Review

Research Progress and Reaction Mechanism of CO₂ Methanation over Ni-Based Catalysts at Low Temperature: A Review

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Abstract: The combustion of fossil fuels has led to a large amount of carbon dioxide emissions and increased greenhouse effect. Methanation of carbon dioxide can not only mitigate the greenhouse effect, but also utilize the hydrogen generated by renewable electricity such as wind, solar, tidal energy, and others, which could ameliorate the energy crisis to some extent. Highly efficient catalysts and processes are important to make CO₂ methanation practical. Although noble metal catalysts exhibit higher catalytic activity and CH₄ selectivity at low temperature, their large-scale industrial applications are limited by the high costs. Ni-based catalysts have attracted extensive attention due to their high activity, low cost, and abundance. At the same time, it is of great importance to study the mechanism of CO₂ methanation on Ni-based catalysts in designing high-activity and stability catalysts. Herein, the present review focused on the recent progress of CO₂ methanation and the key parameters of catalysts including the essential nature of nickel active sites, supports, promoters, and preparation methods, and elucidated the reaction mechanism on Ni-based catalysts. The design and preparation of catalysts with high activity and stability at low temperature as well as the investigation of the reaction mechanism are important areas that deserve further study.

Keywords: CO₂; CH₄; reaction mechanism; Ni-based catalysts; low temperature

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1. Introduction

With the continuous advancement of social economy and the unceasing enhancement of human living standards, the overuse of fossil fuels has resulted in an energy crisis while the excessive emission of CO₂ has exacerbated the greenhouse effect, which has induced global climate problems [1–5]. One of the most effective strategies is to replace fossil fuels with clean, renewable, carbon-neutral alternatives. Photocatalytic hydrogen production by solar energy has attracted the extensive attention of researchers, which was considered to be one of the most promising ways of utilizing solar energy because the combustion of H₂ would release a large quantity of energy and the product would not pollute the environment [6–9]. However, it is impossible to achieve an industrial application due to the cost and operational limitations of this technology at present. Moreover, capture and geological sequestration strategies have also been used to remove excessive CO₂ in the atmosphere [10–12]. However, several issues such as energy consumption, unsustainability, and leakage risks prevent these two methods from a large-scale application [13,14]. As the main component of industrial waste gas, CO₂ could also be used as an abundant and cheap chemical feedstock for renewable fuels [15]. Therefore, converting CO₂ into value-added chemicals is considered to be one of the most promising strategies to mitigate the energy crisis and reduce the greenhouse effect. CO₂ reform of methane (DRM) is becoming an interesting strategy to convert the two greenhouse gases into syngas, which can be further converted to value-added products such as methanol or fuels through Fisher–Tropsch synthesis to replace traditional fossil fuels [16–20]. Many studies have also

reported the steam methane reforming reaction to produce H_2 as an alternative energy for fossil fuels [21–24].

Several clean and renewable energy resources such as wind, solar, and tidal energy produce discontinuous and unstable electricity, which cannot be used effectively. Hydrogen can be generated by the electrolysis of water using this kind of unstable electricity [25–29]. With this low cost H_2 supply, CO_2 could be hydrogenated to form a variety of products including methanol [30–35], ethanol [36–39], olefins [40], methane [41–44], and other hydrocarbons [45,46]. At the same time, clean and renewable energy can also be effectively utilized [47]. Compared with the conversion of CO_2 to other value-added chemicals, the CO_2 methanation reaction rate is faster, the reaction conditions are milder, and can be carried out under atmospheric pressure. The hydrogenated product, methane, as the main component of natural gas, can be effectively utilized as a fuel or chemical, thus forming a new carbon cycle. The CO_2 methanation reaction can alleviate the greenhouse effect, solve the problem of natural gas shortage, and reduce humanity's dependence on fossil energy [48–51]. Throughout the years, the CO_2 methanation reaction has been carried out via different methods such as thermo-catalysis [47,52], photo-catalysis [53–62], electro-catalysis [63,64], bio-catalysis [63,65–67], plasma-catalysis [68–70], etc. Figure 1 presents the CO_2 hydrogenation to produce CH_4 through different catalysis methods. Among these CO_2 methanation processes, CO_2 can be hydrogenated to produce CH_4 by photo-catalysis, electro-catalysis, and plasma-catalysis at low temperature. However, there are still some challenges including the low CH_4 selectivity and low efficiency. Thermo-catalysis is one of the most common forms of catalysis, which is mainly attributed to its high efficiency and applicability for large scale processes. As thermal CO_2 methanation is mature enough to be commercialized, this paper focused on thermal catalytic CO_2 methanation [71].

Figure 1. CO_2 hydrogenation to produce CH_4 via different catalysis methods.

In light of the importance of the CO_2 methanation reaction, it has been widely investigated. This reaction was proposed by Sabatier and Senderens in 1902, which was also called the Sabatier reaction (Equation (1)) [72,73]. The reaction is exothermic, and can be carried out at low temperature to achieve high CO_2 conversion [74–77]. However, CO_2 is the upmost oxidized state of carbon and the activation of the C–O bond in CO_2 faces many challenges. The hydrogenation of CO_2 to methane is an eight-electron process with high kinetic barrier that requires a catalyst to achieve acceptable rates and selectivity [78–80]. More and more researchers are interested in designing a CO_2 methanation catalyst. As reported, the sintering of metal particles and carbon deposition would result in the deactivation of catalysts at high temperature. At the same time, the reverse water–gas shift reaction (RWGS) (Equation (2)) would also occur at high temperature, and produce CO as a by-product [46]. The presence of CO might induce the Boudouard reaction, resulting in the formation of coke. Furthermore, the Tammann temperature of nickel is about 590 °C, so the sintering would occur at high temperature. Therefore, sintering-resistant and coke-resistant characteristics would be facilitated at low temperature (below 300 °C), where the life of the catalysts could also be prolonged [77]. The active metals usually affect the catalytic

activity and selectivity of the catalysts. Many noble metals such as Rh [2,49], Ru [81–83], and Pd [84,85] have been widely applied in CO₂ methanation due to their excellent activity and CH₄ selectivity at low temperature. The catalytic performance of some noble metal catalysts on CO₂ methanation is summarized in Table 1. It can be seen that noble metal catalysts with low metal loading exhibited high catalytic activity, especially excellent CH₄ selectivity at low temperature. However, their large-scale industrial applications are limited due to the high costs.

Table 1. The catalytic performance of different noble metal catalysts for CO₂ methanation.

Catalysts	Metal Loading (%)	Synthesis Method	Reaction Conditions			CO ₂ Con. (%)	CH ₄ Yie. (%)	CH ₄ Sel. (%)	Ref.
			Temp. (°C)	H ₂ :CO ₂	GHSV/h ^{−1}				
Ru-CeO ₂ /Al ₂ O ₃	2	Impregnation	300	5:1	1000	60	nd	99	[86]
Ru/TiO ₂	2.5	Impregnation	350	4:1	6000	90	nd	~99	[87]
Ru/TiO ₂	0.8	“Dry” modification	180	4:1	nd	nd	nd	100	[88]
Ru/UIO-66	1	Impregnation	250	4:1	nd	60	nd	100	[89]
Ru/Al ₂ O ₃	4	Impregnation	375	5:1	10,000	85	nd	nd	[90]
RhY	6	Ion-exchange	150	3:1	6000	5.9	nd	99.8	[91]
Rh/MSN	5	Impregnation	350	4:1	5000	99	nd	100	[42]
Rh/ACZ	10	Impregnation	402	4:1	nd	~50	46.8	nd	[92]
Rh/CeO ₂	3	Impregnation	350	4:1	nd	~46	~41	~100	[93]
Pd/UIO-66	6	Sol-gel	340	4:1	15,000	56	nd	97.3	[85]
Pd/Al ₂ O ₃	5	Impregnation	280	4:1	45,000	nd	nd	40	[94]
PdO@LaCoO ₃	3	One-pot	300	3:1	18,000	62.3	nd	>99	[95]
PdO/LaCoO ₃	3	Impregnation	300	3:1	18,000	31.8	nd	87.4	[95]
Pd-Mg/SiO ₂	6.2	Microemulsion	450	4:1	7320	59.2	56.4	95.3	[96]

nd: no data.

In addition to noble metal catalysts, many non-noble metals such as Co and Ni have also been widely used in CO₂ methanation due to their low cost. Co-based catalysts exhibit excellent low temperature catalytic performance and could effectively avoid catalyst sintering deactivation. However, the CH₄ selectivity of the catalysts is generally low. Among the results reported thus far, only a few Co-based catalysts could achieve high CO₂ conversion and high CH₄ selectivity [61,97–99]. Therefore, many researchers have turned their attention to Ni-based catalysts with relatively high activity in this reaction because of their comparable price and abundance [75,79,100–102]. Some Ni-based catalysts also exhibit high catalytic activity and CH₄ selectivity. Zhou et al. [103] prepared Ni/CeO₂ catalyst by using the hard template method and the catalyst exhibited high CO₂ methanation activity with 91.1% CO₂ conversion and 100% CH₄ selectivity at 340 °C, atmospheric pressure. However, Ni-based catalysts still face several challenges in the application of CO₂ methanation at present. First, the activity of Ni-based catalysts at low temperature needs to be improved. Second, the sintering of nickel particles due to the exothermic methanation reaction and the formation of carbon deposition could all result in deactivation of the catalyst during the reaction process [104]. Third, the precise elucidation of the CO₂ methanation mechanism is still a challenging task.

Many papers have reviewed the progress of the CO₂ methanation reaction. Fan et al. [46] mainly reviewed various active metals and heterogeneous catalyst supports used for the thermal hydrogenation of CO₂ to methane. Lee et al. [105] mainly focused on the recent work around low temperature CO₂ methanation on a wide range of catalysts including

reaction thermodynamics and kinetics, catalyst materials including supports and promoters, and suitable reactor technologies. Ashok et al. [51] mainly reviewed the research progress of three kinds of CO₂ methanation reaction systems including thermo-catalytic systems, CO₂ methanation in a catalytic membrane reactor, and the CO₂ hydrogenation under plasma process in detail. Insightful guidance was provided in these review papers. The present work highlighted, in particular, CO₂ methanation on Ni-based catalysts and elaborated the CO₂ methanation mechanism, which was focused on discussing the research progress and present status of CO₂ methanation with an emphasis on designing catalysts with high activity and stability at low temperature. We summarized the recent development of Ni-based catalysts used in CO₂ methanation including the effects of nickel active sites, supports, promoters, and preparation methods on CO₂ methanation as well as the two kinds of reaction mechanisms. Several suggestions for the future development of Ni-based catalysts for CO₂ methanation at low temperature are also proposed.

2. CO₂ Methanation at Low Temperature

As reported, Ni-based catalysts have been widely studied in CO₂ methanation. Many key parameters including the essential nature of nickel active sites, supports, promoters, and preparation methods could influence the catalytic performance of Ni-based catalysts for CO₂ methanation [106].

We summarized the catalytic activity and selectivity of most of the previously reported Ni-based catalysts for CO₂ methanation with different reaction conditions, as listed in Tables 2 and 3. Many studies added the balance gas in the reaction mixture such as Ar, N₂, and He, which could improve heat and mass transfer during the reaction process, thus improving the CO₂ conversion. Tables 2 and 3 summarize the catalytic performance of different Ni-based catalysts for CO₂ methanation without the balance gas and with balance gas, respectively. Here, we also review the recent research progress of CO₂ methanation and discuss the effect of different factors through some detailed representative examples.

Table 2. The catalytic activity of different Ni-based catalysts for CO₂ methanation without balance gas.

Catalysts	Synthesis Method	Reaction Conditions			CO ₂ Con. (%)	CH ₄ Yie. (%)	CH ₄ Sel. (%)	Ref.
		Temp. (°C)	H ₂ :CO ₂	GHSV/h ^{−1}				
Ni/Pr ₂ O ₃ -CeO ₂	Impregnation	350	4:1	25,000	54.5	54.5	100	[107]
Ni-CeO ₂ /γ-Al ₂ O ₃	Impregnation	300	4:1	36,000	79	nd	100	[26]
Ni/NaY	Impregnation	500	4:1	nd	67	nd	94	[108]
Ca-NiTiO ₃ /γ-Al ₂ O ₃	Precipitation	350	4:1	2000	84.73	78.84	99.95	[109]
Ni/CaZrO ₂	Impregnation	350	4:1	24,000	~75	nd	99	[110]
Ni-5Mg/SBA-15	Ammonia evaporation (AE)	400	4:1	30,000	75	nd	100	[111]
Ni/γ-Al ₂ O ₃	Impregnation	500	4:1	6000	77.2	nd	99.9	[112]
Ni/F-SBA-15	Impregnation	450	4:1	24,900	99.7	98.2	nd	[113]
Ni/CeO ₂	Sol-gel	250	4:1	10,000	80.5	nd	95.8	[114]
Ni-Nb ₂ O ₅	Impregnation	350	4:1	20,600	92	nd	99	[115]
Ni/Al ₂ O ₃ -SiO ₂	Sol-gel	350	3.5:1	12,000	82.38	nd	98.19	[116]
Ni/bentonite	Solution combustion	300	4:1	3600	85	nd	100	[117]
Ni-Mn/Bn	Impregnation	270	4:1	3600	85.2	nd	99.8	[118]
Ni/Al ₂ O ₃ -ZrO ₂	Sol-gel	300	4:1	6000	77	nd	~100	[119]
Ru-Ni/Ce _{0.9} Zr _{0.1} O ₂	One-pot hydrolysis	300	4:1	2400	98.2	nd	100	[120]
Ni-CeO ₂ /MCM-41	Deposition precipitation	380	4:1	9000	85.6	nd	99.8	[121]
Y ₂ O ₃ -Ni/MgO-MCM-41	Direct synthesis	400	4:1	9000	65.55	nd	84.44	[122]
Ni-Ce/CNT	Ultrasonic-assisted co-impregnation	350	4:1	30,000	83.8	nd	~100	[123]
Ni/MSN	Impregnation	350	4:1	50,000	85.4	nd	99.9	[42]

nd: no data.

Table 3. The catalytic activity of different Ni-based catalysts for CO₂ methanation with balance gas.

Catalysts	Synthesis Method	Reaction Conditions			CO ₂ Con. (%)	CH ₄ Yie. (%)	CH ₄ Sel. (%)	Ref.
		Temp. (°C)	H ₂ :CO ₂ :Ar (N ₂ , He)	GHSV/h ^{−1}				
Ni/Y ₂ O ₃	Impregnation	300	4:1:5	20,000	77	80	99.5	[124]
CA-Ni/Y ₂ O ₃	Impregnation	350	4:1:5	6000	92	~90	100	[125]
Ca/Ni/Al ₂ O ₃	Impregnation	275	4:1:5	160,000	93	nd	99	[126]
Ni/mpCeO ₂	Precipitation	350	16:4:5	60,000	81	nd	99	[127]
Ni-RuAl	Glycerol Assisted Impregnation (GAI)	400	16:4:5	30,000	60	nd	99.5	[128]
NiCeY	Precipitation	450	12:3:5	30,000	nd	80	95	[129]
NiLaAl-HT	Precipitation	450	4:1:1	480,000	88	nd	98	[130]
Ni/zeolite X	Fusion method	450	12:3:5	12,000	53	nd	>90	[131]
Ni/La ₂ O ₃ CO ₃	Impregnation	450	12:3:5	20,000	91	nd	99.9	[132]
Ni/CeO ₂	Gas discharge plasma	275	16:4:5	56,000	84.2	nd	99.5	[133]
Ni/ZrO ₂	Impregnation	400	4:1:5	43,500	50	nd	100	[76]
Ni-La/Mg-Al	Urea hydrolysis	200	36:9:5	45,000	61	nd	~100	[134]
Ni/ZrO ₂	Plasma decomposition	350	16:4:5	60,000	79.1	76.5	100	[135]
Ni-La ₂ O ₃ /Na-BETA	Impregnation	350	4:1:1.25	10,000	65	nd	99	[136]
Ni-Pd/γ-Al ₂ O ₃	Impregnation	300	4:1:8.5	5700	90.5	nd	98.7	[137]
NiCo/Al ₂ O ₃	Evaporation-induced self-assembly	400	12:3:5	10,000	78	nd	99	[80]
Ni/CeO ₂ -ZrO ₂	Ammonia evaporation	275	8:2:15	20,000	55	nd	99.8	[138]
Ni/USY	Impregnation	450	4:1:15	nd	72.6	nd	95	[139]
Ni/CaO-Al ₂ O ₃	nd	400	12:3:10	15,000	81	80	nd	[140]
Ni/La ₂ O ₃	Impregnation	320	4:1:1	3250	97.1	nd	100	[141]

nd: no data.

2.1. The Nature of Active Sites on CO₂ Methanation

The catalytic performance of Ni-based catalysts can be influenced by characteristics of Ni active sites including the content of Ni [142,143], the size of Ni [125,144–147], the structure and chemical state of Ni [127,148–151], the different nickel precursor salts [152], and the location of Ni active sites [153].

Vita et al. [142] designed Ni/GDC (gadolinium-doped-ceria) catalysts containing different contents (15–50 wt%) of Ni. They found that the catalytic activity increased with an increase in Ni content because of the enhanced Ni–support interaction, basicity, and oxygen vacancies. However, some Ni-based catalysts with low metal loading also exhibited excellent catalytic performance, which are summarized in Table 4. For example, the CO₂ conversion of the 2 wt %Ni/CeZrO₄ catalyst was 63%, and the CH₄ selectivity could reach 100% at 350 °C [154]. Both the catalytic activity and CH₄ selectivity were proposed to also be related to the size of the Ni particles, and Ni-based catalysts can be prepared by controlling the nickel size to achieve higher catalytic performance [144,145,155,156]. Many researchers have devoted themselves to exploring the role of nickel size in CO₂ methanation when designing catalysts with high activity. Citric acid was added during the preparation of the Ni/Y₂O₃ catalyst, which could affect the nickel particle size and the Ni–support interaction [125]. Ni/CeO₂ with different sized Ni particles (2, 4 and 8 nm) were prepared to explore the size effect on CO₂ methanation performance, and Ni/CeO₂ with 8 nm nickel particles exhibited the highest catalytic activity. According to DRIFTS study, the larger Ni over CeO₂ efficiently promoted the hydrogenation of the formate intermediates, which accounted for the excellent CO₂ methanation performance [146]. Hao et al. [147] also explored Ni particle size in CO₂ methanation over Ni/CeO₂ catalyst. Through TGA measurements, the small Ni nanoparticles suffered a temporary loss of activity due to the carbon deposition.

Table 4. The catalytic performance of some Ni-based catalysts with low nickel loading.

Catalysts	Ni Loading (%)	Reaction Temp. (°C)	CO ₂ Con. (%)	CH ₄ Yie. (%)	CH ₄ Sel. (%)	Ref.
Ni/CeZrO ₄	2	350	63	nd	100	[154]
Ni/CaZrO ₂	5	350	~75	nd	99	[110]
Ni/NaY	5	500	67	nd	94	[108]
Ni/Ce _{0.85} Zr _{0.15} O ₂	5	500	70	nd	~100	[157]
Ni/MSN	5	350	85.4	nd	99.9	[42]
Ni/F-SBA-15	5	450	99.7	98.2	nd	[113]
Ni/TiO ₂	6.17	350	73.2	nd	nd	[158]
Ni/MgO- MgH ₂	7.9	300	85.2	nd	99.5	[44]
Ni/CeO ₂	10	275	84.2	nd	99.5	[133]
Ni/SiO ₂	10	310	77.2	nd	~100	[101]
Ni/Y ₂ O ₃	10	300	77	80	99.5	[124]
12CA-Ni/Y ₂ O ₃	10	350	92	~90	100	[125]
Ni/CeO ₂	10	300	84	nd	100	[159]
Ni/mpCeO ₂	10	350	81	nd	99	[127]
Ni-10La ₂ O ₃ /Na-BETA	10	350	65	nd	99	[136]
Ni-Pd/ γ -Al ₂ O ₃	10	300	90.5	nd	98.7	[137]
Ni ₃ Co/Al ₂ O ₃	10	400	78	nd	99	[80]
Ni/CeO ₂ -ZrO ₂	10	275	55	nd	99.8	[138]
Ni/CeO ₂	10	340	91.1	nd	100	[103]
Ni-5Mg/SBA-15	10	400	75	nd	100	[111]
Ni/La ₂ O ₃	10	320	97.1	nd	100	[141]

nd: no data.

Ni-based catalysts with special structure and chemical state also affect the performance of the catalyst [148]. Sponge Ni exhibited excellent CO₂ methanation performance, and the CO₂ conversion could achieve 83% under a high space velocity (0.11 mol_{CO2} g_{cat}^{−1} h^{−1}) at 250 °C [149]. Hongmanorom et al. [127] designed Ni nanoparticles encapsulated in mpCeO₂ using strong electrostatic adsorption with 0.183 s^{−1} TOF, but the TOF of the conventional Ni/CeO₂ catalyst was only 0.057 s^{−1}. The higher activity resulted from more oxygen vacancies provided by the encapsulated structure on the Ni–CeO₂ surface. The Ni@HZSM-5 catalyst was synthesized by the hydrothermal method with a special embedment structure that showed high activity and stability in CO₂ methanation, and Ni@HZSM-5 could retain a structure and content of nickel similar to that of the fresh catalyst due to its special structure, while the conventional Ni/SiO₂ and Ni/HZSM-5 catalysts changed after a long period of reaction [150]. Hu et al. [151] discovered three distinct nickel active phases on Ni/Al₂O₃ obtained by reduction at different temperatures, that is, the catalysts reduced at different temperatures (535, 573, and 673 K, respectively) exhibited different CO₂ conversion and CH₄ yield.

Ni-based catalysts prepared by different nickel salt precursors exhibited different catalytic performance. The Ni-AA catalyst (nickel acetylacetonate precursor) with special coordinating anion showed the best catalytic performance, but the Ni-S catalyst (nickel sulfate precursor) deactivated rapidly due to the presence of Ni₃S₂ after the reduction pre-treatment [152]. In addition, Yan et al. [153] found that the promising catalytic performance was also associated with the location of the nickel. They controlled the location of the nickel by employing the terminal groups of siloxane and varying the solvent used. When nickel was on the interior of adjacent siloxane nanosheets, the activity of Ni@Siloxane was higher, with above 90% CH₄ selectivity. When the location of the nickel was different, there were two disparate reaction pathways accordingly.

2.2. The Support on CO₂ Methanation

The nature of supports plays a critical role in the catalytic process by influencing the morphology, dispersion, stability, and reducibility of the active sites [160,161]. The nickel-support interaction can potentially modify the electronic state of active sites and

suppress nickel sintering, which is important in promoting CO₂ methanation at low temperature [82,111,162]. Therefore, synthesis of highly efficient supported Ni catalysts is one of the major directions of CO₂ methanation. According to the reported study, we divided the supports of Ni-based catalysts into single supports, composite oxide supports (MOF, zeolite, and activated biochar), as shown in Figure 2.

Figure 2. The different supports of Ni-based catalysts.

2.2.1. Ni-Based Catalysts Supported on Single Oxide Supports

Various oxides such as Al₂O₃ [143,163–165], TiO₂ [158,166], ZrO₂ [110,167], CeO₂ [145,168], and SiO₂ [25,101] have been explored for Ni-based CO₂ methanation catalysts. Muroyama and co-workers [124] compared the catalytic activity of different metal oxide supported Ni catalysts and found that Ni/Y₂O₃ exhibited the highest catalytic activity with 80% CH₄ yield at 300 °C. Italiano et al. [162] also found that Ni/Y₂O₃ exhibited the highest activity and no deactivation was observed after 200 h of testing, resulting from its good anti-coking and anti-sintering ability among Ni/CeO₂, Ni/Al₂O₃, and Ni/Y₂O₃ catalysts. As reported, the oxygen vacancies on the support played a significant role in the adsorption/activation of CO₂ species. CeO₂ supported Ni-based catalysts have been widely used in CO₂ methanation due to the high concentration of oxygen vacancies on the surface [103]. Le et al. [169] reported that Ni/CeO₂ was the most active for CO₂ methanation due to the smallest Ni particle size among Ni-based catalysts on different supports. The Ni/ZrO₂ catalyst is also one of the most active systems for CO₂ methanation, and ZrO₂ is very relevant for the generation of active sites of the methanation reaction, and the high concentration of oxygen vacancies on ZrO₂ also play an essential role in CO₂ methanation [110,170,171]. Therefore, ZrO₂ has also received extensive attention in CO₂ methanation because of its high mechanical and thermal stability [172]. Martínez et al. [76] reported the outstanding catalytic performance of Ni/ZrO₂, where the conversion of CO₂ was close to 60% and CH₄ selectivity was 100% at 500 °C, with high stability after a 250 h reaction.

2.2.2. Ni-Based Catalysts Supported on Composite Oxide Supports

Composite supports could modify Ni-support interaction more easily and exhibited better properties compared with single oxide support. Zhu et al. [129] prepared a Y₂O₃-promoted NiO–CeO₂ catalyst and compared the catalytic activity of NiO–CeO₂ and NiO–CeO₂–Y₂O₃ catalysts. They found that the introduction of Y₂O₃ to CeO₂ greatly facilitated the generation of surface oxygen vacancies during the reaction, which promoted the dissociation of CO₂ and thus improved the catalytic activity. Siakavelas et al. [107] also reported binary CeO₂-based oxides Sm₂O₃–CeO₂, Pr₂O₃–CeO₂, and MgO–CeO₂ supported Ni catalysts used in CO₂ methanation. The addition of Sm³⁺ and Pr³⁺ increased the amount of oxygen vacancies of the catalysts, which improved CO₂ methanation activity. The strong nickel-support interaction on the Ni/MgO–CeO₂ increased the anti-sintering ability of the

catalyst. The oxygen vacancies and coordinatively unsaturated sites formed cation pairs on the Ca doped Ni/ZrO₂. The number of these pairs on Ni/CaZrO₂ was higher than the Ni/ZrO₂ catalyst, which increased the CO₂ methanation rate [110].

Although Al₂O₃ supported Ni-based catalysts exhibited relatively high catalytic activity because of their high surface area and excellent hydrothermal stability, it needed further improvement [112]. Much research has been conducted on the modification of the Al₂O₃ support by the employment of rare-earth oxides [74]. Furthermore, La³⁺ doping could also enhance the surface basicity of the catalysts [173]. A variable amount of La-doped Ni/ γ -Al₂O₃ catalysts [164] was used in CO₂ methanation, and the activity and selectivity of Ni/La- γ -Al₂O₃ increased compared with Ni/ γ -Al₂O₃. The basicity of the support increased because of the addition of La, which enhanced the adsorption of CO₂. ZrO₂, as a promoter, is also widely used in CO₂ methanation catalysts because of its excellent hydrothermal stability and high oxygen defects. Lin et al. [119] designed a Ni/Al₂O₃-ZrO₂ catalyst with CH₄ selectivity of about 100%, CO₂ conversion of 77% at a lower temperature of 300 °C. The formed Al₂O₃-ZrO₂ solid solution could promote the reduction and dispersion of NiO, and increase the number of nickel active sites and oxygen vacancies because of the higher Zr loading, which results in significant improvement of the catalytic activity at low temperature.

2.2.3. Ni-Based Catalysts Supported on Other Supports

In addition to various oxide carriers, there are many other materials such as zeolite [108,113,131,174], MOF [101,175], and activated biochar [176] supported Ni catalysts, which have also been used in CO₂ methanation. Sholeha and co-workers [108] synthesized zeolite NaY from dealuminated metakaolin and used as a support of the Ni catalyst. The prepared Ni/NaY exhibited significant CO₂ conversion (67%) and CH₄ selectivity (94%) in CO₂ methanation, which could be attributed to the combination of well-defined crystalline structures and the large surface area of NaY. The Ni catalyst with porous zirconia obtained from a Zr-based metal-organic framework with UiO-66 as the support exhibited a turnover frequency of 345 h⁻¹ space-time yield of 5851 mmol·g_{Ni}⁻¹·h⁻¹ with CH₄ selectivity of over 99%, showing only a 4% decrease in activity after testing for 100 h on stream [175]. Ni/zeolite X [131] derived from fly ash was also applied in CO₂ methanation, where around 50% CO₂ conversion could be obtained at 450 °C. Wang et al. prepared a Ni/Ce-ABC (where ABC refers to activated bio-char) catalyst using biomass as the raw material, and the bio-char was modified by highly dispersed CeO₂ [176]. This catalyst showed fantastic catalytic performance in CO₂ methanation, achieving 88.6% CO₂ conversion and 92.3% CH₄ selectivity at 360 °C.

2.3. Promoter Effect on CO₂ Methanation

To obtain satisfactory catalytic performance, doping a second metal into Ni-based catalysts as promoters is also a good idea. The second metal and nickel might form an alloy structure, which tends to modify the geometric and electronic structure of Ni-based catalysts. Based on the literature, these promoters contain alkaline earth oxides [109,126,174,177,178], noble metals [120,137], rare-earth metals [121,130,134,136,163,179–183], and some other typical transition metals and non-metallic elements [3,13,75,80,118,157,166,184–186], as displayed in Figure 3. These promoters could affect the dispersion of nickel active sites, the acid–base properties of the support, the nickel–support interaction, and thus to the catalytic activity and stability of the catalyst.

Figure 3. The promoters used for Ni-based catalysts in CO₂ methanation.

2.3.1. Alkaline Earth Oxides Promoted Ni-Based Catalysts

Various studies have been conducted where alkaline-earth oxides have been widely used in CO₂ methanation catalysts as promoters. As alkaline-earth oxides are cheap, abundant, and can improve the basicity of the catalysts, they can promote the adsorption, activation, and reduction of CO₂ [61,74,130,177]. Ca-doped Ni-based catalysts have shown great potential in CO₂ methanation. The influence of alkaline-earth oxides (Ca, Mg, Sr, and Ba) as promoters on Ni/ γ -Al₂O₃ has also been investigated [126], where Ni and promoters were found to be uniformly dispersed into the pore structure of the support, and the Ca-promoted Ni/Al₂O₃ catalyst exhibited the highest catalytic activity, which could be attributed to the enhanced CO₂ adsorption and the reducibility of Ni active sites. Do et al. [109] applied Ca-inserted NiTiO₃ in CO₂ methanation and found that the addition of Ca generated oxygen vacancies on the catalyst, and 84.73% CO₂ conversion and 99.95% CH₄ selectivity were observed. Xu and co-workers [178] reported that the Ca promoter increased the surface basicity of Ni–Al composite oxide catalysts, which enhanced the adsorption and activation of CO₂. Bacariza et al. [174] prepared a Mg-promoted Ni/USY zeolite catalyst using different incorporation methods. They found that lower contents of Mg could enhance the catalytic performance because of the increase in nickel dispersion, while a higher amount of Mg would decrease CO₂ conversion due to the formation of a NiO–MgO solid solution, and the dispersion and stability of nickel on the Ni/USY zeolite catalyst obtained by ion exchange were higher than that of the impregnated catalysts.

2.3.2. Noble Metals Promoted Ni-Based Catalysts

Bimetallic methanation catalysts were prepared by adding small amounts of noble metals into Ni-based catalysts, which showed a significantly enhanced catalytic performance at low temperature. Shang et al. [120] prepared different Ru content doped 30 wt% Ni/Ce_xZr_{1-x}O₂ catalysts and explored the effects of Ru content on catalytic performance as well as the Ce/Zr molar ratios. 3Ru-30Ni/Ce_{0.9}Zr_{0.1}O₂ exhibited the best catalytic performance with 98.2% CO₂ conversion and 100% CH₄ selectivity at a low reaction temperature (230 °C). The addition of Ru can improve the Ni dispersion and the basicity of the surface of the catalysts. Noble metals as promoters could enhance the reducibility, the dispersion of nickel, and H₂ chemisorption capacity, thus improving the catalytic performance. Mihet et al. [137] also explored the effect of Pt, Pd, or Rh on the Ni/ γ -Al₂O₃ catalyst, and found that Ni-Pd/ γ -Al₂O₃ exhibited the highest activity with 74.6% CO₂ conversion and 96.6% CH₄ selectivity at 250 °C.

2.3.3. Rare-Earth Metal Promoted Ni-Based Catalysts

Rare-earth elements, mainly, La, Ce, and Y, have been used as promoters to increase the catalytic activity at low temperature because they can enhance the basicity of catalysts, Ni reducibility, and smaller Ni particles. Wang et al. [179] explored different rare-earth metals

including La, Y, Ce and Ge promoted Ni/ γ -Al₂O₃ catalyst. They found that the Y promoted Ni/ γ -Al₂O₃ catalyst exhibited the highest catalytic activity, followed by the promoters of Ce, Gd, and La, which could be attributed to the differences in atomic radius, electron layer structure, and oxide basicity of each promoter. Mikhail et al. [173] also found that 4 wt% Gd promoted Ni/CeZrO_x exhibited the highest activity with 85% CO₂ conversion and 100% CH₄ selectivity due to its high metal dispersion and the high percentage of medium basic sites. Many studies have reported that the addition of La could enhance the surface basicity and the adsorption of CO₂, resulting in a significant increase in CO₂ conversion and CH₄ selectivity [136,182]. The effect of La on the catalytic activity was investigated and compared with that of Y and Ce [130]. The highest space velocity (480 L g⁻¹ h⁻¹) and CH₄ productivity (101 L_{CH4} g_{Ni}⁻¹ h⁻¹) were obtained on the La-promoted catalyst, which was related to more reduced, highly dispersed Ni nanoparticles and basic sites in the La₂O₃-Al₂O₃ matrix. Zhang et al. [134] also explored La as a promoter on CO₂ methanation. The NiLa₅/Mg-Al catalyst showed the best catalytic performance, obtaining 61% CO₂ conversion and nearly 100% CH₄ selectivity with a WHSV of 45,000 mL g⁻¹ h⁻¹ at 250 °C, 0.1 MPa. Characterization results showed that La effectively increased Ni dispersion and decreased Ni particle size. In addition, La could significantly increase the amount of moderate basic sites, which could contribute to enhanced CO₂ adsorption capacity.

Ce as a promoter could increase the basicity of the catalyst, thus improving the adsorption and activation of CO₂. In addition, the rapid reduction of Ce⁴⁺ to Ce³⁺ could form oxygen vacancies, which is of great importance for the catalytic activity [163]. Li et al. [180] prepared a Ce-promoted Ni-La₂O₃/ZrO₂ catalyst with high Ni dispersion and excellent resistance to sintering, leading to high activity and stability. Daroughegi et al. [163] found that the Ce promoted Ni-Al₂O₃ catalyst exhibited the highest activity and stability with 76.4% CO₂ conversion and 99.1% CH₄ selectivity at 350 °C. Alarcón et al. [26] also reported a Ce promoted Ni-Al₂O₃ catalyst with high loading CeO₂ (25 wt%), which was highly stable for 120 h.

2.3.4. Other Transition Metals and Non-Metallic Elements Promoted Ni-Based Catalysts

In addition, other typical transition metals such as Fe [3,13,184], Co [80,185], Mn [3,118,166], and non-metallic elements such as Si [75] promoted Ni-based catalysts can also be used in CO₂ methanation.

Serrer et al. [184] reported that the Ni-Fe catalyst exhibited high activity and long-term stability. They found a synergistic effect between nickel and iron on a bimetallic Ni-Fe catalyst that led to higher fractions of reduced nickel compared to a monometallic Ni-based catalyst. The Fe⁰ ⇌ Fe²⁺ ⇌ Fe³⁺ redox mechanism could be observed at the interface of these FeO_x clusters, which could promote CO₂ dissociation. Mn was introduced into Ni/bentonite, and the conversion of CO₂ on 2 wt% Mn-Ni/bentonite was 85.2% with 99.8% CH₄ selectivity at 270 °C. On the other hand, CO₂ conversion on Ni/bentonite needed 300 °C to obtain 84.7% CO₂ conversion. The addition of Mn enhanced the nickel-support interaction and the dispersion of nickel, and increased the amount of oxygen vacancies on the catalyst surface, which promoted the CO₂ methanation reaction [118]. Li et al. [75] prepared a series of Ni-xSi/ZrO₂ catalysts and found that the appropriate amount of Si promoter increased the dispersion of nickel, Ni-support interaction, and the number of active sites. The Ni-0.1Si/ZrO₂ catalyst exhibited the highest catalytic activity with 72.5% CO₂ conversion and 72.2% CH₄ yield at 250 °C.

2.4. The Effect of Preparation Methods on CO₂ Methanation

Diverse methods are applied in the preparation of Ni-based catalysts including the impregnation method (IM), precipitation method (PM), sol-gel method (SGM) as well as other methods. Table 5 summarizes the synthesis methods of different Ni-based catalysts. From Table 5, it can be observed that most catalysts were synthesized by the traditional impregnation method and precipitation method. In addition, a small number of catalysts were prepared by other methods including sol-gel, solution combustion, ammonia evaporation

(AE), and the mechanochemical ball-milling method. Furthermore, catalysts prepared by different methods also exhibited different structures and properties as well as catalytic activity [128,187].

Table 5. The catalytic performance of Ni-based catalysts by different preparation methods.

Catalysts	Synthesis Method	Reaction Temp. (°C)	CO ₂ Con. (%)	CH ₄ Sel. (%)	Ref.
Ni-La ₂ O ₃ /Na-BETA	Impregnation	350	65	99	[136]
Ni/Pr ₂ O ₃ -CeO ₂	Impregnation	350	54.5	100	[107]
Ni/Y ₂ O ₃	Impregnation	300	77	99.5	[124]
Ni/CeO ₂	Impregnation	300	84	100	[159]
Ni/MSN	Impregnation	350	85.4	99.9	[42]
Ni-CeO ₂ /Al ₂ O ₃	Impregnation	350	85	nd	[188]
Ni-La/SiC	Impregnation	250	39.6	99.6	[189]
NiO-CeO ₂ /SBA-15	Impregnation	300	76	93	[168]
Ni/ZrO ₂	Impregnation	400	50	100	[76]
Ni/CeZrO ₄	Impregnation	350	63	100	[154]
Ni-Mn/Bn	Impregnation	270	85.2	99.8	[118]
Ni/TiO ₂	Impregnation	350	73.2	nd	[158]
Ni-Pd/ γ -Al ₂ O ₃	Impregnation	300	90.5	98.7	[137]
NiCeUSY	Impregnation	400	68.3	95.1	[190]
Ni/La ₂ O ₃	Impregnation	320	97.1	100	[141]
Ni-CeO ₂ / γ -Al ₂ O ₃	Impregnation	300	79	100	[26]
Ni/NaY	Impregnation	500	67	94	[108]
Ni/CaZrO ₂	Impregnation	350	~75	99	[110]
Ni/ γ -Al ₂ O ₃	Impregnation	500	77.2	99.9	[112]
Ni/F-SBA-15	Impregnation	450	99.7	nd	[113]
Ni/Ce-ABC	Impregnation	360	88.6	92.3	[176]
Ni-La ₂ O ₃ / γ -Al ₂ O ₃	Impregnation	300	97	>99	[165]
Ni/USY	Impregnation	450	72.6	95	[139]
NiCe/CNT	Ultrasonic-assisted co-impregnation	350	83.8	~100	[123]
Ni-RuAl	Glycerol Assisted Impregnation (GAI)	400	60	99.5	[128]
Ni/mpCeO ₂	Precipitation	350	81	99	[127]
NiCeY	Precipitation	450	nd	95	[129]
NiLaAl-HT	Precipitation	450	88	98	[130]
Ca-NiTiO ₃ / γ -Al ₂ O ₃	Precipitation	350	84.73	99.95	[109]
Ni-Ce-Al ₂ O ₃	Precipitation	350	73.2	99.1	[163]
Ni/Ce _{0.85} Zr _{0.15} O ₂	Precipitation	500	70	~100	[157]
Ni-CeO ₂ /MCM-41	Deposition precipitation	380	85.6	99.8	[121]
Ni/CeO ₂	Sol-gel	250	80.5	95.8	[114]
Ni/Al ₂ O ₃ -SiO ₂	Sol-gel	350	82.38	98.19	[116]
Ni/SiO ₂	Sol-gel	310	77.2	~100	[101]
Ru-Ni/Ce _{0.9} Zr _{0.1} O ₂	One-pot hydrolysis	300	98.2	100	[120]
Ni-La/Mg-Al	Urea hydrolysis	200	61	~100	[134]
Ni/bentonite	Solution combustion	300	85	100	[117]
Ni-Mg/SBA-15	Ammonia evaporation (AE)	400	75	100	[111]
Ni/CeO ₂ -ZrO ₂	Ammonia evaporation (AE)	275	55	99.8	[138]
Y ₂ O ₃ -Ni/MgO-MCM-41	Direct synthesis	400	65.55	84.44	[122]
Ni/zeolite X	Fusion method	450	53	>90	[131]
RhNi/Al ₂ O ₃	Galvanic replacement (GR)	250	97	>90	[191]
Ni/CeO ₂	Gas discharge plasma	275	84.2	99.5	[133]
Ni/MgO-MgH ₂	Mechanochemical ball-milling method	300	85.2	99.5	[44]
Ni/ZrO ₂	Plasma decomposition	350	79.1	100	[135]
NiCo/Al ₂ O ₃	Evaporation-induced self-assembly	400	78	99	[80]
NiRu/CaO-Al ₂ O ₃	Facile evaporation-induced self-assembly method	380	83.8	100	[192]
Ni/CeO ₂	Hard template method	340	91.1	100	[103]
Ni/ZrO ₂	Combustion method	300	60	~97.5	[193]

nd: no data.

Zhang et al. [134] found that the urea hydrolysis method was a more efficient approach compared to the coprecipitation method in the preparation of Ni-based catalysts and obtained a Ni-based catalyst with higher Ni dispersion, larger CO₂ adsorption capacity, and therefore better catalytic performance. The Ni/CeO₂ catalyst prepared via decomposition of the nickel precursor by gas discharge plasma exhibited above 99% CH₄ selectivity at reaction temperatures lower than 300 °C, and more active sites were exposed to the CeO₂ surface, which promoted the splitting of H₂ and the activation of CO₂, thus significantly improving the catalytic activity at low temperature [133]. Bukhari et al. [194] prepared Ni/SBA-15 catalysts using three kinds of hydrothermal treatment techniques (Reflux (R) and Teflon (T)) and without the hydrothermal technique (W), and applied them to CO₂ methanation. The catalytic activity sequence was as follows Ni/SBA-15(R) > Ni/SBA-15(T) > Ni/SBA-15(W). Characterization results showed that Ni/SBA-15(R) possessed excellent catalytic properties due to its high surface area and pore diameter, finest metal particles, strongest metal–support interaction, and highest concentration of basic sites. In addition, Gnanakumar et al. [115] studied the influence of pretreatment method on the catalytic performance of Ni/Nb₂O₅ by calcining the Nb₂O₅ support at different temperatures. Ni/Nb₂O₅ calcined at 700 °C provided higher methanation activity and CH₄ selectivity with good stability in a stream study for 50 h.

3. The Reaction Mechanism of CO₂ Methanation

It is crucially important to understand the key intermediates and reaction mechanisms in depth when designing catalysts with excellent catalytic performance [81]. Many researchers have made efforts to elucidate the possible CO₂ methanation mechanism by in situ FTIR, mass spectrometry (transient-MS) techniques, and DFT calculations. Although there are many arguments on the intermediates and different reaction pathways of CH₄ formation, two widely accepted pathways have been proposed: (1) the formate pathway where formate species are the main intermediate products formed during CO₂ methanation reaction, also called the CO₂ associative methanation: the chemisorbed *CO₂ species can first be converted to bidentate formates (HCOO*) and then to formic acid (HCOOH), then to CH₄, and (2) the CO pathway, also called the CO₂ dissociative methanation: the chemisorbed *CO₂ species can dissociate into *CO and *O. The formed *CO species can further dissociate into carbon species (*C), which can then be hydrogenated to CH₄ by dissociated H₂ still on the metal particles, desorbing from the catalyst surface, whereas the *O species can react with hydrogen to produce H₂O [28,51,128,153,195–197].

The possible reaction pathways are illustrated in Figure 4. CO₂ methanation on different catalysts occur via two different pathways, which are affected by the nature of nickel active sites and the supports [28].

Figure 4. Two different CO₂ methanation reaction routes: formate route and CO route.

3.1. The Formate Pathway

Many studies have reported that CO₂ methanation follows the formate route on different nickel catalysts such as Ni/MgO [198], Ni-Mn/Al@Al₂O₃ [199], Ni/Y₂O₃ [200], Ni/ZrO₂ [196,201], Ni/ultra-stable Y (USY) zeolite [139], and Ni@C [102]. For example, Xu

and coworkers [196] discussed the formation and evolution of CO₂ adsorbed species on Ni/c-ZrO₂ by in situ FTIR and DFT calculations. CO₂ methanation on Ni/c-ZrO₂ was dominated by the formate pathway as follows: CO₂* → HCOO* → H₂COO* → H₂COOH* → H₂CO* → CH₂* → CH₄*, which is the same as that shown in Figure 4. CO was a by-product instead of a reaction intermediate, which could not further form CH₄, and the DFT calculations also confirmed the formate pathway, which was highly consistent with the in situ FTIR results. Solis-Garcia et al. [201] also found that CO₂ methanation follows the formate pathway over Ni/ZrO₂ and no CO species were observed during the reaction. The possible reaction pathway of the CO₂ methanation over Ni@C was also investigated by CO₂-TPD measurements and in situ FTIR characterization. All results demonstrated that CO₂ methanation over Ni@C catalyst proceeded via the formate route without involving CO as an intermediate [102]. Aldana et al. [41] also found that the main CO₂ methanation mechanism on Ni-CZ_{sol-gel} was the formate pathway, which does not require CO as reaction intermediate. They also found that H₂ was dissociated on Ni⁰ sites while CO₂ was activated on the ceria–zirconia support to form carbonates and then further into CH₄, suggesting that a stable metal–support interface is beneficial for the adsorption of CO₂.

In another study, Pan et al. [202] found that the reaction pathway on Ni/γ-Al₂O₃ and Ni/Ce_{0.5}Zr_{0.5}O₂ all followed the formate pathway, only differing in reactive basic sites. On the Ni/Ce_{0.5}Zr_{0.5}O₂ catalyst, CO₂ adsorption on medium basic sites formed bidentate formate, whereas CO₂ adsorption on surface oxygen resulted in the monodentate formate. Due to the faster hydrogenation of monodentate formate, it was assumed to be the main reaction route on the Ni/Ce_{0.5}Zr_{0.5}O₂ catalyst. For CO₂ methanation on Ni/γ-Al₂O₃, hydrogenation of bidentate formate was the main reaction route as bidentate formate was the main adsorption and intermediate species and CO₂ adsorbed on strong basic sites of Ni/γ-Al₂O₃ will not participate in the CO₂ methanation reaction. It was assumed that medium basic sites are responsible for promoting the formation of monodentate formate species, thus enhancing CO₂ methanation activity. CO₂ methanation reaction pathways on Ni/Ce_{0.5}Zr_{0.5}O₂ and Ni/γ-Al₂O₃ are shown in Figure 5.

Figure 5. CO₂ methanation reaction route on (A) Ni/Ce_{0.5}Zr_{0.5}O₂ and (B) Ni/γ-Al₂O₃.

3.2. The CO Pathway

The CO pathway involves the dissociation of CO₂ to CO prior to methanation, and in the subsequent reaction, CO is converted to CH₄ by reacting with H₂ [203]. Karelovic et al. showed the direct dissociation of CO₂. The reactions below summarize the reduction process (Equations (3) and (4)). The excess amount of CO generated in the first reaction deposits on the catalyst, which produces coking effects. To avoid this problem, the methanation of CO must proceed much faster than the CO production, and the CO₂ methanation reaction must take place at low temperatures. Therefore, the direct dissociation of CO₂ to CO_{ads} and O_{ads} often occur over a variety of noble metal-based catalysts at low temperature [49,204,205]. In addition, the formation of nickel carbonyls Ni(CO)₄ would cause the deactivation of Ni-based catalysts [162].

Therefore, CO_2 methanation occurred via the CO pathway only over some Ni-based catalysts including Ni/CeO₂ [103], Ni/F-SBA-15 [113], and Ni-sepiolite [206]. The CO pathway over Ni/CeO₂ could be proven by in situ FTIR. The FTIR adsorption bands at 2017 cm^{−1} were assigned to the CO adsorption state, and the bands at 2120 and 2170 cm^{−1} were ascribed to gas phase CO, which indicated that CO_2 molecules can be converted to CO molecules on the surface of the Ni/CeO₂ catalyst. Characterization results indicated that CO species generated from the reduction of CO_2 molecules by nickel active sites and surface oxygen vacancies promoted CO_2 methanation [103]. Bukhari et al. found that Ni metals on Ni/F-SBA-15 (Fibrous type SBA-15) contributed to the CO_2 dissociation into CO and O species as well as the dissociation of H_2 into atomic hydrogen species. The linear carbonyl group came from the dissociation of CO_2 , which was an intermediate during CO_2 methanation and could be seen at 2055 cm^{−1}. Then, the adsorbed CO species interacted with surface oxygen, producing bidentate and unidentate carbonate groups, thus CH_4 [113]. Cerdá-Moreno et al. [206] also found linearly and bridged bonded CO as intermediates during CO_2 methanation over a Ni-sepiolite catalyst.

3.3. The Key Factors of CO_2 Methanation Reaction Route

There are also many factors influencing the CO_2 methanation mechanism. The addition of promoters affects the formation of intermediates. Mg or Ca modified Ni/Al₂O₃ catalysts promote the formation of the carbonate species due to the increased basicity, while Sr or Ba modified catalysts promoted $^*\text{CO}$ and H_2CO^* formation [177]. The nature of nickel active sites also influence the CO_2 methanation mechanism. Zhou et al. [158] found that CO_2 methanation took the pathway of CO over the Ni/TiO₂ catalyst with Ni (111) as the principal exposing facet, while the catalyst with multi-facets followed the formate route, with which nickel was only functional for hydrogen dissociation. The location of nickel active sites also affects the CO_2 methanation reaction pathways [153]. Controlling nickel being on either the interior or the exterior of adjacent siloxene nanosheets is achieved by employing different solvents in the preparation process, which determines the reaction intermediates and pathways for CO_2 methanation, as shown in Figure 6. CO_2 methanation occurred through the formate pathway over Ni@SiXNS-EtOH with nickel active sites being on the interior of adjacent siloxene nanosheets while CO_2 methanation followed the CO pathway when nickel was at the exterior of adjacent siloxene nanosheets on Ni@SiXNS-H₂O.

Figure 6. CO_2 methanation pathways on (A) Ni@SiXNS-H₂O and (B) Ni@SiXNS-EtOH.

The different preparation methods can also influence the reaction pathway of CO_2 methanation. Jia et al. [135] used the *operando* DRIFT analyses to demonstrate the CO_2

methanation pathway on Ni/ZrO₂ obtained via different preparation methods. CO₂ methanation over the plasma decomposed catalyst follows the Co-hydrogenation route. The exposed high-coordinate Ni (111) facets of the plasma decomposed catalyst facilitate the decomposition of CO₂ and formates into adsorbed CO. The subsequent hydrogenation of adsorbed CO leads to the production of methane. However, the thermally decomposed catalyst with a complex Ni crystal structure and more defects mainly takes the pathway of direct formate hydrogenation.

Although some researchers have reported on the mechanism of CO₂ methanation, it is still hotly debated. Some of the problems are as follows: (1) Why are there two different CO₂ methanation mechanisms on Ni-based catalysts with the same Ni element as the active component? (2) What are the influencing factors of reaction pathways? (3) Are the adsorbed CO₂ species on different Ni-based catalysts the same? (4) What is the approach and process of the adsorbed CO₂ species evolution on the catalysts? (5) What is the effect of Ni on the activation and dissociation of CO₂? (6) Ni-based catalysts are also used in CO methanation, so why is CO only a by-product and does not react further to form CH₄ on some catalysts? and (7) What is the role of CO across the whole CO₂ methanation reaction process? Regarding these problems, no consensus has been reached. Establishing a reaction network to understand the CO₂ methanation mechanism at the molecular-level is extremely important. These mechanistic insights will have great potential to guide the rational design of catalysts with high activity and CH₄ selectivity.

4. Summary and Perspective

This review encompassed the recent development of Ni-based catalysts used in CO₂ methanation including the effects of nickel active sites, supports, promoters, and preparation methods on CO₂ methanation as well as the two kinds of reaction mechanism, with emphasis on designing catalysts with high activity and stability at low temperature. By discussing the research progress and present status of CO₂ methanation over Ni-based catalysts, some conclusions could be obtained. First, interactions between Ni and the support seem to be a key parameter for the methanation reaction. The appropriate nickel–support interaction could suppress nickel sintering, resulting in high activity and good stability. Second, the promoters could affect the dispersion of the active phase, the acid–base properties of catalysts, and thus the catalytic activity and stability. Adding noble metals into Ni-based catalysts as promoters could improve the catalytic activity at low temperature. In addition, alkaline-earth oxides as promoters could improve the alkaline properties of the catalysts, which could promote the adsorption, activation, and reduction in CO₂, thus enhancing the catalytic activity at low temperature. Third, CO₂ methanation occurred via the formate pathway and CO pathway over Ni-based catalysts, and the addition of promoters and the nature of active metal affects the formation of intermediates, thus affecting the reaction mechanism. Fourth, appropriate basic sites on catalysts could promote the formation of monodentate formate species, thus enhancing CO₂ methanation activity. Using different basic oxides as supports could adjust the basicity of the catalysts, enhancing the adsorption of CO₂.

Although Ni-based catalysts have been widely used in CO₂ methanation, many challenges and problems remain. To increase the activity of Ni-based catalysts at low temperature, the activation of CO₂ and H₂ at low temperature is important, and the properties of the nickel metal, support, and promoter would influence this. Some new technologies have been applied in CO₂ methanation such as photo-catalysis, electro-catalysis, and plasma-catalysis. CO₂ could be hydrogenated to produce CH₄ by these methods at low temperature, but there are some challenges including the low CH₄ selectivity and low efficiency. One recommended advancement to overcome these issues is to couple these new technologies with traditional thermo-catalysis such as thermal-photo catalysis, which could significantly improve the selectivity and yield of CH₄. For example, solar-thermal CO₂ reduction could achieve high-efficient conversion CO₂ at mild conditions, which could overcome the low efficiency and very high operating temperature of photo-catalysis and

thermo-catalysis, and achieve higher solar energy utilization efficiency. In addition, it is still a big challenge to experimentally determine CO₂ methanation reaction pathways, and the effects of active sites, supports, and promoters on the reaction mechanism are still being debated. The precise elucidation of the activation of the C–O bond in CO₂ and the relationship between CO₂ activation and H₂ activation are also challenging tasks.

Based on the above discussions, the following suggestions on CO₂ methanation on Ni-based catalysts are proposed.

- (1) Design of CO₂ methanation catalysts with high activity at low temperature simultaneously with high carbon deposition resistance and anti-sintering properties;
- (2) Try new materials and technologies such as MOF, alloy material, and plasma assisted technology for the design and preparation of CO₂ methanation catalysts;
- (3) Combine photo-catalysis, electro-catalysis, and plasma-catalysis with traditional thermo-catalysis to integrate their advantages;
- (4) Investigate the mechanism of the activation and cleavage of C–O in CO₂, and the relationship between CO₂ activation and H₂ activation as well as provide deep insights into the CO₂ methanation reaction pathways and the key factors in the reaction mechanism; and
- (5) Combine the theoretical calculations with experiments to explore the role of the active metal, support, and the nickel–support surface in the CO₂ methanation reaction process.

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