation is another conventional way for catalyst preparation, in which a certain amount of distilled water is used to dissolve the metal precursor. The water amount exceeds the pore volume of the support in wet impregnation, while it is equal to the pore volume of the support in incipient wetness impregnation. The sorbent is added to the solution, and the water in the mixture solution is removed by filtering or evaporation after several hours of stirring. The obtained solid is then dried further in an oven before calcination (Wei et al., 2020).

Other considerations for the bifunctional material preparation

Sub-nanometer or single-atom-based materials are the desired option, as they typically display high activity and they should largely retain their water-adsorption capacity after metal loading as low loadings can be used due to the high dispersion and pore blockage should then be avoided due to the small cluster size. Several strategies exist for synthesizing sub-nano/single-atom catalysts (Chen et al., 2018; Zhang et al., 2018a), of which mass-selected soft loading (Abbet et al., 2000) and atomic layer deposition (Peters et al., 2015; Yan et al., 2015) are limited by high cost and are complicated methods for large-scale catalyst production. In recent years, other synthesis strategies have emerged for single-atom catalyst preparation, such as defect engineering (Qiu et al., 2015; Zhang et al., 2018b), coordination pyrolysis (Chen et al., 2017; Han et al., 2017; Yin et al., 2016), and gas migration using volatile metal complexes (Qu et al., 2018). However, it is difficult to keep the material's structure intact since the high calcination or pyrolysis temperatures needed are prone to damage the structure of the support irreversibly. Furthermore, there is the possibility of sintering of the metal (nano) particles. Additionally, these preparation routes are difficult to scale up because of the complicated and expensive methods involved. Nevertheless, if solutions can be found for the drawbacks mentioned above, it will be feasible to prepare an extremely highly dispersed (maybe down to single-atom) catalyst and combined with a sorbent for sorption enhanced CO_2 methanation. However, physical mixtures are mainly the possible option in many of the cases.

It is possible to prepare highly dispersed zeolite catalysts by a novel strategy or by modifying conventional methods (Kistler et al., 2014; Lee et al., 2019a; Liu et al., 2019a). Liu et al. reported a general strategy to prepare a highly dispersed (even single atom) Pt, Pd, Ru, Rh, Co, Ni, and Cu on Y zeolite by adding ethylenediamine (EDA) as ligand to adjust the size the of precursors (Fig. 4.10) (Liu et al., 2019b).

Moreover, the metal precursor has also been observed to play an important role in the metal dispersion during the catalyst preparation, which influences the catalyst performance in CO_2 methanation. Wei et al. clearly showed how the selection of the precursor can influence the properties of a nickel-modified catalyst, in which nickel citrate precursor resulted in better dispersion compared to nitrate and acetate (Wei et al., 2021).

Characterization of the material

Similar to conventional catalysts, the bifunctional material has some important properties which relate to its performance in CO_2 methanation, such as the crystal structure and size, the dispersion of the active metal, the actual loading of active and promoter metal, the cluster size of metal, the acidity and basicity of the material, the pore size, volume and surface area, etc. Those properties can be characterized by conventional techniques such as X-ray powder diffraction (XRD) for crystal structure and size, scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX) for material morphology and surface elemental content, transmission electron microscopy (TEM) for metal particle size on the support, scanning transmission electron microscopy equipped with energy-dispersive X-ray spectroscopy (STEM-EDX) for elemental distribution, X-ray photoelectron spectroscopy (XPS) for chemical valence states, hydrogen-temperature programmed reduction (H_2-TPR) for catalyst reduction behavior, CO_2-temperature programmed desorption (CO_2-TPD) for basicity, pyridine-FTIR for acidity distribution, and N_2 adsorption for pore size, volume and surface area, etc.

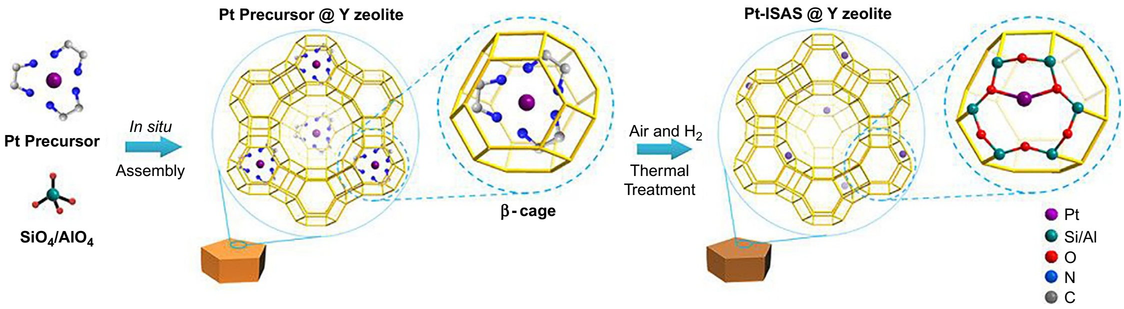

FIG. 4.10 A schematic illustration of the in-situ separation and confinement of platinum precursor in β-cage followed by thermal treatments. *Reprinted (adapted) with permission from Liu, Y., et al. (2019b). A general strategy for fabricating isolated single metal atomic site catalysts in Y zeolite.* Journal of the American Chemical Society, 141*(23), 9305–9311. Copyright (2019) American Chemical Society.*

Single-atom catalyst is a challenging topic in the analysis, HAADF-STEM (High-angle annular dark-field-scanning transmission electron microscope) has in some cases been successfully used to characterize the single atoms catalyst to get direct evidence of metal dispersion (Liu et al., 2019b).

For most single-atom catalyst, XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-Ray Absorption Fine Structure) are useful spectroscopic techniques to further determine the dispersion and coordination of the active metal in the zeolite (Liu et al., 2019b).

Performance of the material

Around 100% CO_2 conversion and 100% CH_4 selectivity have been obtained by using bifunctional material 6%Ni/5A in sorption-enhanced CO_2 methanation at temperatures lower than 200°C (Borgschulte et al., 2013), and 100% CH_4 selectivity was obtained using 5%Ni/5A and 5%Ni/13X under atmospheric pressure in fixed bed reactor (Delmelle et al., 2016). These materials are easily regenerated under H_2 or air atmosphere at elevated temperatures (Delmelle et al., 2016; Walspurger et al., 2014). The results of the studies are summarized in Table 4.2.

However, the number of publications on utilization of bifunctional materials for CO_2 hydrogenation is low so far, and the published papers are mainly focused on nickel-based LTA and FAU (13X) zeolite. Another zeolite, USY has been widely studied for CO_2 methanation, however, the sorption effect of the USY has been ignored. Results found in the literature are presented in Table 4.3. Other metals besides Ni have been explored in CO_2 methanation, with the aim of obtaining high low-temperature activity.

A study has shown that there are at least three possible reaction pathways for CO_2 methanation, (I) formate pathway; (II) carbide pathway; (III) carboxyl pathway (Fig. 4.11) (Vogt et al., 2019). The water removal might influence the reaction pathway, therefore the reaction rate and product distribution could be different. The reaction mechanisms of sorption enhanced CO_2 methanation are not yet exhaustively studied, including the bifunctional catalysts with or without promoters. The presence of promoters such as Ce could change the reaction pathway of CO_2 methanation, and there exist reports that the detected intermediates were different when a promoter was added (Westermann et al., 2017). However, this has not been extensively studied for sorption-enhanced CO_2 methanation.

TABLE 4.2 Performance of representative bifunctional materials for sorption-enhanced CO_2 methanation.

Bifunctional catalyst	Metal loading (wt%)	Pressure (bar)	Temp. (°C)	X_{CO2} (%)	S_{CH4} (%)	$T_{reg.}$[a] (°C)	Reference
Ni/5A	6	1.2	170	100	100	N.A.	Borgschulte et al. (2013)
Ni/Al_2O_3 mix 4A	N.A.	1	250–350	100	100	350–450	Walspurger et al. (2014)
Ni/5A	5	1	300	100	100	300	Delmelle et al. (2016)
Ni/13X	5	1	300	100	100	300	Delmelle et al. (2016)

[a] *T_{reg}, regeneration temperature of bifunctional material; X_{CO2}, CO_2 conversion; S_{CH4}, CH_4 selectivity.*

TABLE 4.3 Performance of representative zeolite catalysts for conventional CO_2 methanation.

Zeolite catalyst	Metal loading (wt %)	Prep. method[a]	Pressure (bar)	Temp. (°C)	X_{CO2} (%)	S_{CH4} (%)	Reference
Ru/5A	2–5	Impregnation	23	320	92	99.5	Hastings et al. (1988, 2002)
Rh/Y	6	Ion-exchange	30	150	5.9	99.8	Hastings et al. (1988)
Ru/HZSM-5	2	Impregnation	1	350	20	99	Scirè et al. (1998)
Ru/Y	3	Ion-exchange	30	150	12.4	96	Bando et al. (1999)
Ni/Beta	10	Impregnation	1	280	20	N.A.	Jwa et al. (2013)
Ni/HY	5	Impregnation	1	300	48.5	96.4	Aziz et al. (2014)
Ni/USY	5	IWI	1	400	24.7	61.4	Graça et al. (2014)
Ni/USY	14	Impregnation	1	300	8	36	Azzolina-Jury and Thibault-Starzyk (2017)
Ni/USY	4.8	IWI	1	300	10	95	Bacariza et al. (2017a)
Ni/HUSY	15	IWI	1	340	12	80	Bacariza et al. (2017b)
Ni/USY	5	IWI	1	350	12	72	Westermann et al. (2017)
Ni	15	IWI	1	337	12	80	Bacariza et al. (2018a)
Ni/Na-USY	15	IWI	1	305	14	95	Bacariza et al. (2018b)
Ni/USY	5	IWI	1	350	8	73	Bacariza et al. (2018c)
Ni/Na-Y	9.9	IWI	1	350	32	84	Quindimil et al. (2018)
Ni/Na-USY	15	IWI	1	360	62	96	Bacariza et al. (2019b)
Ni/ZSM-5	5	Impregnation	N.A.	450	44	84	Rasmussen et al. (2019)
Rh/HZSM-5	0.42	Seed-directing	10	300	20	100	Wang et al. (2019)
Ni/HZSM-5	10	IWI	1	400	68.4	94.8	Chen et al. (2020)
Ni/X	10	IWI	1	470	49	96	Czuma et al. (2020)
Ni/ITQ-2	5	IWI	1	250	6	97	da Costa-Serra, Cerdá-Moreno, and Chica (2020)
Fe/13X	5	Impregnation	1	350	13	11	Franken and Heel (2020)
Ru/13X	2.5	Impregnation	1	240	10	100	Wei et al. (2020)
Ni/13X	5	Impregnation	1	240	17	70	Wei et al. (2021)

[a] *IWI-incipient wetness impregnation.* X_{CO2}, *CO_2 conversion;* S_{CH4}, *CH_4 selectivity.*

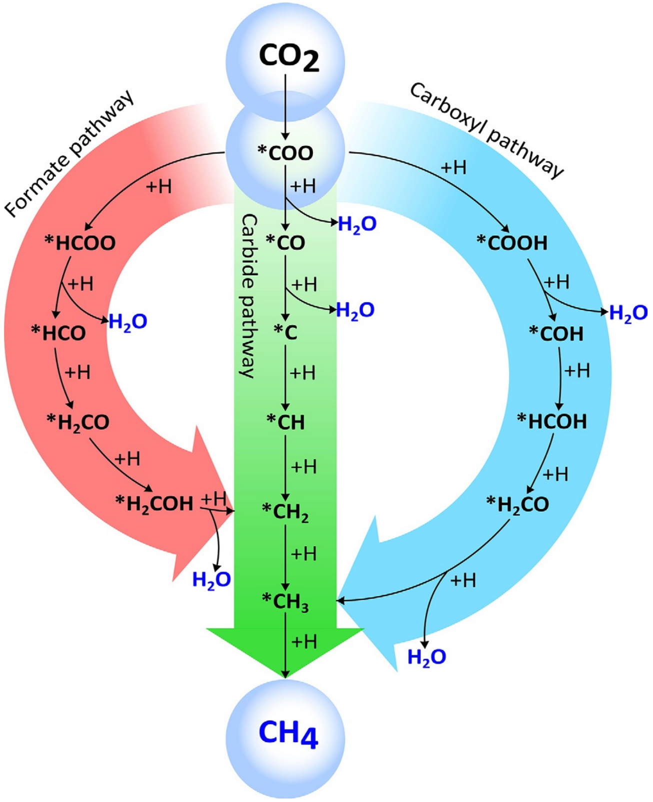

FIG. 4.11 Possible reaction pathways for the methanation of CO_2 (Vogt et al., 2019).

Stability of the material

The longevity and stability test of the catalyst/sorptive materials is extremely important for future commercial and large-scale projects on sorption-enhanced CO_2 methanation.

The factors which influence the stability and performance of the materials include two main parts: the deactivation of the catalytic metal and the change in water uptake capacity of the sorbent. Compared to the conventional CO_2 methanation processes, the bifunctional sorption catalyst can work at relatively mild reaction conditions. The calculated results of equilibrium in CO_2 methanation reaction confirm the extremely low carbon depositions present, although water removal in sorption enhanced CO_2 methanation can result in significant carbon generation at high temperature (higher than 400°C) (Catarina Faria, Miguel, & Madeira, 2018; Massa, Coppola, & Scala, 2020). On the other hand, carbon formation can be avoided by supplying H_2 in slight excess (Massa et al., 2020), however, a balance should be achieved in getting a high-quality product CH_4 with low H_2 concentration. Therefore, a good solution for avoiding carbon formation in bifunctional material is to operate the CO_2 methanation at low temperature. It has been shown that a CO_2 conversion of around 100% can be obtained at around 170°C using Ni-5A zeolite bifunctional material (Borgschulte et al., 2013), and it is also possible to obtain around full CO_2 conversion at 250–300°C using physical

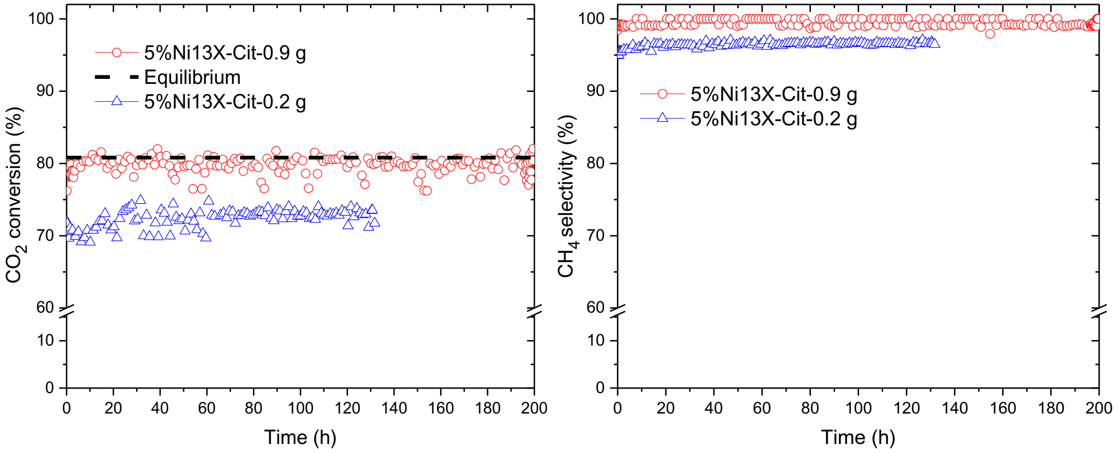

FIG. 4.12 CO_2 conversion *(left)* and CH_4 selectivity *(right)* of 5%Ni13X-Cit at 360°C with 150 mL/min N_2, 40 mL/min H_2, 10 mL/min CO_2 (Wei et al., 2021).

mixtures (commercial Ni/Al_2O_3 catalyst with 4A zeolite) (Walspurger et al., 2014). In fact, even coking of catalyst was not found from the bifunctional material at around 100 to 200-h time scale operation (Fig. 4.12), it showed that Ni zeolite bifunctional materials are very stable for the CO_2 methanation (Delmelle et al., 2018; Walspurger et al., 2014; Wei et al., 2020, 2021).

Moreover, some promoter metals such as Ce and La might also be an option for decreasing the carbon formation on the bifunctional materials in sorption enhanced CO_2 methanation. It would be necessary to further study the catalyst poisoning in practical operation of sorption enhanced CO_2 methanation, depending on the source, because some poisoning gases, H_2S for instance in biomass-derived CO_2, would lead to the catalyst deactivation as in conventional catalysis.

A high water uptake capacity of the bifunctional material is vital in sorption enhanced CO_2 methanation. Delmelle et al. reported that no change in sorption performance was observed within six cycles of drying procedure for both 5Ni/5A and 5Ni/13X (Delmelle et al., 2016). However, they found a degradation mechanism for Ni/5A specific to the sorption catalysis under cyclic methanation/drying periods, which affects water diffusion kinetics in the zeolite support and showed a decrease of water-diffusion coefficient during multiple cycling (Delmelle et al., 2018). To understand the mechanism of decreased water sorption for different sorbents, further studies and many more operation cycles would be needed for further application of sorption enhanced CO_2 methanation.

Research systems and scale

Sorption enhanced CO_2 methanation is based on the conventional CO_2 methanation reaction (Sabatier reaction (4.1)). The CO_2 conversion values reported in the literature (around 80%) (Ashok et al., 2020; Rönsch et al., 2016) are typically far from 100% under currently viable reaction conditions because conventional CO_2 methanation is hampered by thermodynamic limitations (Alvarez et al., 2017; Ashok et al., 2020; Rönsch et al., 2016). The sorption enhanced CO_2 methanation has the potential to provide high purity of CH_4 even meeting the requirements of the gas grid (Walspurger et al., 2014).

To obtain high purity product gas in a conventional CO_2 methanation system (Fig. 4.13),

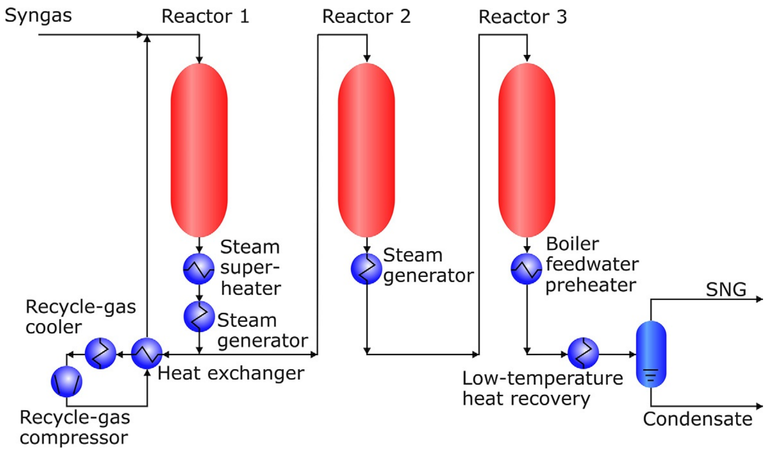

FIG. 4.13 Exemplary fixed-bed methanation process configuration with intermediate cooling and gas recycle. *Adapted from Rönsch, S., et al. (2016). Review on methanation—From fundamentals to current projects.* Fuel, 166, *276–296.*

several consecutive reactors combined with water condensers are needed to be employed, and separation of CO_2 and CH_4 is typically also implemented on site (Fig. 4.14) (Uebbing et al., 2019). In conventional CO_2 methanation, a high operating pressure must be used for obtaining a high CO_2 conversion and CH_4 yield due to kinetics (Fig. 4.2) (Catarina Faria et al., 2018). The sorption enhanced CO_2 methanation route has the potential to produce high purity CH_4 with water removal in situ and it is operated at lower pressure as well as at relatively low temperatures. This provides an opportunity for process simplification and cost savings by decreasing the number of reactors needed and by elimination of the downstream separation steps (Carvill et al., 1996). The sorbent will be saturated after some time in operation, and needs to be regenerated. There are two basic options for regeneration in a continuous process, which are a double parallel fixed bed reactor system and a circulating fluidized reactor system. A system which combines the fixed bed reactor, circulating fluidized reactor, and integrates the heat of reaction utilization is a promising solution for getting a high system energetic efficiency.

Fixed bed reactor system

Sorption enhanced CO_2 methanation was first reported by Borgschulte et al. in 2013 (Haije & Geerlings, 2011) in a study where the experiments were performed in a lab-scale stainless steel tubular fixed bed reactor system. Some publications on sorption enhanced CO_2 methanation have been published since then of which all are lab-scale experimental research as commercial operation and review papers are scarce to date (van Kampen et al., 2019). The utilization of zeolites as supports for CO_2 methanation catalysts was reported by M. Carmen Bacariza et al. (Bacariza et al., 2019a) and, Walspurger et al. described preliminary results from sorption enhanced CO_2 methanation experiment performed in a quartz reactor (lab scale) system in 2014 (Walspurger et al., 2014). In 2015, Borgschulte et al. described the Sabatier reaction kinetics using Ni supported on zeolite 3A and 5A in a lab-scale fixed bed reactor system (Borgschulte et al., 2015).

A mechanistic study was performed by Borgschulte et al. in a lab-scale fixed bed reactor system. They used time-resolved neutron radiography on the reactor. Using this technique, they clearly showed that water accumulated in

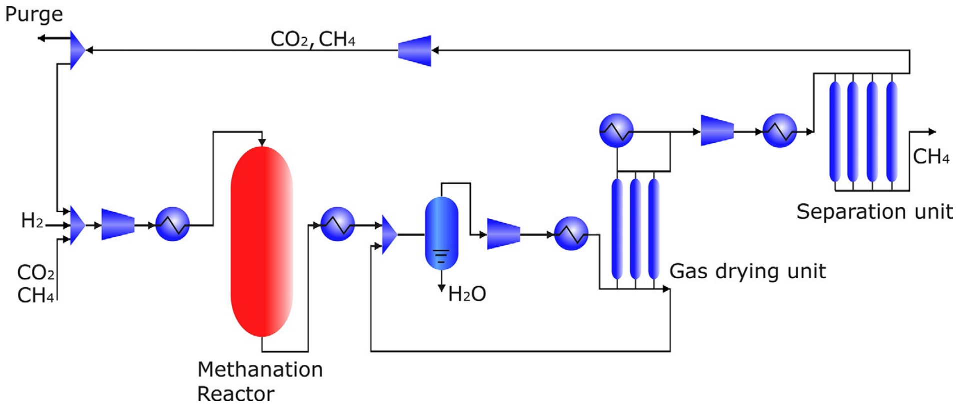

FIG. 4.14 Schematic figure of the process configuration for CO_2 methanation with separation unit. *Adapted from Uebbing, J., Rihko-Struckmann, L.K., Sundmacher, K. (2019). Exergetic assessment of CO_2 methanation processes for the chemical storage of renewable energies.* Applied Energy, *233–234, 271–282.*

the reactor during the sorption enhanced methanation, and was released from the reactor inventory gradually in the regeneration process (Borgschulte et al., 2016).

Fluidized bed reactor system

Compared to fixed bed reactor systems, fluidized bed reactor systems have advantages related to heat and mass transfer and they are favorable for integrating the sorbent regeneration involving large-scale operation of exothermic reactions (Rönsch et al., 2016). Compared to fixed beds, the application of fluidized bed reactors can also lead to energy-saving and favorable reaction conditions due to much higher efficiency in heat exchange as a result of the turbulent gas flow and rapid solids circulation flows (Lappas & Heracleous, 2016). However, the studies on sorption enhanced CO_2 methanation in fluidized bed reactor systems are scarce. Recently, Coppola et al. reported that they evaluated 3A zeolite and CaO for water removal in a lab-scale fluidized bed (40mm inner diameter) system. They investigated the sorbents hydration in steam (balance air) at 200–300°C and dehydration in air at 350–450°C. The results show that zeolite 3A has a higher steam adsorption capacity compared to CaO, and that the capacity of CaO reduced as a result of the carbonation reaction (Coppola et al., 2020). However, the sorbents were not used in combination with CO_2 processing.

Membrane reactor system

Compared to conventional CO_2 methanation, besides the advantage on methane yield and achieving zero CO_2 and CO outlet concentration, the operating temperature, pressure, and CO_2/H_2 ratio range can also be extended significantly in sorption enhanced CO_2 methanation systems (Borgschulte et al., 2013; Catarina Faria et al., 2018; Massa et al., 2020).

A membrane reactor can be used in CO_2 methanation to enhance the conversion of CO_2 by removing H_2O from the product mixture (Ashok et al., 2020; Lee et al., 2019b). In other reaction setups, typically at least two reactors are needed for obtaining continuous operation, one is used for the sorption enhanced reaction, another is for the regeneration of the sorbent. However, the high cost of membrane reactors and operation costs due to the required high driving force (pressure) often outweigh the benefits of having a single reactor (Catarina Faria et al., 2018).

Other considerations and novel reactor system application

The Sabatier reaction (4.1) is highly exothermic, while the sorbent regeneration is endothermic, therefore the energy efficiency of the whole system can be improved by integrating the heat from the Sabatier reaction performed in a first stage reactor at relatively high temperature for sorbent regeneration. This would be beneficial for lowering the cost of a large-scale commercial application of sorption enhanced CO_2 methanation. It is also beneficial to remove heat efficiently from the methanation reactor to avoid hotspots in the catalyst bed. One option would be to combine a circulating fluidized bed reactor with a fixed bed reactor according to the scheme presented in Fig. 4.15. The system integrates the heat utilization for obtaining a high-system energetic efficiency.

In the proposed system, the conventional CO_2 methanation technologies can be used well for the fixed bed reactor. The operating conditions such as the input ratio of H_2/CO_2, temperature, and pressure of the fixed bed reactor could be regulated to optimize the output composition, which is then fed into the sorption enhanced fluidized bed reactor. For example, thermal oil could be cycled in the system for carrying the heat from the fixed bed reactor to the generator. The bifunctional material (sorptive catalyst) is cycled between the circulating fluidized bed and the regenerator. The removal of water from the methanation reactor results in the equilibrium shift for achieving high conversion of CO_2 and very pure CH_4.

The above-described sorption enhanced CO_2 methanation system is not only beneficial for achieving 100% purity for CH_4, but it is also beneficial for lower temperature and pressure operation and process simplification. In addition to the application on earth, it may also have the potential for undertaking the role of H_2O and carbon cycle in space (Fig. 4.16), e.g., planet Mars (Vogt et al., 2019).

4.3 Conclusions and outlook

In summary, sorption enhanced CO_2 methanation has a great potential in the utilization of CO_2 and H_2 transfer for energy storage. It has been proven, that loading Ni on a water sorbents (LTA or FAU zeolite) is a feasible method to enhance the CH_4 yield significantly during CO_2 methanation and that it is possible to obtain full CO_2 conversion and high purity of CH_4 with the sorption enhanced CO_2 methanation route. Moreover, the sorption enhanced CO_2 methanation is also beneficial for lower temperature and pressure operation and process simplification. In addition to the application on earth, it may

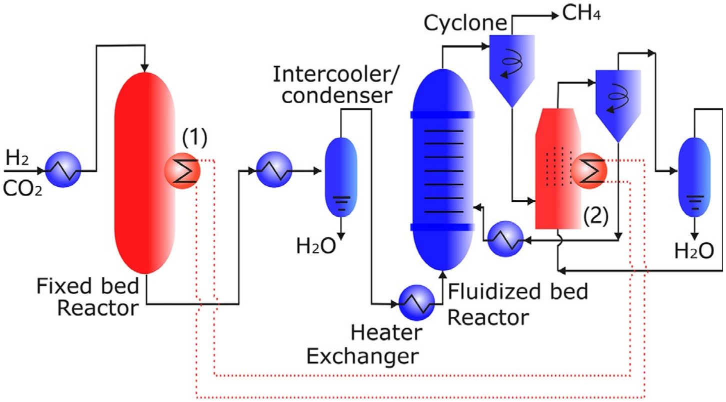

FIG. 4.15 A schematic diagram of sorption enhanced CO_2 methanation with circulating fluidized bed reactor setup and heat utilization for sorbents regeneration. (1) Heater exchanger in reactor or regenerator, (2) Fluidized bed regenerator.

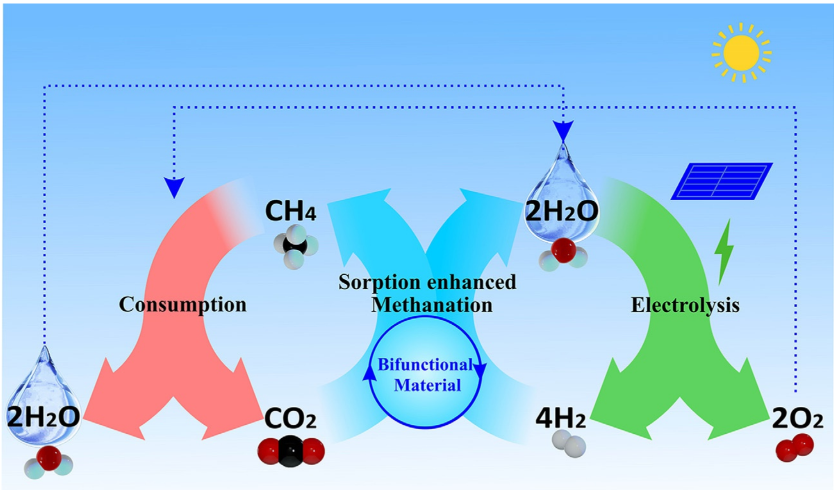

FIG. 4.16 A schematic diagram of sorption enhanced CO_2 methanation system with carbon and hydrogen cycle.

also have the potential for undertaking the role of H_2O and carbon cycle in space, e.g., in Mars.

However, there are still some unclear aspects in sorption enhanced CO_2 methanation. Even though the basic concept has been presented previously, there are still many fundamental and practical aspects unclear and unresolved in sorption enhanced CO_2 methanation. Before the commercial application of sorption enhanced CO_2 methanation, further studies are needed, which include the structure and properties (pore size, acidity, basicity, metal dispersion, etc.) tuning of sorbent and catalyst, the possibility for applying prolonged time and many regeneration cycles, bifunctional performance evaluation under practical operation conditions well as considering systematic scale-up for sorption enhanced CO_2 methanation by taking into account, e.g., mass and heat transfer phenomena.

To select a proper zeolite, or tune the zeolite property or synthesize a new zeolite for sorption enhanced CO_2 methanation is tedious. The zeolite water sorption capacity has a direct relationship to the sorption temperature, and a lower temperature is favored for a higher water sorption capacity. To develop a bifunctional catalyst which can work at a low temperature is regarded for a future sorption enhanced CO_2 methanation. This kind of bifunctional material should have a high dispersion of catalytic metal and activity. The loading of the catalytic metal should also have limited effect on the sorption capacity of the sorbent.

Further work regarding the mechanism of sorption enhanced CO_2 methanation will give a clearer image about the pathway of CH_4 formation under water sorption enhanced condition, which will reveal the selectivity of the bifunctional material.

It would be worth to study sorption enhanced CO_2 methanation with a systematic design which considers the heat utilization and mass cycle.

Some harsh conditions in the presence of poisoning gases such as CO and sulfur compounds are needed for further study in sorption enhanced CO_2 methanation, as it is an important issue to avoid the catalyst poisoning and water capacity decay for the bifunctional material.

Further study on more cycles for sorbent (bifunctional material) on sorption enhanced CO_2 methanation is needed before industrial application.

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