Current Developments in Catalytic Methanation of Carbon Dioxide—A Review

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The utilization of fossil fuel has increased atmospheric carbon dioxide (CO₂) concentrations drastically over the last few decades. This leads to global warming and climate change, increasing the occurrence of more severe weather around the world. One promising solution to reduce anthropogenic CO₂ emissions is methanation. Many researchers and industries are interested in CO₂ methanation as a power-to-gas technology and carbon capture and storage (CCS) system. Producing an energy carrier, methane (CH₄), via CO₂ methanation and water electrolysis is an exceptionally effective method of capturing energy generated by renewables. To enhance methanation efficiency, numerous researches have been conducted to develop catalysts with high activity, CH₄ selectivity, and stability against the reaction heat. Therefore, in this mini-review, the characteristics and recent advances of metal-based catalysts in methanation of CO₂ is discussed.

Keywords: noble metal, methane, CO₂ methanation, catalyst, nickel

INTRODUCTION

Solving climate change represents one of mankind's biggest challenges in the 21st century (Wang and Gong, 2011). The dominant greenhouse gases (GHGs) that raise Earth's temperature are water vapor, carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). Water vapor makes up roughly 75% of the total greenhouse effect, CO₂ and CH₄ contribute roughly 24%, while N₂O and ozone (O₃) accounts for the remaining 1%. Despite being the major GHG, water vapor behaves as feedback of greenhouse effect and is temperature-dependent. Instead, CO₂ is the main driver of greenhouse effect. This is due to high concentration and long retention time of CO₂ in the atmosphere compared to other GHGs (Tan et al., 2021). The substantial effect of CO₂ on global warming has prompted worldwide effort to curb anthropogenic GHG emissions (Wang and Gong, 2011). One promising solution is CO₂ methanation. Methanation, uncovered by Paul Sabatier and Jean-Baptiste Senderens in 1902, refers to the reaction between CO_x and hydrogen (H₂) to produce methane (CH₄) (Eqs. 1, 2). Methanation can turn emitted CO₂ into the valuable energy carrier CH₄, potentially creating power-to-gas platform and circular carbon economy. Since renewable energy is increasingly used for global electricity generation, power-to-gas systems utilizing CO₂ methanation can solve the issue of intermittent power production from renewables such as solar and wind. The green CH₄ produced from renewable electricity can be stored and converted back to electricity when needed (Rönsch et al., 2016; Frontera et al., 2017).

CO₂ methanation is also a pivotal process for future manned space travel as its reactants, CO₂ and H₂, are continuously produced from respiration and water electrolysis (Sheehan, 2021).

Despite the highly exothermic nature of CO₂ methanation (Eq. 2), the reaction is thermodynamically favored at low temperatures. However, catalysts are necessary to lower the high activation barriers and speed up the reaction (Su et al., 2016). Methanation catalysts must fulfil two requirements: (1) display high efficiency and activity at low temperatures, and (2) remain stable against the reaction heat (Xu et al., 2016a). The most common catalysts are nickel (Ni)-based due to the cheap and abundant Ni metal. But Ni-based catalysts suffer from sintering, creation of mobile Ni sub-carbonyls, and creation of carbon deposits. In contrast, ruthenium (Ru)-based catalysts show high activity and stability across a broad range of operating conditions. Other transition metals [iron (Fe), cobalt (Co)] and noble metals [rhodium (Rh), palladium (Pd)] have also shown catalytic activity in CO₂ methanation (Su et al., 2016; Frontera et al., 2017; Dębek et al., 2019). Therefore, this mini-review aims to discuss the characteristics of different metal-based catalysts in CO₂ methanation and provide a comparison of their recent advances.

RECENT DEVELOPMENTS IN NI-BASED CATALYSTS

Ni is the most thoroughly researched metal for CO₂ methanation due to its relatively high activity, exceptional CH₄ selectivity, and lower cost compared to noble metals (Rönsch et al., 2016). Numerous researches have highlighted that Ni-based catalyst activity is enhanced by smaller Ni particles and greater degree of dispersion (Dębek et al.,

2019). The key breakthroughs for Ni-based catalysts in CO₂ methanation lies in enhancing their reactivity, stability at lower temperatures (typically operate around 400°C), and CH₄ selectivity. However, at lower temperatures, the appearance of mobile Ni subcarbonyls causes sintering which reduces catalytic ability and increases carbon deposits. Besides lower temperature operation, catalyst basicity is another important parameter since active sites with moderate basicity are key locations for creation of monodentate formate species. These species are crucial as they amplify catalytic performance and CH₄ selectivity of Ni-based catalysts (Figure 1) (He et al., 2014; Darouhegi et al., 2017; Wierzbicki et al., 2017). All these characteristics of Ni-based catalysts can be altered by choosing different supports, promoters, catalyst synthesis method, and catalyst pretreatment (Dębek et al., 2019). Using five different mesoporous supports, Guo et al. (2018) found that Ni catalyst activity decreased along this trend: Ni/ZSM-5 > Ni/SBA-15 > Ni/Al₂O₃ > Ni/SiO₂ > Ni/MCM-41. The basicity of Ni/ZSM-5 enhanced monodentate formate creation on the catalyst surface, which displayed higher activity compared to bidentate formate created on Ni/MCM-41 (Guo et al., 2018). Meanwhile, Fukuhara et al. (2017) found that highly basic support, like MgO, strongly adsorbed CO₂ on the catalyst surface which reduced catalytic performance (Fukuhara et al., 2017). Among various supports for Ni-based catalysts, ceria (Ce) has been shown to achieve better performance. This is because the existence of oxygen vacancies on Ce surface increases catalyst basicity and establishes redox interactions between Ni particles and Ce support (Zhou et al., 2016). But this structural advantage can show negative impacts when unsuitable catalyst synthesis technique is used. This was validated by Konishcheva et al. (2016) who documented diminished activity from Ni(Cl)/CeO₂ catalyst compared to Ni/CeO₂. This was because chlorine (Cl) particles hindered CO₂ methanation reaction pathway, resulting in lower activity (Konishcheva et al., 2016). A performance comparison of different Ni-based catalysts in CO₂ methanation is found in Table 1.

TABLE 1 | Performance comparison of different nickel (Ni)-based catalysts in CO₂ methanation.

Catalyst	CO ₂ conversion	CH ₄ selectivity	Operating conditions	References
20Ni/Al ₂ O ₃	81%	96%	400°C, 1 atm, CO ₂ :H ₂ :N ₂ = 6:30:64, GHSV = 55,000 h ⁻¹	Garbarino et al. (2015)
75Ni25Fe/Al ₂ O ₃	3.39 × 10 ⁶ mol g _{cat} ⁻¹ s ⁻¹	97.6%	250°C, CO ₂ :H ₂ = 1:24, m _{cat} = 0.1 g, reduced at 550°C for 4 h	Ray and Deo, (2017)
15Ni/Al ₂ O ₃	1.07 × 10 ⁶ mol g _{cat} ⁻¹ s ⁻¹	100%	250°C, CO ₂ :H ₂ = 1:24, m _{cat} = 0.1 g, reduced at 550°C for 4 h	Ray and Deo, (2017)
Sponge Ni	83%	>95%	250°C, CO ₂ :H ₂ :He = 1:4:5, m _{cat} = 0.3 g, WGHSV = 0.11 mol _{CO2} g _{cat} ⁻¹ h ⁻¹ , stored underwater at room temperature, dried in air at room temperature for 48 h before use	Tada et al. (2017)
90Ni10Fe	≈0.8 μmol m ⁻² s ⁻¹	≈98%	250°C, 1 atm, CO ₂ :H ₂ = 4:96, m _{cat} = 0.15 g, calcined at 500°C for 6 h	Pandey et al. (2018)
Ni/ZrO ₂	71.9%	69.5%	300°C, CO ₂ :H ₂ :N ₂ = 4:16:5, GHSV = 60,000 h ⁻¹ , calcined at 500°C for 3 h	Jia et al. (2019)
Ni/ZrO ₂	32.9%	30.3%	300°C, CO ₂ :H ₂ :N ₂ = 4:16:5, GHSV = 60,000 h ⁻¹ , decomposed with dielectric barrier discharge plasma for 1 h	Jia et al. (2019)
Ni/Pr ₂ O ₃ -CeO ₂	54.5%	100%	350°C, CO ₂ :H ₂ = 1:4, WGHSV = 25,000 ml g ⁻¹ h ⁻¹	Siakavelas et al. (2021)
Ni/Sm ₂ O ₃ -CeO ₂	44.9%	100%	350°C, CO ₂ :H ₂ = 1:4, WGHSV = 25,000 ml g ⁻¹ h ⁻¹	Siakavelas et al. (2021)
Ni/MgO-CeO ₂	43.2%	100%	350°C, CO ₂ :H ₂ = 1:4, WGHSV = 25,000 ml g ⁻¹ h ⁻¹	Siakavelas et al. (2021)

TABLE 2 | Performance comparison of different transition- and noble-metal-based catalysts for CO₂ methanation.

Catalyst	CO ₂ conversion	CH ₄ selectivity	Operating conditions	References
3Ru/Al ₂ O ₃	96%	96%	300°C, 1 atm, CO ₂ :H ₂ :N ₂ = 6:30:64, GHSV = 15,000 h ⁻¹	Garbarino et al. (2015)
10Ru-30Mn-60Cu/Al ₂ O ₃	98.5%	–	220°C, CO ₂ :H ₂ = 1:4, m _{cat} = 5 g, calcined at 1,000°C for 5 h	Zamani et al. (2015)
2Ru/TiO ₂	≈20%	100%	250°C, CO ₂ :H ₂ :He = 5:20:75, m _{cat} = 100 g	Panagiotopoulou, (2017)
5Ru/Al ₂ O ₃	TOF/I ₀ ≈ 1 × 10 ⁻¹⁰ m _{Ru} ² m _{interface} ⁻¹ s ⁻¹	100%	250°C, CO ₂ :H ₂ :He = 5:20:75, m _{cat} = 100 g, calcined at 650°C for 4 h	Panagiotopoulou, (2017)
Rh@S-1-OH	≈75%	≈99%	450°C, 1 MPa, CO ₂ :H ₂ :Ar = 1:3:1, m _{cat} = 0.5 g, calcined at 550°C for 4 h	Wang et al. (2019)
Rh@HZSM-5	≈70%	≈99%	450°C, 1 MPa, CO ₂ :H ₂ :Ar = 1:3:1, m _{cat} = 0.5 g	Wang et al. (2019)
Rh@KZSM-5	≈55%	≈73%	500°C, 1 MPa, CO ₂ :H ₂ :Ar = 1:3:1, m _{cat} = 0.5 g, calcined at 500°C for 4 h	Wang et al. (2019)
Rh@S-1	≈51%	≈20%	500°C, 1 MPa, CO ₂ :H ₂ :Ar = 1:3:1, m _{cat} = 0.5 g, calcined at 550°C for 4 h	Wang et al. (2019)
6Pd/UiO-66	56.0%	97.3%	340°C, 4 MPa, CO ₂ :H ₂ :N ₂ = 16:64:20, m _{cat} = 0.6 g, GHSV = 15,000 h ⁻¹ , calcined at 360°C for 3 h	Jiang et al. (2019)
PdO@LaCoO ₃	62.3%	99%	300°C, 3 MPa, CO ₂ :H ₂ :He = 24:72:4, m _{cat} = 0.15 g, calcined at 500°C for 1 h	Wang et al. (2021)
PdO/LaCoO ₃	31.8%	87.4%	300°C, 3 MPa, CO ₂ :H ₂ :He = 24:72:4, m _{cat} = 0.15 g, calcined at 500°C for 1 h	Wang et al. (2021)
CoO	73%	94%	400°C, CO ₂ :H ₂ = 1:4, GHSV = 1,500 cm ³ h ⁻¹ g _{cat} ⁻¹ , calcined under argon atmosphere (0.1 MPa) at 500°C for 2 h	Kierzkowska-Pawlak et al. (2019)
2Co/ZrO ₂	85%	≈99%	400°C, 3 MPa, CO ₂ :H ₂ = 1:4, m _{cat} = 0.5 g, citric acid-assisted impregnation where molar ratio of citric acid to Co was 2, calcined at 500°C for 4 h	Li et al. (2019)
Co-Zr _{0.1} -B-O	78.1%	97.8%	180°C, 8 MPa, CO ₂ :H ₂ = 1:1, m _{cat} = 0.04 g	Tu et al. (2021)
2Mg/Fe ₂ O ₃	32%	65%	400°C, 8 bar, CO ₂ :H ₂ :N ₂ = 1:4:5, GHSV = 10,000 h ⁻¹ , m _{cat} = 4 g, calcined at 400°C for 2 h	Baysal and Kureti, (2020)
α-Fe ₂ O ₃	≈24%	≈7%	400°C, 1 bar, CO ₂ :H ₂ :N ₂ = 1:4:5, GHSV = 52,000 h ⁻¹ , m _{cat} = 0.2 g	Kirchner et al. (2020)
15Fe/SiO ₂	≈19%	≈3.5%	400°C, 1 bar, CO ₂ :H ₂ :N ₂ = 1:4:5, GHSV = 52,000 h ⁻¹ , m _{cat} = 0.2 g, calcined at 400°C for 2 h	Kirchner et al. (2020)

RECENT DEVELOPMENTS IN OTHER METAL-BASED CATALYSTS

Ruthenium

Ruthenium (Ru) is also one of the most reactive catalysts for methanation. However, its catalytic ability and CH₄ selectivity are

greatly influenced by the choice of support, dispersion of metallic Ru on the supports (greater dispersion lowers the apparent activation energy), and inclusion of promoters that enhances the Ru activity (Garbarino et al., 2015; Garbarino et al., 2016; Toemen et al., 2016). Ru-based catalysts display higher reactivity and lower reduction temperatures compared to Ni-based

catalysts (Garbarino et al., 2015; Garbarino et al., 2016). Studies on Ru/Al₂O₃ catalyst discovered that its activity was enhanced when activated via reaction with the CO₂/H₂ stream compared to the pre-reduced version (Garbarino et al., 2015). The Ru/Al₂O₃ catalyst also became more active with smaller Ru particle size (Li et al., 2013; Zheng et al., 2016). When using TiO₂ as support, Xu et al., 2016b showed that pretreatment temperature of Ru/rutile-TiO₂ at 600°C achieved a maximum CO₂ turnover frequency (TOF) of 1.59 s⁻¹. The high activity of Ru/rutile-TiO₂ was due to the increased encapsulation of Ru particles by TiO₂ layers and higher concentrations of hydroxyl groups on the TiO₂ layers, which enhanced CO₂ dissociation (Xu et al., 2016b). In a separate study, a binary supported Ru/TiO₂-Al₂O₃ catalyst showed 3.1-fold increase in CO₂ methanation reaction rate compared to Ru/Al₂O₃ catalyst. The smaller mean Ru particle size of 2.8 nm in Ru/TiO₂-Al₂O₃ contributed to its higher activity compared to 4.3 nm in Ru/Al₂O₃. The small particle size was maintained by the presence of rutile-TiO₂, which obstructed the agglomeration of Ru particles (Xu et al., 2016a). **Table 2** shows the performance comparison of different noble metal- and transition metal-based catalysts for CO₂ methanation.

Rhodium

Many studies have demonstrated Rh as among the most reactive catalysts for methanation of CO₂ at low temperatures (100–200°C). The primary benefit of Rh-based catalyst is its lower reduction temperature (less than 400°C) compared to the commonly used Ni-based catalyst (typically more than 500°C) (Dębek et al., 2019). It was hypothesized that CO₂ methanation on Rh-based catalysts followed two mechanisms: (1) dissociation of CO₂ into CO followed by hydrogenation of CO, or (2) direct hydrogenation of chemisorbed CO₂ molecules. However, mechanistic studies performed by Beuls et al. (2012) verified the former mechanism as well as showing that surface gem-dicarbonyl species had higher reactivity compared to surface linear species (**Figure 2**). The formation of gem-dicarbonyls was boosted by the interactions between surface Rh⁺ molecules and

CO₂ (Beuls et al., 2012). In one study, CO₂ methanation using Rh/γ-Al₂O₃ catalysts at low temperature was investigated. Selectivity to CH₄ was 100% under all test conditions. At higher temperatures of 185–200°C, Rh particle size did not affect methanation, whereas at lower temperatures, bigger particle size enhanced the methanation reaction (Karelovic and Ruiz, 2012). During methanation, the presence of oxygen (O₂) in low concentrations could increase CH₄ yield by encouraging the formation of more surface reactive species like gem-dicarbonyls. But when O₂ concentrations rose above the optimum, it would inevitably oxidize the metal Rh atoms, reducing the effectiveness of the catalysts (Jacquemin et al., 2010; Beuls et al., 2012).

Palladium

Since Pd can catalyze both methanol synthesis and reverse water gas shift (RWGS) reaction, its methanation capability was also investigated (Rui et al., 2017; Nelson et al., 2020). Numerous researches have demonstrated good catalytic ability for Pd-based catalysts in CO₂ methanation. However, the drawbacks of Pd-based catalysts include higher cost of Pd compared to transition metals, low activity (acceptable performance usually observed beyond 400°C), lesser CH₄ selectivity, and greater selectivity towards methanol and heavier hydrocarbons (Dębek et al., 2019). A recent study by Jiang et al. (2019) demonstrated the use of UiO-66 support and Pd nanoparticles for CO₂ methanation. Synergy was observed in the Pd/UiO-66 catalyst whereby CO₂, activated by Zr₆O₄(OH)₄ molecules on UiO-66, was hydrogenated by H₂ molecules dissociated by Pd. At 340°C, 4 MPa and 6 wt% Pd loading, high CO₂ conversion, CH₄ selectivity and space-time yield of 56.0%, 97.3% and 856 g h⁻¹ kg_{cat}⁻¹ were observed (Jiang et al., 2019). Luo et al. (2020) described the remarkable activity and stability of PdFe intermetallic nanocrystals for CO₂ methanation. At 180°C, CO₂:H₂ ratio of 1:4 and 1 bar, the maximum yield of *face-centered-tetragonal* (fct) PdFe catalyst was 5.3 mmol g⁻¹ h⁻¹, an increase of 6.6, 1.6, 3.3, and 5.3-fold compared to *face-*

centered-cubic (fcc) PdFe nanocrystals, Ru/C, Ni/C, and Pd/C catalysts. The fct-PdFe nanocrystals also maintained 98% activity after 20 successive runs. Mechanistic studies found that PdFe nanocrystals could renew their Fe species via reversible oxidation-reduction process during CO₂ methanation, thereby maintaining the catalytic ability of Fe species in dissociating CO₂ into an intermediate CO* (Luo et al., 2020).

Cobalt

Since Co is an active catalyst in Fischer-Tropsch reaction, its catalytic ability in CO₂ methanation was also studied (Chen et al., 2018). The synthesis of long-chain hydrocarbons from syngas (CO and H₂) by Co catalyst implies that Co does not catalyze water-gas shift reaction. This beneficial characteristic of Co may become disadvantageous for CH₄ selectivity during methanation. Numerous researches have described higher Co activity under smaller Co particle sizes and increased particles dispersion, whereas sintering lowers Co activity (Dębek et al., 2019). An investigation by Le et al. (2017) revealed that Co activity and type of end-product relied on the choice of support. Co activity was reduced along this sequence: CeO₂ > SiO₂ > ZrO₂ > Al₂O₃ > TiO₂. The primary product for all catalysts was CH₄, with ethane and CO as by-products in high and low activity catalysts, respectively (Le et al., 2017). In a recent study, Tu et al. (2021) discovered that adding zirconium (Zr) promoter enabled amorphous Co-Zr_{0.1}-B-O catalyst to commence CO₂ methanation at temperatures as low as 140°C. Maximum catalyst activity was achieved at 180°C (10.7 mmol_{CO2} g_{cat}⁻¹ h⁻¹) with 78.1% CH₄ yield and 97.8% CH₄ selectivity, on par with noble metal catalysts under similar conditions. The high catalyst performance could be attributed to: (1) prevalent surface defects and inherent active sites in the amorphous structure, and (2) expansion of active surface area and tuning of oxidation state of surface particles by Zr promoter (Tu et al., 2021). Another study by Li et al. (2019) examined the effects of organic acid-assisted incipient wetness impregnation for Co catalyst preparation. Citric acid-assisted 2Co/ZrO₂ catalyst attained 85% CO₂ conversion and ≈99% CH₄ selectivity. Molar ratio of citric acid to Co between 0 and 2 resulted in highly dispersed Co particles and improved activity. Adequate particle dispersion allowed optimal interaction between Co-ZrO₂ and oxygen vacancy, giving rise to more active sites (Li et al., 2019).

Iron

Iron Fe is the second most widely used catalyst for Fischer-Tropsch reaction and a common catalyst for RWGS reaction. As such, it was hypothesized that Fe catalyst could dissociate CO₂ to CO *via* RWGS pathway followed by methanation of CO (Dörner et al., 2010; Mahmoudi et al., 2017). The benefits of Fe-based catalysts include cheaper Fe metal and lesser toxicological effect compared to Ni. But Fe-based catalysts suffer from low CH₄ selectivity (Dębek et al., 2019). Kirchner et al. (2018) synthesized Fe-based catalysts from commercial iron oxides and activated the catalyst in the CO₂/H₂ stream without reduction pretreatment. During methanation, iron carbides and carbon deposits appeared on the catalyst surface. Large quantities of CO were observed due

to RWGS reaction. Nano-sized γ-Fe₂O₃ catalyst achieved the best result due to the high concentrations of surface carbon species compared to low reactivity carbides that formed on α-Fe₂O₃ catalyst (Kirchner et al., 2018). In another study, De Masi et al. (2020) magnetically-induced heating on bimetallic catalyst Fe₃₀Ni₇₀/SiAlOx to trigger CO₂ methanation. Acceptable CO₂ conversion (71%) but low CH₄ selectivity (65%) were obtained due to formation of Fe-rich shell on the catalyst surface. After covering the catalyst with a thin Ni layer, the catalyst performance was enhanced to 100% conversion and 100% CH₄ selectivity under low magnetic field and moderate conditions (25 ml min⁻¹, 19 mT, 300 kHz) (De Masi et al., 2020).

CONCLUSION

Presently, methanation is receiving ever-growing attention due to global warming, climate change, depleting fossil fuels, and increasing usage of renewables in global energy generation. The reutilization of atmospheric CO₂ to produce valuable energy carrier CH₄ presents a promising pathway towards net zero carbon future. The CH₄ synthesized from methanation is compatible with existing gas pipelines and energy infrastructures. CO₂ methanation process is greatly dependent on catalysts performance. Hence, improving and developing catalysts with high activity, CH₄ selectivity, stability, and lifetime is among the key areas of intense research. Ni-based catalysts are the most widely commercialized catalysts due to its cheaper price and relatively high activity. But Ni-based catalysts suffer from deactivation due to sintering and oxidation. Conversely, Ru-based catalysts have the highest activity and better stability, but more expensive Ru metal. Generating H₂ from water electrolysis using inexpensive renewables may improve the commercialization of more expensive catalysts. More research is required to solve these technological and economic issues. However, once solved, CO₂ methanation will become a key technology for a sustainable future.

AUTHOR CONTRIBUTIONS

CHT: conceptualization, writing, writing – review and editing; SN: funding acquisition, supervision, writing; AHS: formal analysis, validation, funding acquisition, supervision, writing; Y-KP: writing – review and editing, validation; HH-C: writing – review and editing, validation; PLS: supervision, writing.

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