

Synthesis and Mechanistic Study of Ni-based Catalysts for CO₂ Methanation

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Summary

Ni-based catalysts, due to its high CH₄ selectivity and attractive cost-effectiveness, is the most widely studied catalyst for CO₂ methanation. However, achieving a high methanation activity at low-temperature (especially below 250 °C) for Ni-based catalyst is a great challenge, and the methanation mechanism over Ni-based catalyst is still controversial. In this thesis, three kinds of Ni catalysts have been prepared by sol-gel method in chapter 5 and chapter 6 and by C₃N₄-assited one-pot method in chapter 7. Furthermore, the methanation mechanism focusing on Ni itself has been studied in chapter 4, and the effect of dopant on the catalytic performance has been studied in chapter 5.

Chapter 5 has disclosed the sol-gel preparation of high-loading mesoporous Ni/SiO₂ catalysts with small Ni particles. Being based on inert silica, these catalysts are ideal model materials to elucidate the reaction mechanism on nickel. Based on CO₂-TPD, in-situ CO₂-DRIFTS,TPSR, and DFT calculations, CO₂ methanation follows mostly the RWGS+CO-hydrogenation and the formate pathways, the former being dominant at low temperature.

Chapter 6 has revealed the effect of dopant (Mn, Co, and Cu) on the catalytic performance of Ni-based catalyst. The effect of promoters is not directly related to improvement of dispersion, reducibility, or basicity. Instead, the promoters orient the reaction mechanism and favor the conversion of key intermediates. Mn addition has the highest promoting effect on the hydrogenation of formaldehyde intermediate (*OCH₂) to methoxy intermediate (*OCH₃), i.e. the rate determining step of the “RWGS+CO hydrogenation” pathway which is shown to predominate at low reaction temperature. Co addition facilitates the formation of formate species, i.e. the rate determining step of the formate pathway which is also active at high reaction temperature. Cu addition has a negative effect on the rate determining step of those two pathways, resulting a lower performance of Ni-Cu/SiO₂.

In chapter 7, Ni/CeO₂ catalyst is prepared by one-pot method assisted

with the C_3N_4 . The activity of the obtained catalyst shows a significantly high CO_2 conversion and CH_4 selectivity even at a temperature as low as 250 °C. The assistance of C_3N_4 and the one-pot preparation method increase the number of surface oxygen vacancies and medium basic sites. CO_2 methanation on Ni/CeO₂ catalysts followed RWGS+CO hydrogenation pathway and the formate pathway, with the former being dominant at low temperatures. The copromotion of those two pathways by the higher amount of oxygen vacancy and medium basic site of Ni/CeO₂-CN-OP is responsible for its outstanding low temperature methanation performance.

Key words: CO_2 methanation, Ni-based catalysts, high loading, dopant, sol-gel, C_3N_4 , methanation mechanism

Thesis organization

This thesis is composed of seven chapters. After the general introduction of Chapter 1, Chapter 2 presents a detailed literature review on the key properties (physico-chemical properties of catalysts and methanation pathway) dictating the performance of catalyst for CO₂ methanation. The effect of support, promoters, and preparation method on the properties of catalyst are reviewed in a systematic and critical way. After that, the research objection and strategies applied in this thesis are given in Chapter 3. In Chapter 4, the experimental methodologies are described including catalyst characterizations and catalytic activity. In the following three chapters, three kinds of Ni-based catalyst are prepared and applied for CO₂ methanation. The details are as follows. In Chapter 5, high loading Ni/SiO₂ catalyst are prepared by an original sol-gel method and applied for CO₂ methanation reaction. The method is shown to allow reaching high specific productivity. The methanation mechanism is investigated based on this model catalyst. In Chapter 6, the preparation method is extended to bimetallic Ni-M/SiO₂ catalysts. The effect of second metal addition on the methanation performance is studied and the insights gained in Chapter 5 regarding the reaction mechanisms are used in conjunction with advanced characterization to decipher the role of the metal promoters. Chapter 7 discloses the original preparation of Ni/CeO₂ catalysts performed with the assistance of C₃N₄. This system is shown to feature high intrinsic activity. On the fundamental science side, it is used to examine the importance of oxygen vacancy concentration and medium basic site in CO₂ adsorption and activation during CO₂ methanation reaction. The final Chapter 8 presents the general conclusion, giving a brief summary of the findings, and the recommendations for future work

List of abbreviation

BET	Brunauer-Emmett-Teller
CN	Carbon nitride
CNT	Carbon nano tube
DFT	Density functional theory
DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy
FTIR	Fourier transform infrared
GHSV	Gas hourly space velocity
HAADF-STEM	High angle annular dark field-scanning transmission electron microscopy
NMR	Nuclear magnetic resonance
RWGS	Reverse water-gas shift
SMSI	Strong metal-support interaction
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilicate
TOF	Turnover frequency

TPD	Temperature programmed desorption
TPR	Temperature programmed reduction
TPSR	Temperature programmed surface reaction
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Chapter 1 CO₂ methanation – general background

Fossil fuels (coal, petroleum and natural gas) is still the major energy source for the global society. However, enormous amount of carbon dioxide (CO₂) is produced during their combustion process, which is causing a series of environmental issues such as global warming, sea acidification, and extreme climate changes.[1, 2] Carbon capture and storage (CCS) applied in the point sources is the most straightforward strategy to reduce anthropogenic CO₂ emission. However, energy consumption in the separation, purification, compression, transportation, and storage processes and high regeneration temperature of the adsorbents is a key drawback of this strategy.[3, 4] Taking into account that CO₂ is an alternative carbon feedstock, CO₂ conversion and utilization (CCU) provides a more attractive and promising strategy, with the condition that renewable energy is used to feed the conversion process.[5, 6] Simultaneously, using “green H₂” obtained by water electrolysis and photolysis to CO₂ hydrogenation constitutes a potentially scalable method to store renewable energy in a product with a high energy density (Fig. 1.1), which is of great meaning for the today’s world of high energy demands.[7, 8] Among the various CO₂ hydrogenation products (e.g., formate, methanol, and dimethyl ether)[9-12], CH₄ is preferred due to the great market demand and due to the fact that cost-effective distributions solutions are already available using the existing natural gas grid.[13] Additionally, CO₂ methanation is a simple and fast reaction, which can be operated under atmospheric pressure.

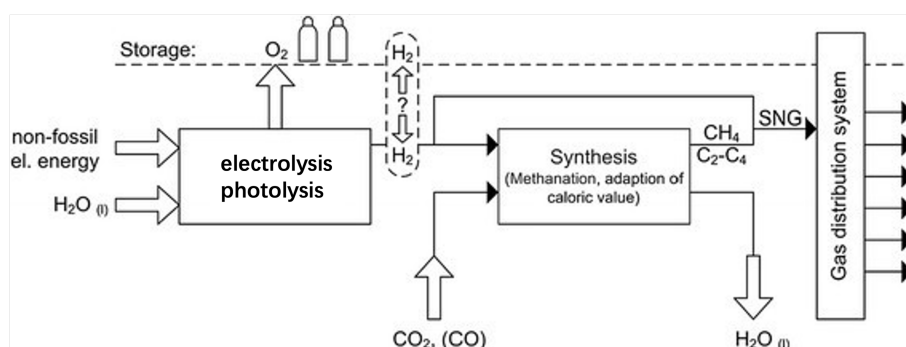


Fig. 1.1 Concept for the storage of renewable energy in a gas distribution system.[14]

The CO₂ methanation reaction (the so-called the Sabatier reaction) is exothermic, and therefore favored thermodynamically at low temperature ($\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$; $\Delta H = -165 \text{ kJ/mol}$). However, it is limited kinetically because of the high stability of CO₂. [15, 16] There a compromise has to be found and the reaction is usually operated in the 200-500 °C range. Obviously, the quest of catalysis scientists is to develop highly active catalysts that would allow reaching high productivity in the lower temperature range. The chemically stable C=O bond possesses a dissociation energy of ca. 750 kJ/mol, requiring an equally high energy input. This high energetic demand emerges as a bottleneck in the large-scale implementation of the currently developed technologies for CO₂ hydrogenation to methane. Above 450 °C, the endothermic back reaction and the reverse water-gas shift reaction ($\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$; $\Delta H = -41 \text{ kJ/mol}$) diminish the CO₂ conversion and produce CO as a byproduct. [17] Therefore, a catalyst enhancing the hydrogenation rate and methane selectivity is essential and indispensable.

The facilitated separation of heterogeneous catalysts and formed products and reactants is of prime concern in the design of large scale commercially practical processes and is notably advantageous in comparison with homogeneous systems. The currently available heterogeneous metal-based catalysts are divided into two main categories: (1) precious metals and/or their alloys and carbides such as Ru [18-20], Rh [21], and Pd [22, 23]; (2) transition metals and/or their alloys and carbides such as Ni [24, 25], Co [26-28], and Fe [29]. The first category has better CO₂ conversion and CH₄ selectivity, especially Ru-based catalysts. Notwithstanding their excellent hydrogenation performance, the large-scale industrial application of noble metals is limited by their high cost. Among the second category catalysts, nickel-based catalysts are the most commonly used catalyst for CO₂ methanation because they are found to have high activity and CH₄ selectivity. However, because of the high activation energy required, high CO₂ conversion was difficult to achieve at low temperatures on Ni thermocatalysts. High temperature methanation also often results in

undesirable effects on the stability (coking) and lifetime of the catalysts as well as increased energy consumption.[2, 30] Thus, fundamental studies on the development of highly active, selective and stable catalysts for CO₂ methanation are of great importance.

Chapter 2 Influence of promoter, support and preparation method on the physico-chemical properties and methanation pathway that dictate catalyst performance

CO₂ conversion using the H₂ obtained by water electrolysis and photolysis not only provides a solution for mitigating the excessive carbon dioxide emissions but also can potentially be employed for the storage and transportation of low-grade energies. Among the numerous target CO₂ hydrogenation products, methane is a promising one as it is in great demand and feasible for cost-effective distributions. However, due to the high stability of CO₂, the CO₂ methanation reaction is limited kinetically. Therefore, high active catalysts are required. Understanding the key properties that dictate catalyst performance is essential for the rational design of CO₂ methanation catalysts. Herein, we elaborate on the effect of particle size and dispersion, metal-support interaction, reducibility, basicity, and mechanism on the catalytic performance. Furthermore, the influence of promoter, support, and preparation method on those five factors is elucidated.

2.1. Introduction

CO₂ methanation is a topical reaction with many papers coming out. Conflicting conclusions and unsolved debates still existed. It is important to understand all of these if we want to develop better catalysts. In this chapter, we propose a detailed state of the art. First, we define the main physical and chemical properties that are thought to govern methanation activity: dispersion, metal support interactions, reducibility and basicity. Second, we explain the possible reaction pathways for CO₂ methanation. Third, we embark into a systematic review of the parameters of the catalyst formulations (nature of the metal, nature of the support, preparation method, etc.) that directly impact these key properties, and possible orient the catalytic mechanisms in one route to another, with marked effects on catalyst properties. The purpose of this chapter is to gain the keys to understand how catalysis scientists can play with catalyst formulation and preparation to try and develop high performance catalysts. This is then exploited in the following chapters, where we focus on model Ni-based catalysts to further gain some fundamental insights and push the

systems towards high performance.

2.2. The physico-chemical properties that dictate catalyst performance

To have a good methanation catalyst, we need to boost intrinsic activity (conversion), maintain high selectivity towards methane over carbon monoxide, and promote catalyst stability (against deactivation by sintering, coking, and poisoning). Any gain in production cost (i.e., less use of the expensive metals) is interesting as well, potentially offering economic benefits. This section has reviewed the four key aspects that need to be considered when designing and tailoring methanation catalysts: (1) particle size and dispersion, (2) metal-support interaction, (3) reducibility, (4) basicity.

2.2.1 Particle size and dispersion

For the CO₂ methanation reaction, the activation of CO₂ and H₂ is the prerequisite for achieving catalytic activity and selectivity. Charge transfer in the activation of reactant molecules are influenced by the metal-support interfacial effect in supported metal catalysts. Among the various factors influencing the interfacial effect, the most debated is particle size. The dependence of the catalytic activity on the particle size of deposited metals is referred to as structure-sensitivity. Although structure-sensitivity is vital from a catalytic design perspective, the exact contribution of size effect in catalyzing the CO₂ methanation reaction is still inexplicit, and the reported optimal sizes of metal particles vary greatly, depending on the catalytic formulations (for instance: 15 nm for Rh/ γ -Al₂O₃ [31], 17 nm for Rh/TiO₂[32] and 2.5 nm for Ru/TiO₂[33]). Strikingly, also for a given catalyst type, various studies come up with contrasted conclusions on the optimal metal NP size. Marconi *et al.* reported a structure-sensitivity of CO₂ methanation on Ni/CeO₂, where the turnover frequency showed a linearly increasing trend with Ni nanoparticle size (3–44 nm) and decreased with Ni size >

45 nm under various Ce^{3+} contents.[34] Differently, Varvoutis *et al.* explored the structure sensitivity of CO_2 methanation over nickel particles (10–25 nm) supported on CeO_2 nanorods, and an optimum Ni particle size of ca. 20 nm was revealed.[35]

The particle size effect in supported hydrogenation catalysts could operate through strong metal-support interactions (SMSI) and H-spillover effects.[36] Guo *et al.* altered the size range of Ru deposits in Ru/ CeO_2 formulations and uncovered a competitive relationship between the SMSI and the H-spillover effect in determining the methanation activities. Comparing with CeO_2 nanowire supported single Ru atoms and large Ru nanoparticles (ca. 4.0 nm in size), CeO_2 nanowire supported Ru nanoclusters (ca. 1.2 nm in size) showed the most outstanding low-temperature CO_2 methanation activity and 98–100% selectivity, with a turnover frequency (TOF) of $7.41 \times 10^{-3} \text{ s}^{-1}$ at 190 °C. As illustrated in Fig. 2.1a, the strongest metal-support interaction and H-spillover effect are respectively encountered in supported single Ru atoms and large Ru nanoparticles, with the activation of metal carbonyls and the dehydration of the support surfaces suppressed correspondingly. The two factors reach a balance in CeO_2 -supported Ru nanoclusters, and the methanation activity is therefore maximized.

Not only the particle size of supported metal, the particle size of support also has an influence on the metal-support interaction. Parastaev *et al.* presented a simple method to control the metal-support interaction strength in Co/ CeZrO_4 by varying the size of the support particles.[37] The particle size of the CeZrO_4 support was varied in a range of 9–120 nm by increasing the calcination temperature of the initial precipitate between 500 °C and 1000 °C. The preparation of cobalt nanoparticles on CeZrO_4 supports with an intermediate particle size of ~20 nm leads to a higher dispersion of metallic cobalt as compared to CeZrO_4 with larger and smaller particle sizes due to an optimal strength of the interfacial cobalt- CeZrO_4 interaction without sacrificing surface area (Fig. 2.1b), which results in the highest CO_2 methanation activity.

Particle size also has an influence on the CO/CH₄ selectivity of CO₂ methanation.[38, 39] Specifically, the reaction pathways followed for CO₂ hydrogenation depends on the Ni particles size, as shown in Fig. 2.1c. On small and large Ni nanoparticles, the key intermediate is monodentate HCOO⁻ formed from co-adsorbed CO₂ and H₂. On small Ni particles, this intermediate is decomposed to CO, which may be further hydrogenated to CH₄, following a consecutive reaction pathway. However, the low H₂ coverage on small Ni particles favors the CO formation. On the contrary, over large Ni particles the m-HCOO⁻ intermediate may be directly hydrogenated to CH₄ due to the large H₂ surface coverage and a higher CH₄ production rate rather than CO production rate is obtained.[39] Likewise, CO is preferably formed over atomically dispersed Ru of 0.1 wt.% Ru/Al₂O₃ catalyst, whereas CH₄ production is favored on relatively large 3D metal clusters formed at Ru loadings of 1 wt.% and above. Additionally, the apparent activation energies for CO and CH₄ formation over Ru/Al₂O₃ catalyst exhibit ~20 kJ/mol difference, suggesting different reaction pathways for CO and CH₄ formation and/or different nature of active centers.[38]

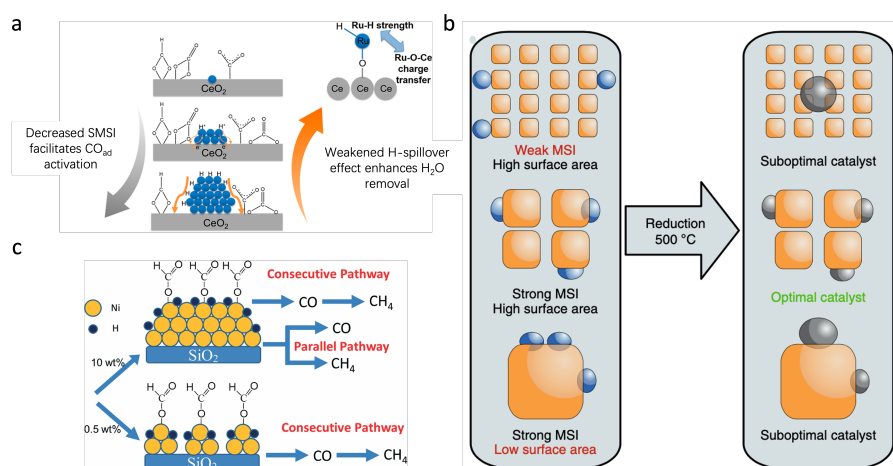


Fig. 2.1. (a) Schematic illustration of competitive SMSI and H-Spillover effect leading to competing CO activation and surface dehydration for CeO₂-supported single Ru atoms, Ru nanoclusters, and large Ru nanoparticles.[41] (b) Schematic representation of the

interplay between the MSI and support particle size on the properties of Co- CeZrO₄ catalysts. Blue and grey spheres represent oxidized and reduced cobalt particles, respectively; orange particles represent the CeZrO₄ support.[42] (c) Proposed mechanism for CO₂ hydrogenation on Ni/SiO₂. [44]

Apart from having an influence on the intrinsic activity of the catalysts, particle size obviously also has an influence on the number of active site (per unit mass of catalyst or unit mass of metal). Smaller particle size feature a higher surface to volume ratio and therefore, in general, more active sites. Fan *et al.* synthesized an atomic-scale Ru catalyst supported by the defect-engineered pyrolytic boron nitride (pBN) through a simple vacuum filtration process, reducing the Ru loading and simultaneously maintaining its high catalytic activity. The as-prepared catalyst with low Ru loading (0.58 wt%) exhibited CH₄ selectivity up to 93.5%, catalytic stability after 110 h, and a higher reaction rate (1.86 mmol_{CO2}/(g_{cat} s)) at 350 °C and 1.0 MPa compared to other nanoparticle catalysts.[18]

2.2.2. Metal support interaction

As a widely recognized effect in heterogeneous catalysis, metal-support interaction can significantly modulate catalytic activities. In general, enhanced metal-support interactions benefit metal dispersion. Li *et al.* synthesized a series of Ni nanoparticles supported on oxygen-functionalized carbon nanotube (CNT) and observed an anomalous metal-support interaction mode (i.e., a higher calcination temperature would lead to a weakened Ni-CNT interaction).[40] The robust Ni-CNT interaction formed through surface oxygen groups was responsible for high dispersion of Ni nanoparticles. The CO₂ conversion and CH₄ selectivity gradually decreased as the calcination temperature increased from 350 to 550 °C since higher thermal treatment temperature could result in the decomposition of surface oxygen groups and the loss of anchoring sites, and the weakened Ni-CNT interaction could thus cause Ni particle growth and sintering. Al₂O₃ has been employed as the support mainly for nickel- and cobalt-based catalysts

in methanation reaction since Ni-aluminate and Co-aluminate spinel structures can be considered as a well-distributed mixed metal oxide precursor.[41, 42]

In contrast, metal-support interactions could decrease the reducibility of the catalysts. The metal oxide species of catalysts need to be turned under a reducing environment into the catalytically active metallic nanoparticles, on which the adsorption and dissociation of CO₂ and H₂ occur. Meanwhile, high reduction temperature could lead to the agglomeration of metal particles and thus decrease the catalytic activity. Furthermore, for catalysts based on a reducible support, the so-called “strong metal-support interaction” effect (SMSI) is frequently observed. This consists in the formation of an over-layer of oxides during high temperature reduction.[43-45] Wang *et al.* found that higher reduction temperature strengthened the SMSI effect, thus a thicker overlayer (amorphous ZnO) was formed on the surface of Ni nanoparticles for the Ni/ZnO catalysts.[46] A similar phenomenon was observed for the Ni/CeO₂, in which the partially reduced cerium oxide migrates onto Ni nanocrystalline under higher reduction temperature and then decorate/encapsulate Ni nanoparticles by ceria layer.[47] Unlike many other catalytic systems where the SMSI effect is beneficial, such a surface reconstruction process was considered detrimental to the CO₂ methanation activity. Therefore, it is essential to adjust the nature and intensity of the metal-support interactions in methanation catalysts to balance the reducibility and dispersion.

2.2.3. Reducibility

Enhancing the reducibility of catalysts is important for their catalytic performance because metal oxide species in the as-prepared catalysts need to be turned – under the reducing reaction environment or via a specific thermal pretreatment – into the catalytically active metallic nanoparticles. Furthermore, the reducibility of support itself also may influence on the activity of catalyst. The generally accepted mechanism for CO₂ methanation over Ru supported on reducible oxides involves two key steps involving the support, i.e., CO₂ activation by filling an

oxygen vacancy (oxidation of the support) and the regeneration of oxygen vacancy by H_2 (reduction of the support). Sakpal *et al.* synthesized CeO_2 with two different morphologies (nanorod CeO_2/r and nano cube CeO_2/c) to study the correlation between the support redox properties and the catalyst performance in CO_2 methanation.[48] $Ru/CeO_2/r$ has a higher support reducibility and oxygen vacancy concentration compared with $Ru/CeO_2/c$, resulting in more sites for CO_2 adsorption and activation. At 250 °C, $Ru/CeO_2/r$ is ~2 times more active ($11.0 \times 10^{-8} \text{ mol m}_{Ru}^{-2} \text{ s}^{-1}$) than $Ru/CeO_2/c$ ($5.1 \times 10^{-8} \text{ mol m}_{Ru}^{-2} \text{ s}^{-1}$). In addition to good redox properties, the efficient hydrogenation of the intermediate species by the H atoms dissociated over the metal sites are crucial to improve the catalyst activity for CO_2 methanation at low temperatures. Dreyer *et al.* synthesized Ru-based catalysts supported on different kinds of supports, which included strong Lewis acid and irreducible Al_2O_3 , amphoteric and reducible CeO_2 and MnO_x , and strongly basic and reducible ZnO . [27] Combining thorough reaction kinetic analysis with quantitative gas chemisorption and in situ DRIFTS, they found that an enhanced support reducibility decreased the Ru-CO coverage, which increased the number of H_2 dissociation sites but in turn strengthened the C-O bonds. Therefore, a slightly reducible support resulting in (i) an increased number of H_2 dissociation sites on Ru due to weaker CO adsorption, and (ii) sufficiently weak C-O bonds, would result in the highest catalytic activity. CeO_2 is such a support and an excellent CO_2 conversion and CH_4 selectivity was observed for the Ru/CeO_2 catalyst.[27]

2.2.4. Basicity

CO_2 adsorption behavior can be tuned by manipulating catalyst basicity since CO_2 is an acid and tends to adsorb on basic sites. Basic sites can be divided into weak, medium, and strong basic sites depending on the chemical nature of surface oxygen species. In the literature, the weak basic sites can originate from surface hydroxyl groups on which CO_2 molecules are adsorbed to form bicarbonate species. The metal-oxygen pairs (M^+-O^{2-}) or acid-base pairs, e.g. $Zr^{4+}-O^{2-}$, $Al^{3+}-O^{2-}$, $Mg^{2+}-O^{2-}$,

can be the source of moderate basic sites, while low-coordination oxygen anions can serve as the strong basic sites for CO₂ adsorption (Fig. 2.2a).[49-51] According to the ‘Sabatier principle’, optimal catalysis occurs when interactions between catalyst and reactant are of intermediary strength. Consistently with this principle, medium basicity is widely accepted as optimal for CO₂ methanation.[52-54] Pan *et al.* combined CO₂-TPD and in-situ FTIR analyses and proposed that intermediate species formed on the medium basic sites of Ni/Ce_{0.5}Zr_{0.5}O₂ could be converted to methane more quickly than those on the weak basic sites. [52] Additionally, they reported that the strong basic sites of Ni/ γ -Al₂O₃ could hinder further hydrogenation of carbonate intermediates.

In some studies, the promotion effect of strong and weak basic sites is also reported. He *et al.* prepared Ni-Al hydrotalcite derived catalyst (Ni-Al₂O₃-HT).[55] Methanation of CO₂ over this catalyst initiated at 225 °C and reached 82.5% CO₂ conversion with 99.5% CH₄ selectivity at 350 °C, which was much better than its impregnated counterpart. Characterizations by means of CO₂ microcalorimetry and ²⁷Al NMR indicated that large amount of strong basic sites existed on Ni-Al₂O₃-HT, originating from the formation of Ni-O-Al structure. The existence of strong basic sites facilitated the activation of CO₂ and consequently promoted the activity. Jia *et al.* prepared Ni/ZrO₂ catalysts via a rapid plasma decomposition of nickel precursor (Ni/ZrO₂-P) and reported the increase in strong basic sites compared with that prepared via a conventional thermal decomposition (Ni/ZrO₂-C), based on CO₂-TPD studies. The formation of more strong basic site ascribed to the increase of oxygen vacancies is one of the reasons for the greatly enhanced CO₂ methanation activity of Ni/ZrO₂-P.[49] On the contrary, the role of weak basic sites in CO₂ adsorption and activation was highlighted in the other studies. Aldana *et al.* found that the better activity of Ni-ceria-zirconia catalysts compared to Ni-silica can be explained by the importance of weak basic sites, which prevents CO₂ from competitive adsorption against H₂ on the Ni active sites.[56] Anastasiia *et al.* tested different types of Co₃O₄ (synthetically prepared mesoporous m-Co₃O₄ and

commercial c-Co₃O₄) for the CO₂ methanation reaction, and m-Co₃O₄ was more active compared to c-Co₃O₄. From the CO₂-TPD results, weak basic sites could be detected exclusively on m-Co₃O₄, promoting the CO₂ activation and resulting in the formate intermediate.[57]

Different kinds of basic sites could jointly contribute to enhanced CO₂ adsorption and activation in the same catalyst system. Hongmanorom *et al.* prepared Ni-Mg phyllosilicate mesoporous SBA-15 catalysts via the ammonia evaporation (AE) method. The catalyst prepared by AE method could form more surface hydroxyl groups serving as weakly basic sites for CO₂ adsorption and activation. Furthermore, the incorporated Mg species could lead to the presence of medium strength basic sites. As a results, the high concentration of both weak and medium basic sites leads to the better catalytic performance of Ni-5Mg/SBA-15-AE catalyst.[58] In another study, Świrk *et al.* prepared vanadium promoted Ni(Mg,Al)O hydrotalcite-derived catalysts and demonstrated that the highest sum of weak and medium basic sites in the sample with 2 wt% V loading could positively influence the catalytic activity in CO₂ methanation.[59]

A number of studies have revealed the correlation between the methanation activity in term of turnover frequency (TOF) and the concentration of basic sites. Aziz *et al.* used pyrrole-FTIR spectroscopy to determine the basic sites of the catalysts based on the intensity of the peak ascribed to N–H stretching vibrations.[60] In more recent studies, the amount of basic sites were measured by CO₂-TPD analysis, and TOF of CO₂ conversion was plotted as a function of the medium-strength basicity (Fig. 2.2b)[61]. Regardless of the method used for measuring the basicity, the activity data in these studies could be positively correlated with the concentration of basic sites, clearly indicating that a large number of basic sites is crucial for high CO₂ adsorption and activation.

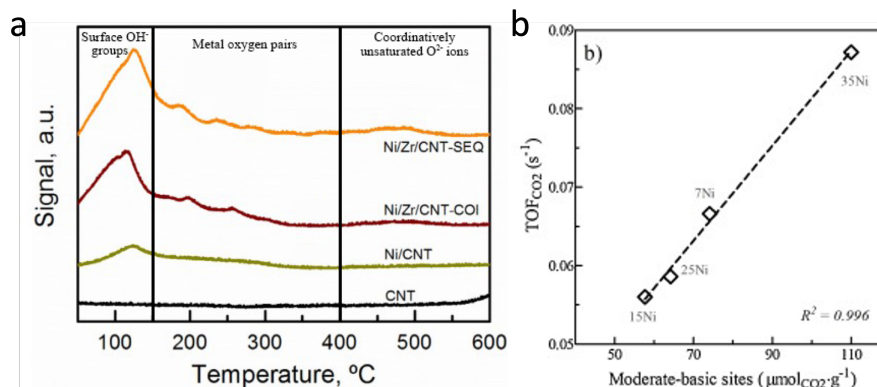


Fig. 2.2. (a) CO₂-TPD profiles of nickel-based catalysts containing different basic sites[50]. (b) The plot of TOF of CO₂ conversion as a function of medium-strength basicity of Ni/Y₂O₃ catalysts.[61]

2.3. The effect of methanation pathway on the catalyst performance

The mechanism of CO₂ methanation reaction has been extensively studied with both experimental and theoretical methods, but a consensus has still not been reached. Generally, the CO₂ methanation reaction is proposed to occur through three pathway categories: the formate pathway[62-64], the RWGS + CO hydrogenation pathway[49, 65, 66], and the direct C–O bond cleavage pathway[67, 68]. The discrepancy for the different pathways is mainly reflected in the pathway of CO₂ adsorption/activation and formed intermediates, the H₂ chemisorption and the rate determining step (RDS). As shown in Fig. 2.3, the formate pathway involves the formation of carbonates (*HCO₃) and formates (*HCOO), which are directly hydrogenated into CH₄, without the dissociative adsorption of CO₂ and the formation of carbonyl CO species. In the CO pathway, carbonyl (*CO) species are the important intermediates formed via CO₂ dissociation into *CO and *O. The decomposition of formates into *CO is also possible.[49, 69] Subsequently, the *CO is hydrogenated into CH₄. In the C–O bond

cleavage pathway, the adsorbed CO dissociates into $\ast\text{C}$ and $\ast\text{O}$ on the metal sites before undergoing subsequent hydrogenation into CH_4 . In general, CO_2 methanation mechanism is dependent on the nature of the catalyst employed, including aspects such as the active species, support, and promoters. It is also possible that some pathways are favored in specific operating conditions (temperature, partial pressure of CO_2 or H_2).

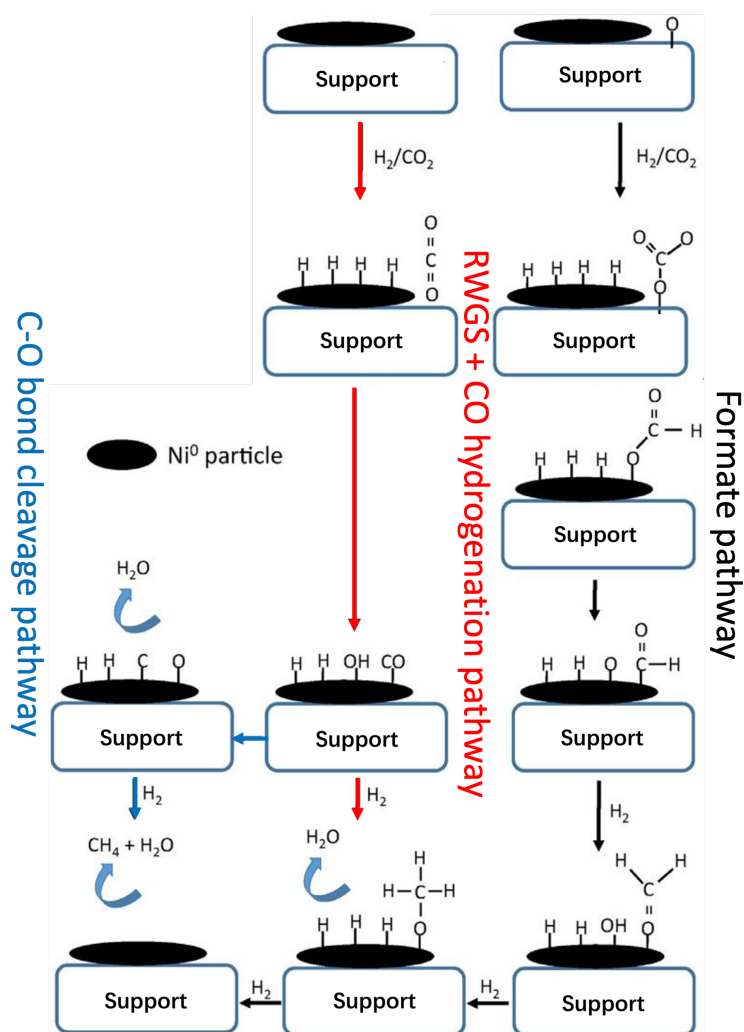


Fig. 2.3. Possible reaction pathways for the methanation of CO_2 .
Adapted from Mebrahtu et al. [70]

It should be noted that different CO₂ methanation pathways are not mutually exclusive; they may occur in parallel at the same time. Killet *et al.* observed a change of the apparent activation energy of Ni/Ni_xMg_{1-x}O for the CO₂ conversion in different temperature regimes, which is usually attributed to simultaneous and competing reactions or reaction mechanisms to which different activation energies are associated.[71] Alfredo *et al.* prepared ZrO₂-supported Rh catalyst for CO₂ methanation and found Rh carbonyls and formate species bonded to the support.[72] To verify their individual involvement in the catalysis, the catalyst was treated by CO and isotopically labelled formic acid. The data showed the coexistence of the RWGS + CO hydrogenation pathway and the formate pathway, that is, both Rh carbonyls and surface formate species participate in CO₂ methanation.

2.4. Systematic overview of the effect of support, promoter, and preparation method on the physico-chemical properties and methanation pathway

2.4.1. Effect of the support

2.4.1.1. Effect of the support on particle size (dispersion)

Increasing the active species content is a direct and efficient approach to increase the amount of active site. This is why catalytically active metal are usually dispersed at the surface of a carrier. Graça *et al.* prepared a series of nickel-based catalysts supported on a HNaUSY zeolite. In this case, CO₂ conversion increased with the Ni content from 2 to 14%, due to the higher amount of Ni species after reduction.[73] However, in most cases, there is an optimal loading because high loadings usually causes sintering and decreased surface metal availability. Zhao *et al.* studied the activity of Ni@UiO-66 with different Ni loadings. At 300 °C, CO₂ conversion firstly increased with the increase of Ni loading, and then a maximum conversion of 57.6%

was obtained at an optimal 20 wt% Ni loading. When further increasing the Ni loading over 20 wt%, the catalytic activity decreased, which was attributed to aggregation of large Ni NPs caused by overloading.[74]

To inhibit the adverse effect of aggregation of active phase led by the high loading, increasing the dispersion is pivotal. Using the supports with high surface areas is beneficial for the dispersion of metal nanoparticles.[60] Zhen *et al.* prepared a series of Ni@MOF-5 for CO₂ methanation, which exhibited a higher activity than 10Ni@SiO₂. The uniformly dispersed Ni in the framework in MOF-5 is the main contributor to the significant activity enhancement.[25] Hongmanorom *et al.* synthesized a well-defined mesoporous ceria support with large surface area using SBA-15 as a starting template, and then utilized it to encapsulate Ni species.[75] The unique encapsulated structure, compared with the conventional CeO₂, provided smaller and higher dispersed Ni nanoparticles, which facilitate H₂ dissociation and thus improve hydrogenation activity.

Using the modified support to enhance its interaction with metal is also beneficial for the dispersion of supported metal. Yang *et al.* reported one kind of Ni-based catalysts with high dispersion fabricated with the amine functionalized nanosponge zeolite as support. The functionalized amine group induced the precisely regioselective precipitation of the Ni precursor in the mesoporous channels and highly dispersed Ni nanoparticles were obtained.[76] As a result, Ni/AF-NSZ displayed higher CO₂ conversion than Ni/NSZ reference catalyst. The reason for this could be attributed to the high dispersion of metallic Ni active sites over Ni/AF-NSZ catalyst owing to the amine functionalization of the support. This would be beneficial to the activation and dissociation of the H₂ over metallic Ni active sites.

2.4.1.2. Effect of the support on metal-support interaction

The nature of support has an obvious influence on the interaction developed with the supported metal. Kim *et al.* prepared Ru based catalysts supported on different titania supports (anatase, rutile, and a

mixture of both (P25)) to unravel the origin of this support effect.[77] This study found that the calcination step provokes intense modifications of the catalyst properties, and these modifications are strongly dependent on the crystal structure of the support. The weak interactions between RuO₂ and anatase TiO₂ cause sintering and growth of RuO₂ crystals, whereas the strong interactions (i.e., lattice-matched interfacial structure) between RuO₂ and rutile TiO₂ lead to a transformation of nanoparticles into epitaxial RuO₂ layers sandwiched between rutile TiO₂ rods. In both cases, specific activity is decreased because the amount of surface-accessible Ru dropped significantly. On the surface of P25 TiO₂, the mixing of anatase and rutile particles gave rise to a more favorable situation where Ru does interact strongly with rutile but remains fully accessible.

2.4.1.3. Effect of support on metal reducibility

The reducibility of the catalysts is related to the nature of support. Li *et al.* compared ZrO₂ and Al₂O₃ loaded with 10 wt% Co and found that ZrO₂-supported Co catalyst was significantly superior over the corresponding Al₂O₃-supported Co catalyst for CO₂ methanation, which was related to the fact that the reduction temperature of Co/ZrO₂ was much lower than that of Co/Al₂O₃. [78] For the Co/Al₂O₃, formation of the spinel CoAl₂O₄ was identified, which is regarded as non-active species in CO₂ hydrogenation [79] and leads to poor reduction of cobalt species on the 10Co/Al₂O₃.

2.4.1.4. Effect of support on basicity

The correlation between support basicity and CO₂ methanation activity has also been studied. For example, Muyoyama *et al.* prepared a series of supported nickel-based catalysts (Y₂O₃, Sm₂O₃, ZrO₂, CeO₂, Al₂O₃, La₂O₃) and found that Ni/Y₂O₃ with larger amount of medium basic sites exhibited the best activity.[80]

2.4.1.5. Effect of support on orienting the methanation mechanism

The CO₂ adsorption and activation ability of the support may directly

influence the CO₂ methanation mechanism. Cerda-Moreno *et al.* proposed different mechanisms for the Ni catalysts with different supports.[69] In Ni-todorokite catalysts, CO₂ easily adsorbs on the basic MnO_x support, and carbonate species are identified as additional intermediates. The carbonate species can be hydrogenated to formates and then hydrogenated to methane. On the contrary, in Ni-sepiolite catalysts, the support itself is not able to adsorb CO₂. H₂ is activated into H atoms on Ni particles, and then CO₂ is dissociative adsorbed on the same site. Consequently, linearly and bridged bonded carbonyl species are identified on Ni NP as the intermediates, and the latter is preferentially hydrogenated to methane. That is, there is a competition between the CO₂ dissociation and H₂ dissociation. The same cases was found by Cárdenas-Arenas *et al.* For the Ni/CeO₂, CO₂ dissociation and H₂ dissociation occur at the NiO-ceria interface and on reduced Ni⁰ particles, respectively, while for Ni/Al₂O₃, H₂ dissociation occurs on the same site with CO₂ dissociation.[81] In addition, they found that the RDS is the water desorption, as indicated by pulse experiments. For Ni/Al₂O₃, all the steps of the mechanism take place on the same active sites, and the slow release of water on these sites delays the further chemisorption of CO₂ molecules. In contrast, the NiO-CeO₂ interface is not blocked by water molecules because the formation of water does not necessarily occur on the CO₂ chemisorption sites, which is attributed to the presence of two types of active sites and to the high oxygen mobility throughout the ceria lattice.

2.4.2. Effect of promoters on CO₂ methanation Catalysts

While CO₂ methanation are often based on an active metal and a support, extensive literature data show that the addition of promoters, either directly to the metal active phase or to the support, is a useful and effective strategy to tune the key catalyst properties and reach higher catalytic performance. These promotion effects are reviewed below, focusing first on the promoters that are added to the active metal, and then on the promoters that accompany the catalyst support.

2.4.2.1. Promoters of the active metal

2.4.2.1.1. Ni-based catalysts

Supported Ni catalysts have been extensively studied for hydrogenation of CO₂ toward methane. Due to its low cost and highly selective toward methane, Ni-based catalysts are the most effective choice and have been widely investigated for industrial purposes. Various types of dopants have been reported for Ni, as reviewed below.

Ni-Fe catalysts. The effect of Fe metal as promoter on Ni-based catalyst has been widely studied. Introducing Fe into the Ni-based catalyst tends to form NiFe alloys, reportedly leading to synergistic effects between Ni and Fe.[82] Mutz *et al.* prepared an alumina-supported Ni-Fe catalyst via a deposition–precipitation method. A large fraction of the Ni and Fe formed the desired Ni₃Fe alloy resulting in small and well-defined nanoparticles of ~4 nm and a dispersion of 24%, which resulted in a better low-temperature performance compared to a monometallic Ni reference catalyst, especially at elevated pressures.[83]

Fe addition can also change the reducibility of support. Ren *et al.* prepared Ni/ZrO₂ catalysts containing a second metal by co-impregnation method. The addition of Fe enhanced the partial reduction of zirconia, further promoting CO₂ activation and leading to a higher catalytic activity at low temperature.[84] Furthermore, the active Ni surface sites of monometallic nickel-based catalysts are prone to surface oxidation (“passivation”) under hydrogen-deficient conditions. Iron can act as “protective” dopant. Indeed, Serrer *et al.* used operando X-ray absorption spectroscopy and X-ray diffraction with quantitative on-line product analysis to make a comparison of Ni/Al₂O₃ and Ni_{3.2}Fe/Al₂O₃ model catalysts under dynamic reaction conditions. They found that Fe act as “sacrificial” or “protective” metal, which protects Ni from oxidation as it is itself more dynamic in the oxidation and reduction process.[85]

Nickel-support interaction can be adjusted by Fe addition. Hwang *et al.* prepared a series of mesoporous Ni-M-alumina xerogel (35Ni5MAX) catalysts with different second metal (M = Fe, Zr, Ni, Y, and Mg) by a

single-step sol-gel method. Among the catalysts tested, 35Ni5FeAX catalyst, which retained the weakest metal-support interaction, showed the best catalytic performance in the carbon dioxide methanation reaction.[86] It has been reported that electron-deficient metal particles are more active in CO_x methanation reaction than electron-rich metal particles.[87] In the case of basic support, a strong metal-support interaction, which might generate a charge transfer between metal and support, should yield an electron-rich metal surface.

Addition of Fe can also influence the CO₂ methanation pathway. Huynh *et al.* studied the role of Fe combining in situ XRD, DRIFTS and DFT. The obtained results indicated the formate pathway was the most plausible reaction scheme on both Ni and NiFe alloy catalysts, but that a moderate addition of Fe facilitated the activation of CO₂ via hydrogenation to *HCOO (Fig. 2.4).[88]

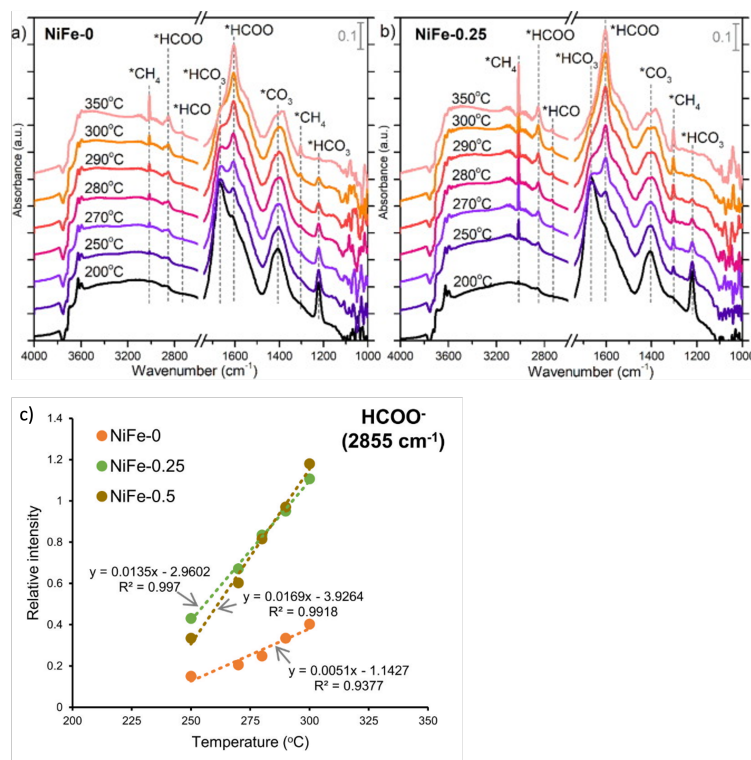


Fig. 2.4. In situ DRIFTS spectra of (a) NiFe-0 and (b) NiFe-0.25

catalysts under CO₂ methanation condition (CO₂/H₂/N₂ vol.% = 1/4/5) at increasing temperatures. c) Formation rate of adsorbed species formate HCOO from in situ DRIFTS spectra over NiFe-0, NiFe-0.25 and NiFe-0.5 under CO₂ methanation condition.[87]

Ni-Co catalysts. In addition to being used as the active phase, Co has also been employed as a promoter to the Ni-catalysts for CO₂ methanation. Liu *et al.* prepared ordered mesoporous Ni-Co/Al₂O₃ catalysts by the facile one-pot EISA method. The synergy between Ni and Co can not only improve the reducibility of Ni species but also reduce the metal particle size.[89].

Co addition can also facilitate the CO₂ activation. Xu *et al.* prepared ordered mesoporous Co-Ni-Al₂O₃ catalysts by a one-pot EISA method. A kinetic study demonstrated that the synergistic effect between Ni and Co could decrease the apparent activation energy by coordinating the activation of H₂ and CO₂ process over Ni and Co active centers (Fig. 2.5).[90]

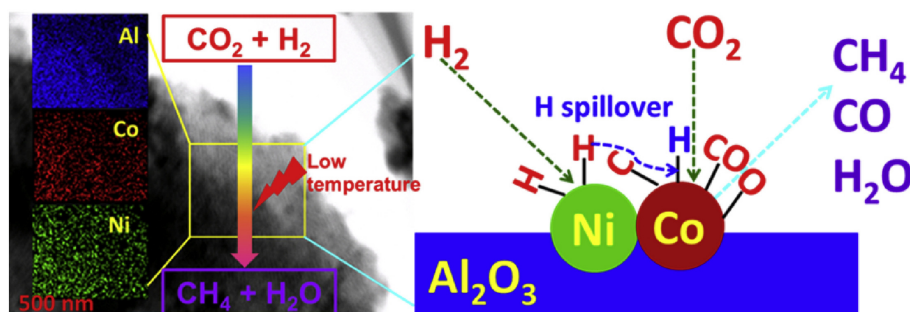


Fig. 2.5. STEM and EDS element mapping images of NiCo/Al₂O₃ catalyst and scheme of coordinating the activation of H₂ and CO₂ process over Ni and Co active centers.[89]

Ni-Ru catalysts. Ru is more active in CO₂ methanation than Ni, but it is also considerably more expensive.[91] Shang *et al.* prepared a series of Ni/Ce_xZr_{1-x}O₂ catalysts doped with Ru and found that CO₂ methanation performance at low temperature was enhanced, which could be attributed to the improved metal dispersion in bimetallic Ru-

Ni/Ce_xZr_{1-x}O₂ catalysts.[92]

Ru addition could also increase the surface basicity, especially the density of medium basic sites. Indeed, Bustinza *et al.* prepared NiRu/Al₂O₃ catalyst by consecutive adsorption method, which consists of 2–4 nm Ni nanoparticles with atomic Ru. According to the CO₂-TPD results, the density of medium basic sites in NiRu/Al₂O₃ catalyst was higher (0.301 mmol g⁻¹) than that in the pristine Ni/Al₂O₃ (0.138 mmol g⁻¹), leading to better performance for the former catalyst.[93]

H₂ chemisorption is found to be enhanced by Ru addition.[94] Liu *et al.* prepared ordered mesoporous NiRu-doped CaO-Al₂O₃ nanocomposites via a facile evaporation-induced self-assembly method. The ordered mesoporous catalyst exhibited enhanced catalytic activity and selectivity, owing to the improved H₂ chemisorption capacities after the addition of Ru promoter.[95] Ru addition also is reported to provide a higher supply of dissociated H₂. Quindimil prepared Ni-Ru/Al₂O₃ catalysts for CO₂ methanation. From the results of operando FTIR experiments, they found that in the bimetallic system, the potentially most reactive species is CO linearly adsorbed over Ru, and this species is more easily hydrogenated by H atoms. Ru could boost the Ni capacity to adsorb H atoms and thus enhance the catalytic performance.[96]

Ni-Rh catalysts. Rh addition in Ni-based catalyst could influence the methanation pathway. Wang *et al.* prepared RhNi/Al₂O₃ by galvanic replacement, exhibiting a 2-fold rate enhancement for CO₂ methanation relative to Rh/Al₂O₃. [97] Operando IR spectroscopy identified reactively formed CO from the dissociative chemisorption of CO₂ over Rh as the key intermediate for methane production, while the surface formate from the dissociative chemisorption of CO₂ and subsequent hydrogenation (via spillover from Rh sites) over alumina is a catalytic spectator because the subsequent hydrogenation of formate is extremely slow.

Ni-Pt catalysts. The addition of Pt into the Ni catalyst is expected to promote the dissociation of H₂, but this also has the potential to lead to

undesired side-reactions (e.g. reverse water-gas-shift reaction).[98, 99] Interestingly, the excellent selectivity toward CH₄ was shown to be maintained after adding Pt species into Ni-based catalyst. Kikkawa *et al.* reported on a Ni-Pt/Al₂O₃ catalyst, which exhibited a relatively high activity and selectivity for CH₄ evolution. the isolated-Pt species in the Ni-Pt alloy is to provide H₂ dissociation sites at low temperature, resulting in high CO₂ methanation activity.[100]

Ni-Mn catalyst. An efficient promoter element for Ni-based catalysts is Mn. Mn addition was shown to enhance the Ni²⁺ reducibility by weakening the interaction between the Ni-oxide precursor and the support.[101, 102] Lower reduction temperature is beneficial to improve the Ni dispersion. In the same vein, Zhao *et al.* observed higher Ni dispersion of Mn-promoted 15 wt% Ni/Al₂O₃ catalysts prepared by an incipient wetness impregnation method. Additionally, the presence of Mn was shown to increase the number of CO₂ adsorption sites.[103] The idea of improving CO₂ adsorption capacity and facilitating CO₂ activation by adding manganese has been strongly supported by several studies.

Li *et al.* synthesized Mn-promoted Ni nanoparticles (NPs) supported on oxygen-functionalized carbon nanotubes (CNTs). Mn promotion notably boosted the activity compared with unpromoted catalysts, which was associated to the enhanced CO₂ adsorption.[40] Burger *et al.* prepared an equimolar NiAlO_x benchmark catalyst (44 wt.% Ni loading) and modified it by doping with Fe or Mn up to 10 wt.% of promoter by co-precipitation. They observed that promotion with Mn led to a significant enhancement of the catalytic activity, which was shown to be attributed to a higher density of medium basic sites and an enhanced CO₂ adsorption capacity.[53] Vrijburg *et al.* observed a similar phenomenon for NiMn/TiO₂ prepared by a wet-impregnation method.[104] The obtained NiMn-based catalysts consist of metallic Ni particles decorated by oxidic Mn²⁺ species. Apart from the function of enhancing CO₂ adsorption, the existence of Mn²⁺ species was thought to also facilitate CO₂ activation. Indeed, the observed higher rate of CO₂

methanation for NiMn catalysts was related to more facile CO₂ activation, enabled by the oxophilic nature of defect sites on MnO. Wu *et al.* also reported Mn-modified Ni catalysts supported on Al₂O₃–ZrO₂, prepared via a single-step sol-gel method. In the low temperature CO₂ methanation, the addition of Mn was shown to facilitate the formation of surface oxygen vacancies, which is beneficial to the CO₂ activation, thus improving the low temperature CO₂ methanation performance significantly.[105]

Ni-alkaline earth metal oxides catalysts. The main role of alkaline earth metal oxides as promoter for Ni-based catalyst is to modify the surface basicity.[106] Yang *et al.* reported that the addition of MgO could obviously promote the number and the strength of the basic sites, which intensified the CO₂ adsorption and activation. Thus, the apparent activation energy of MgO-doped Ni-based catalysts in CO₂ methanation evidently decreased and the low-temperature activity was greatly promoted.[76] Ca has a similar role. Xu *et al.* fabricated a series of Ca doped ordered mesoporous Ni-Al composite oxides by a one-pot EISA strategy. The doping was shown to remarkably increase the surface basicity, driving effective chemisorption of CO₂. [107] The CO₂ conversion rapidly increased and finally reached the maximum point at 8% when the Ca/Al molar ratio gradually increased from 0% to 8%. Nevertheless, the CO₂ conversion suffered some decline when the Ca/Al molar ratio further increased to 10%.

Mg addition was also claimed to increase Ni dispersion. Bacariza *et al.* studied the CO₂ methanation over Ni–Mg–USY zeolite catalysts. At relatively low Mg contents (below 2.5 wt%), an enhancement of the CO₂ conversion into methane of 15% at 350–450 °C was obtained mainly due to the induced increase of the Ni particle dispersion, as well as the possible activation of CO₂ on the defects present on the MgO surface. However, higher contents of Mg (over 5.6 wt%) had a reverse effect due to the formation of NiO–MgO solid solutions, reducing the reducibility of the Ni species and decreasing the amount of metallic nickel available to form active sites and thus the catalytic

performance.[108]

Ni-La catalysts. La_2O_3 was also used as promoter for Ni-based catalysts.[109-112] Zhang *et al.* prepared La-promoted Ni/Mg-Al catalysts using a urea hydrolysis method. The unpromoted Ni-based catalyst showed poor Ni dispersion with Ni particles 8.16 nm. After doping with La, the Ni particles were uniformly dispersed on the catalysts and the Ni particle sizes became smaller. In the study, the catalyst doped with 5 wt.% of La exhibited the smallest Ni particle size (6.57 nm).[109] A group of La-modified mesostructured cellular foam (MCF)-derived nickel phyllosilicates was synthesized by a hydrothermal method followed by the impregnation of La_2O_3 . The formed nickel phyllosilicate was beneficial to obtain small Ni nanoparticles (<5 nm) due to its strong metal-support interaction and high specific surface area; the addition of the La_2O_3 modifier was shown to further reduce the Ni particle size.[110] As a result, the nickel phyllosilicate catalyst showed higher catalytic activity than the impregnated one, and the La modifier could further improve the catalytic activity especially at low temperature. It should be noted that the method used to incorporate La_2O_3 can have a noticeable effect on the structures of the catalysts and their catalytic performances. For example, Wang *et al.* prepared a Ni- La_2O_3 /SBA-15 catalyst by a citrate complex method. The prepared catalyst showed a high dispersion of Ni with a small particle size less than 5 nm, which is one-third of the particle size of that prepared by conventional impregnation method.[112]

Modifying the basicity of the catalyst is another significant role of La promoter. Quindimil *et al.* reported that the surface basicity of Ni/BETA zeolite catalysts were considerably promoted by impregnation of La_2O_3 , which increased the amount of CO_2 adsorption sites and even active hydrogenation sites resulting in a significant increase of activity and selectivity towards CH_4 . [113] La could significantly increase the amount of moderate basic sites.[109, 114, 115] Wierzbicki reported that hydrotalcite-derived Ni-based catalyst and the corresponding La-

promoted catalysts showed very high activity in CO₂ methanation. A considerable increase in the amount of medium-strength sites as well as the total number of basic sites (almost double) were observed for the later one. [115]

In some cases, La addition also has an influence on the CO₂ methanation pathway. Ho *et al.* studied the interaction of CO₂ with NiAl and NiLaAl catalysts by DRIFTS. The activation of CO₂ on the surface occurs by both dissociative (CO_{ads} on Ni⁰ particles) and associative (formation bicarbonate and carbonate on the support) pathways over both NiAl and NiLaAl. The addition of La, however, modifies the CO₂ interaction with the catalysts. For NiLaAl, CO₂ is simultaneously activated on both Ni and the support, resulting in the concomitant formation of carbonyl and bicarbonate/carbonate (Fig. 2.6), while for NiAl, these two steps process separately. A higher contribution of the associative mechanism (i.e. carbonate and bicarbonate intermediates) over NiLaAl was proposed to explain its higher activity at lower temperatures.[111]

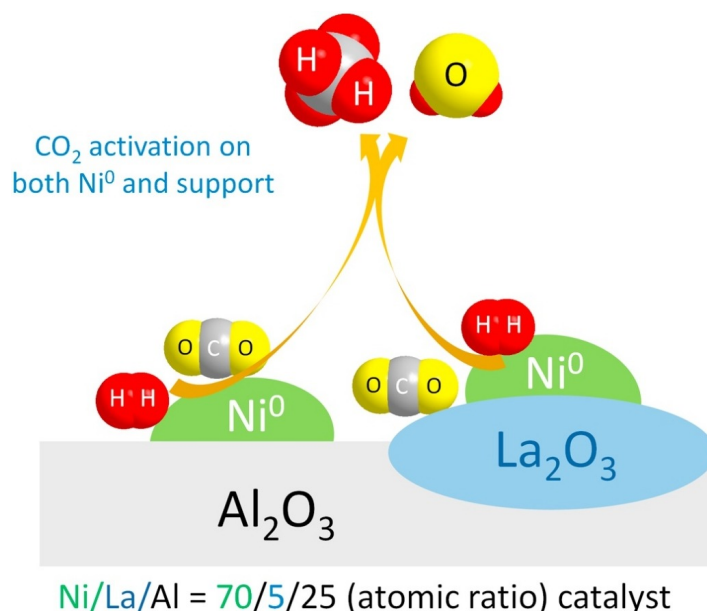


Fig. 2.6. Scheme of CO₂ adsorption and hydrogenation on the NiLaAl catalysts.

It should be noted that the promoter addition needs to be adapted, depending on the chosen support. Riani *et al.* found that the activity of Ni/Al₂O₃ catalyst increased firstly and then decreases with the La addition loading (14% > 4% > 37% > 0% wt. La₂O₃). However, the presence of SiO₂ allowed the dispersion of higher lanthanum loading, i.e. 37% wt. La₂O₃, giving rise to even higher performances.[116]

Ni-Ce catalysts. CeO₂, in addition to be applied as support, has also been widely employed as a promoter to the catalysts for CH₄ methanation. The most important function of Ce oxide is its electronic promotion. Ce is able to store and release oxygen (a redox property), which helps creating an appropriate electron transfer environment and therefore additional driving force for CO₂ activation. Li *et al.* prepared cerium-modified Ni-La₂O₃/ZrO₂ catalysts using a perovskite phase as the precursor. They found that Ce modification resulted in the introduction of oxygen vacancies and improved the effective activation of CO₂, thus enhancing the CO₂ methanation activity at low temperature.[117] In addition, the oxygen vacancies are likely to release free electrons, which migrate from the CeO₂ to the metallic Ni centers through the Ni-CeO₂ interface, thus increasing the d-electron density of the Ni atom.[118] The electron-rich character of the Ni atoms naturally inhibits the cracking of CH₄, which is the reverse reaction of CO₂ methanation.[119]

Ce addition can also be used to help shaping the catalyst structure. Darouhegi *et al.* prepared ceria-promoted Ni-Al₂O₃ catalyst by ultrasound assisted coprecipitation method. The addition of Ce led to the formation of larger mesopores in the prepared samples and stronger interaction between nickel species and alumina, resulting in the formation of smaller Ni crystallite size with high dispersion on the catalyst surface. Moderate basic site were observed after introducing the Ce promoter, which was beneficial to the adsorption and activation of CO₂. Furthermore, the redox properties of CeO₂ favored carbon removal. Specifically, the electron transition between Ce⁴⁺ and Ce³⁺ provides the well oxygen storage capacity in CeO₂ and oxidation of

carbonaceous species by oxygen anions lead to removal of the deposited coke during the CO₂ methanation reaction.[120]

The order of metals introduced into bimetallic catalytic systems has been shown to be important.[121, 122] Bacariza *et al.* studied the effect of the Ce incorporation order used in the preparation of Ni-based catalysts supported by ultra-stable Y (USY) zeolite for CO₂ methanation. Co-impregnation led to stronger interactions between Ni and Ce species, improving the reducibility of the Ni species and reducing the Ni average size to about 2.5 nm. even if the same result was observed when the incorporation of Ce was done before Ni, the CO₂ adsorption capacity of this catalyst was smaller due to the blockage of some Ce particles by the Ni particles. On the contrary, when Ni was impregnated first the CO₂ adsorption capacity remained comparable to that obtained for the co-impregnation catalysts but larger Ni particles (13.3 nm) were formed. Thus, in this example, co-impregnation was identified as the best preparation method.[123]

Table 2.1. Summary of the effect of different promoter on the Ni-based catalysts.

promoter	role	function
Fe	formation of Ni ₃ Fe alloy	lead to the formation of small and well-defined nanoparticles
	-	improve the reducibility of reducible support
	“sacrificial” or “protective” metal	protect Ni from oxidation
	adjust metal-support interaction	form an electron-deficient metal
	-	facilitate the format pathway
Co		reduce the metal particle size

		improve the reducibility of Ni species
	coordinating the activation of H ₂ and CO ₂ process	facilitate the CO ₂ activation
	-	increase the Ni dispersion
	-	increase the amount of medium basic sites
Ru	provide the site for H ₂ adsorption and dissociation	enhance H ₂ chemisorption
Rh	-	facilitate the RWGS+CO hydrogenation pathway
Pt	provide the site for H ₂ adsorption and dissociation	promote the dissociation of H ₂
	weak the metal-support interaction	improve the reducibility of Ni species
Mn	-	increase the amount of total basic site
	formation of oxygen vacancy	facilitate the CO ₂ activation
Mg	-	increase the surface basicity
	-	reduce the Ni particle size
	-	increase the amount of medium basic sites
	-	enhance the RWGS+CO hydrogenation pathway
	introduction of oxygen vacancy	facilitate the CO ₂ activation
Ce	-	increase the amount of medium basic site

2.4.2.1.2. Co-based catalysts

Apart from Ni-based catalysts, Co was also tested to determine the potential of catalyzing CO₂ methanation reaction.[26, 124-128]

Co-Pt catalyst. Pt and other precious metals are known to promote Co catalysts for CO₂ methanation and Fischer-Tropsch synthesis. Like the function of Pt addition in Ni-based catalyst, Pt addition in Co-based catalyst could also provide the site for H₂ dissociation and thus increase the catalytic performance (Fig. 2.7).[129] Furthermore, the presence of nearby Pt NPs is able to significantly enhance reduction of the Co at temperatures relevant to CO₂ methanation. Beaumont *et al.* studied the promotional effect of Pt, using a realistic model which contains discrete monometallic NPs of both Pt and Co deposited in close proximity within the pores of a mesoporous silica, MCF-17. Pt NPs deposited near Co NPs can enhance the CO₂ methanation rate by up to a factor of 6 per Co surface atom, which is due to the higher reducibility of Pt-Co alloyed NPs revealed by the in situ NEXAFS spectroscopy.[130]

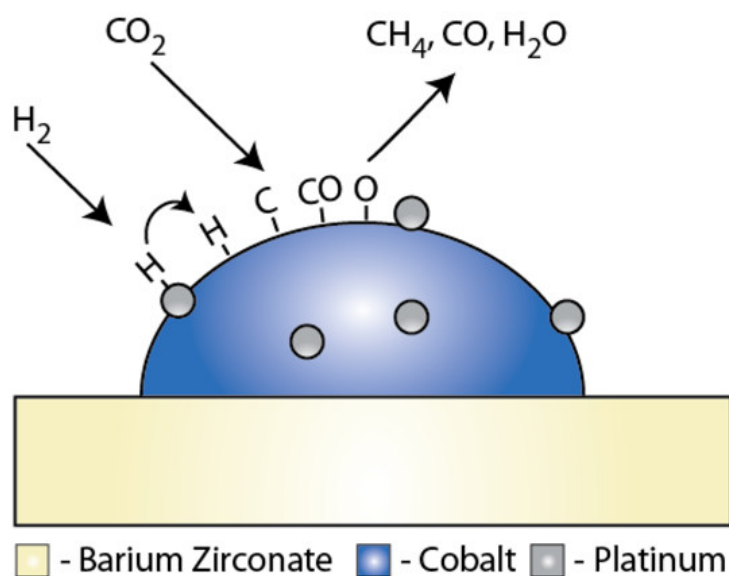


Fig. 2.7. Scheme of CO₂ adsorption and hydrogenation on the Co-Pt catalysts. [128]

Co-Zr catalyst. Tu *et al.* reported an amorphous Co-Zr catalyst for CO₂

methanation, the activity of which reached $10.7 \text{ mmol}_{\text{CO}_2} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ at 180°C with a methane selectivity of 97.8%. The promoting factor brought by Zr in the Co-Zr catalyst was as high as 12.3, which was attributed to the fact that Zr addition resulted in an increased surface area and increased the Co surface concentration.[131]

Zhou *et al.* prepared Zr-Co₃O₄ catalyst for CO₂ methanation. Compared to pristine Co₃O₄, the Zr-Co₃O₄ exhibited a higher CO₂ conversion and CH₄ selectivity. Apart from the effect of Zr on the structure, i.e., decreasing the crystallite sizes of Co and increasing the surface area, the addition of Zr was shown to change the reducibility of Co₃O₄ significantly and to provide more active site. Moreover, the introduction of Zr also changed the surface basicity. The basic intensity of weak and medium basic sites increases over the surface of Zr-Co₃O₄ catalyst.[132]

Co-alkaline earth metal oxides catalyst. In contrast to the positive role of alkaline earth metal oxides addition on the Ni-based catalysts, Mg and Ca addition were shown to decrease the CO₂ methanation performance of Co-based catalyst. Zhang *et al.* prepared the Co/Al₂O₃ catalysts modified by Mg and Ca. Mg species reacted with alumina, forming MgAl₂O₄ spinel structure, leading to the re-structuring of the catalysts and a remarkable decrease of the specific surface area. In addition, the alkaline earth metals additives remarkably enhanced the affinity of catalyst to the reaction intermediates such as HCOO* and CO₃²⁻, slowing down their further reduction to CH₄. [133]

Table 2.2. Summary of the effect of different promoter on the Co-based catalysts.

promoter	role	function
Pt	provide the site for H ₂	promote the dissociation
	adsorption and dissociation	of H ₂
		enhance the reduction of Co
Zr	increased the Co surface concentration	increase the active site

	-	increase the reducibility
	-	increase the amount of weak and medium basic site
Mg, Ca	-	negative effect (inhibit the format pathway)

2.4.2.1.3. Fe-based catalysts

Comparing to Ni- and Co-based catalysts, Fe-based catalysts have not gained much attention for methanation possibly due to their lower selectivity towards CH₄, although they bring in certain advantages, such as environmental compatibility, high abundance, and considerably lower costs[134]. Baysal *et al.* evaluated Fe catalysts for CO₂ methanation with a special focus on suitable promoters to achieve enhanced yield of CH₄. A wide range of potential promoters, i.e., alkali, earth alkali, transition, rare earth and group III metals, were investigated using an active α -Fe₂O₃ as base catalyst, and Mg was found as the most effective promoter. It was proposed that the strong carbon adsorptive property of MgO promotes the adsorption and dissociation of CO₂. Furthermore, Mg promoter could increase the BET surface areas and total pore volumes, resulting in the formation of more bulk carbon moieties during CO₂ hydrogenation. These additional carbon deposits were proposed to eventually incorporate into the carbidic bulk, which led to particle disintegration, formation of more catalytically active sites and enhanced CH₄ formation.[29]

2.4.2.1.4. Ru, Rh-based catalysts

There are not many reports on the metal doped Ru- and Rh-based catalysts for the CO₂ methanation, since Ru, Rh-based catalysts themselves exhibit high performance even at lower temperature. In most power-to-gas (PtG) applications, CO₂ comes from conventional capture technologies, which often rely on the use of an aqueous amine-based sorbent and solid adsorbents. However, to regenerate the adsorbent and release captured CO₂ is energy intensive. To increase the

efficiency of whole process and reduce the cost, one of the possible solutions is the combination of capture and hydrogenation process using the “dual functional materials” (DFM). The DFM used for CO₂ adsorption and methanation is composed of alkali metal oxide and alkaline earth metal oxides for CO₂ adsorption and Ru and Rh for CO₂ methanation. There are many research and reviews on this aspect[135-139], we will not make a detailed description in here.

2.4.2.2. Promoters in the reducible support

2.4.2.2.1. ZrO₂ addition.

Iglesias *et al.* prepared 15 at.% Zr-doped ceria supports by precipitation and then used it to prepare Ni/Ce_{0.85}Zr_{0.15}O₂ catalyst by impregnation method. A higher reaction rate was determined for the Zr-doped catalyst. In addition to a higher Ni dispersion in Ni/Ce_{0.85}Zr_{0.15}O₂, the reducibility of this sample led to the notable improvement of the catalytic activity. Furthermore, the beneficial effect of Zr on the catalyst stability was ascribed to higher oxygen mobility and the consequent enhancement of gasification reactions.[140]

Moon *et al.* manufactured a series of Ni-Ce-Zr ternary disk-shaped catalysts using a simple mixing method. These showed excellent catalytic performance for CO₂ methanation. The oxygen storage capacity was enhanced by the Ce-Zr composite, which was beneficial to the CO₂ adsorption. In addition, the reactive metals in Ni-Ce-Zr catalyst distributed evenly, which successfully prevented the occurrence of the sintering phenomenon.[119]

2.4.2.2.2. Cr addition.

Xu *et al.* reported that the CO₂ methanation activity of a Ru/CeO₂ catalyst can be enhanced by doping Cr cations in the support, with the turnover frequency value on Ru/Ce_{0.9}Cr_{0.1}O_x at 150 °C being 5.3 times higher than that on Ru/CeO₂. [141] More reactive surface oxygen species and hydroxyl group formed on the Ce_{0.9}Cr_{0.1}O_x support due to the Cr³⁺ doping in the lattice of the CeO₂ support, thus increasing the

amount of bicarbonates and formates.(Fig. 2.8). Consequently, Cr doping strongly promoted the formate pathway, greatly improving the activity of the Ru/Ce_{0.9}Cr_{0.1}O_x catalyst at low temperatures.

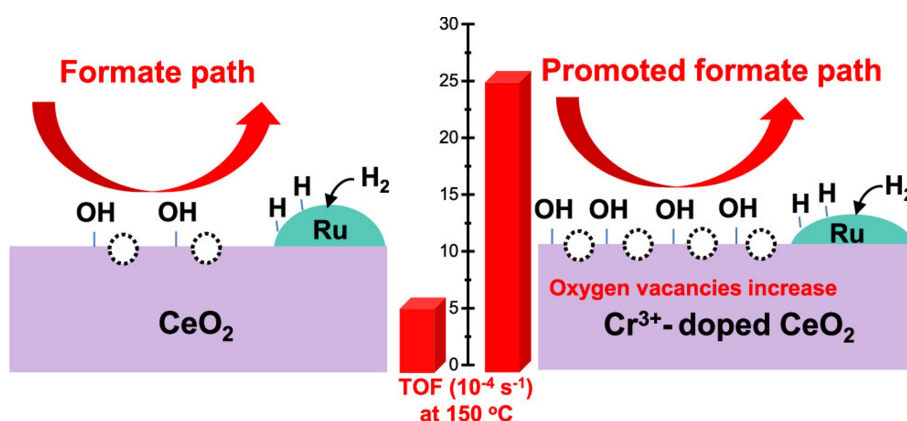


Fig. 2.8. Scheme of effect of Cr dopant on the amount of surface hydroxyl group and oxygen vacancy.[140]

2.4.2.2.3. Y₂O₃ addition.

Zhu *et al.* prepared Y₂O₃-promoted NiO-CeO₂ catalysts, which exhibited an outstanding methanation activity that is up to three folds higher than the corresponding NiO-CeO₂ and six folds higher than NiO-Y₂O₃ at mild reaction temperatures (<300 °C).[142] Combining theoretical and experimental methods, they found that the introduction of Y₂O₃ to CeO₂ greatly facilitated the generation of surface oxygen vacancies during the reaction (Fig. 2.9), and these sites promoted the direct dissociation of CO₂, which is kinetically more favorable than the associative route.

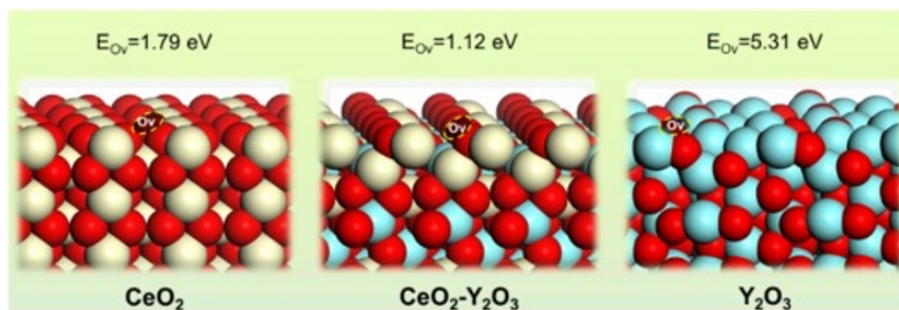


Fig. 2.9. Schematic representations of CeO_2 , $\text{CeO}_2\text{-Y}_2\text{O}_3$, and Y_2O_3 , as well as their oxygen vacancy formation energy values (E_{Ov}). Yellow, blue and red spheres are Ce, Y and O atoms, respectively (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Takano *et al.* carried out the catalytic methanation of CO_2 on Ni catalysts supported on Y-doped ZrO_2 , which showed higher catalytic activity than the Ni catalyst supported on pristine ZrO_2 . The highest activity was obtained when the $\text{Y}/(\text{Zr}+\text{Y})$ molar ratio was 0.333. At this composition, the number of oxygen vacancies was maximum. The oxygen vacancies in the oxide contributed to the formation of bidentate carbonate and formate adsorption species, which are the main adsorption species under the reaction condition at $T \geq 300^\circ\text{C}$. [143]

Qin *et al.* prepared the $\text{Co}/\text{Y-TiO}_2$ catalysts by the precipitation-deposition method and investigated the effects of Y on the catalytic performance and stability. Y addition affected the TiO_2 pore structure and increased the specific surface area of the catalysts. Besides, Y addition increased the reducibility of Co_3O_4 . In addition, the CO_2 adsorption and activation were enhanced due to the increase of surface basicity and oxygen vacancies after Y doping. [144]

2.4.2.2.4. Gd addition.

Frontera *et al.* studied the role of Gd-doping in CeO_2 support on the promotion of CO_2 methanation over Ni catalyst. They found that the Gd-doped CeO_2 support was prone to generate surface oxygen

vacancies able to weaken the carbon-oxygen bond of CO₂ adsorbed on Ni sites and to increase its dissociation.[145]

2.4.2.2.5. Other addition (Sm, Pr, Mg).

Siakavelas *et al.* compared the catalytic performance, in terms of activity and stability, of Ni catalysts based on Sm-Ce, Pr-Ce and Mg-Ce with a Ni/Ce catalyst for the CO₂ methanation reaction. It was found that Sm³⁺, Pr³⁺ and Mg²⁺ addition led to the formation of smaller Ni nanoparticles. Also, the addition of Sm³⁺ or Pr³⁺, incorporated into the lattice of CeO₂, generated oxygen vacancies. The addition of Mg²⁺ resulted in stronger metal support interactions reinforcing the resistance of the Ni/Mg-Ce catalyst against sintering. Moreover, the addition of Sm³⁺, Pr³⁺ and Mg²⁺ increased the overall basicity and the amount of moderate adsorption sites. These physico-chemical properties enhanced CO₂ methanation reaction.[146] The improvement effect of Pr addition was also observed for Ru/CeO₂ catalysts. Sergio *et al.* prepared Ru catalysts with Pr-doping (3 wt%) CeO₂ supports, which was shown to be moderately more active than pristine Ru/CeO₂ from 250 °C onward.[147] On the contrary, high Pr concentration had a negative effect on the catalytic activity, which was attributed to the fact that the negative effect on the Ru-CeO₂ interaction overcompensated the positive effect in oxygen mobility in the ceria support.

2.4.2.2.6. Ca addition.

Everett *et al.* synthesized Ni/CaZrO₂ by wet impregnation method. Ca²⁺ was inserted in the ZrO₂ lattice surface of the support, leading to the formation of oxygen vacancies and coordinatively unsaturated sites pairs. Increasing the concentration of these pairs was shown to facilitate the CO₂ adsorption and activation.[148] Petala *et al.* investigated the effect of alkali promotion of TiO₂ on the CO₂ methanation activity and selectivity of dispersed Ru catalysts. It was shown that the CO₂ methanation activity of Ru/TiO₂ catalysts can be enhanced significantly by the addition of small amounts of alkalis (Li, Na, K, Cs) on the TiO₂ support, with the Na-promoted sample showing the best catalytic

performance and being around 3 times more active compared to the unpromoted catalyst. This was proposed to be due to the promotion of CO intermediate hydrogenation to CH₄ over better dispersed Ru particles.[149] The following research from the same group indicated the alkali additives also has an effect on the reaction pathway. Results showed that hydrogenation of CO₂ proceeds with intermediate formation of carbonyl species via the RWGS reaction, the nature of which vary significantly in the presence of alkalis. Alkali addition results in an increase of the relative population of carbonyl species adsorbed on reduced Ru sites, which is responsible for the improved CO₂ methanation activity.[150]

2.4.2.2.7. Carbonate addition.

Dai prepared La₂O₂CO₃-supported Ni NPs atmospheric CO₂ methanation reaction, and their catalytic performance is superior than that of Ni/La₂O₃ catalyst.[151] Surface carbonate species could provide moderate basic sites contributing to the high ability for CO₂ chemisorption and activation. Besides, the carbonate-modified interface facilitates the formation of monodentate and bidentate formates as the reaction intermediates (Fig. 2.10), which are highly reactive for further transformation into CH₄.

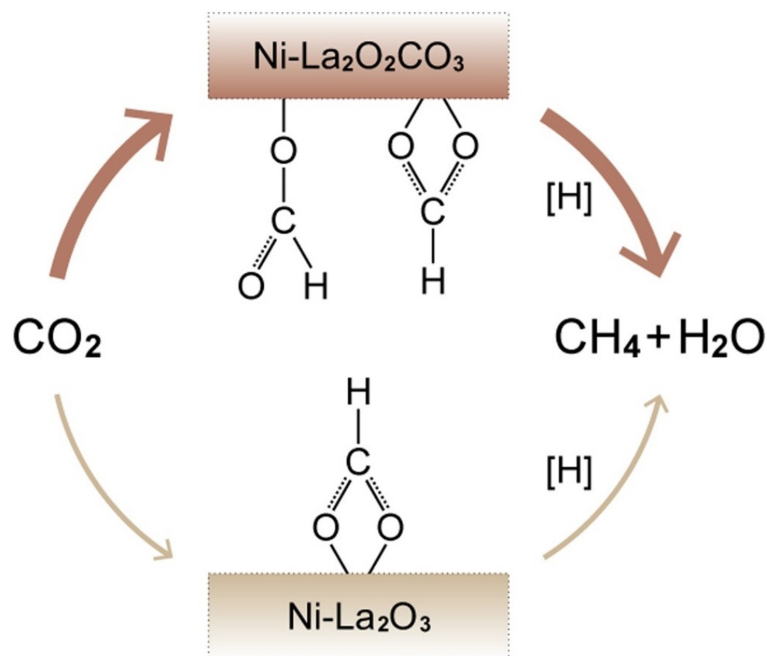


Fig. 2.10. Scheme of effect of carbonate addition on the CO₂ adsorption.

Table 2.3. Summary of the effect of different addition to reducible supports.

addition	support	role	function
Zr addition	CeO ₂	higher Ni dispersion	increase the amount of active site
		higher oxygen mobility	
Cr addition	CeO ₂	more surface oxygen vacancy	promote the CO ₂ dissociation
			increase the amount of weak basic site
Y addition	CeO ₂	more surface oxygen vacancy	promote the CO ₂ dissociation

		higher specific surface area	
	TiO ₂		increase the reducibility of Co ₃ O ₄
			higher surface basicity
		more surface oxygen vacancy	promote the CO ₂ activation
Gd addition	CeO ₂	more surface oxygen vacancy	promote the CO ₂ activation
		smaller Ni nanoparticles	more active site
Sm, Pr, Mg addition	CeO ₂		more medium basic site
		more surface oxygen vacancy	promote the CO ₂ activation
Ca addition	ZrO ₂	smaller Ni nanoparticles	more active site
Na addition	TiO ₂		enhance the RWGS+CO hydrogenation pathway
carbonate addition	La ₂ O ₃		enhance the formate pathway

2.4.2.3. Addition to non-reducible supports

2.4.2.3.1. TiO₂ addition.

Xu *et al.* prepared a TiO₂-modified Al₂O₃ materials by a wet-impregnation method and used it as the support for ruthenium-based methanation catalyst. The Ru/TiO₂-Al₂O₃ catalytic system exhibited a much higher activity (0.59 mol_{CO2} g_{Ru}⁻¹ h⁻¹) in CO₂ methanation reaction, which was ~3 times higher than that on Ru/Al₂O₃ (0.19 mol_{CO2} g_{Ru}⁻¹ h⁻¹). The strong interaction between Ru and the rutile-TiO₂ support hindered the aggregation of Ru nanoparticles and thus formed the smaller particle size of ruthenium, which resulted in the improved activity over Ru/TiO₂-Al₂O₃ catalyst.[152] Janlamoo *et al.* synthesized different silica-based supported Co catalysts and used for CO₂

methanation. They found that CoTiMCM catalyst exhibits the highest activity and selectivity, which is attributed to the presence of Ti facilitating the reduction of cobalt oxide species and inhibiting the RWGS.[153]

2.4.2.3.2. ZrO₂ addition.

Lin *et al.* synthesized mesoporous Ni/Al₂O₃-ZrO₂ catalysts by a single-step sol-gel method, which displayed superior lower-temperature activity, CH₄ selectivity and excellent CO₂ methanation stability when compared to pristine Ni/Al₂O₃. ZrO₂ addition was shown to weaken the Ni-Al₂O₃ interaction via the formation of Al₂O₃-ZrO₂ solid solution, increasing the reducibility of NiO. Oxygen vacancies on the composite support increased with the addition of Zr, improving obviously the lower temperature catalytic activity and CH₄ selectivity. In addition, oxygen vacancies provided by the ZrO₂ promoter and the enhanced stability of the Al₂O₃-ZrO₂ support promoted the catalyst stability.[154] Similar results were obtained by Zhan *et al.*. They prepared ZrO₂-doped Ni/Al₂O₃ catalysts by a co-precipitation method. The introduction of ZrO₂ suppressed the formation of NiAl₂O₄ effectively due to the formation of γ -(Al, Zr)₂O₃, leading to the highest activity for the CO₂ methanation.[42] He *et al.* developed a novel Ni-Zr-Al catalysts derived from Ni-Zr-Al ternary hydrotalcites synthesized by a hydrothermal process. The Ni-Zr-Al catalysts showed a remarkably higher low-temperature activity comparing with the Ni-Al catalyst derived from Ni-Al hydrotalcite and with a commercial Ni-based catalyst. This was proposed to be due to the introduction of Zr into the Ni-Al binary hydrotalcite that generated synergetic effects between Ni and ZrO₂, resulting in more surface oxygen vacancies, basic sites, and abundant mesopores (Fig. 2.6a and 2.6b).[155] Yang *et al.* prepared a special catalyst support Zr(x)@MCM-41 by hydrothermal synthesis with in-situ doping of Zr and used it as support to prepare a series of Ni/Zr(x)@MCM-41 catalyst by citric-acid-assisted impregnation. The strengthened interaction between Zr and Ni facilitated the spillover of H absorbed on Ni to the support, promoting the hydrogenation of CO₂

and CO_{ad} intermediates on the support and increasing the CO_2 conversion at low temperature. Simultaneously, the addition of Zr also inhibited the carbon deposition by decreasing the amount of strong basic sites and increasing the amount of surface oxygen species on the surface, which slightly improves the CH_4 selectivity.[156]

2.4.2.3.3. SiO_2 addition.

Moghaddam *et al.* prepared a series of nanocrystalline mesoporous $\text{Ni}/\text{Al}_2\text{O}_3\text{-SiO}_2$ catalysts by the sol-gel method for CO_2 methanation. With the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio, the catalytic performance greatly enhanced, especially at low temperatures due to the obtained improvements in reducibility of the catalysts.[157] Conversely, Riani *et al.* found a negative effect of SiO_2 addition. They found that the addition of Si in Al_2O_3 support decreased the activity of Ni catalysts in CO_2 methanation. This is probably attributable to a lowered CO_2 adsorption. However, for the La-doped $\text{Ni}/\text{Al}_2\text{O}_3\text{-SiO}_2$ catalysts, the presence of SiO_2 allowed the dispersion of higher lanthanum loadings, indicating again that the promoter addition needs to be tailored on the basis of the chosen support.[116]

2.4.2.3.4. Mn addition.

Franken *et al.* reported that spinel based solid solutions are suited to be used as catalyst precursor species for Co based methanation catalysts, and that higher activity could be obtained after modifying their reducibility by the introduction of manganese species. At 300 °C, the catalyst productivity of $\text{CoMn}_{0.5}\text{Al}_{1.5}\text{O}_4$ was 0.6 mol/(mol min), which was significantly higher, by a factor of 24, than that of CoAl_2O_4 (0.025 mol/(mol min)). Mn addition was shown to change the reaction site and pathway from the Co metal surface solely via a CO-mediated reaction path towards the surface of the support via a formate mediated reaction mechanism. Besides, the dissociative CO_2 adsorption was suppressed on the Mn-modified spinel precursor, decreasing the formation of CO as a by-product. Furthermore, the enabled hydrogen spillover (Fig. 2.6d), potentially due to its $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox pairs, facilitated CO_2

hydrogenation on the surface of the support.[41]

2.4.2.3.5. Ca addition.

Yang *et al.* prepared CaO-modified Ni/Al₂O₃ and applied it for the methanation of CO₂. The CaO-modified Ni/Al₂O₃ showed better catalytic activity than pure Ni/Al₂O₃. CaO addition can effectively restrain the growth of NiO nanoparticles (i.e. improve the dispersion of NiO) and weaken the interaction between NiO and Al₂O₃. In addition, CaO can change the environment surrounding of CO₂ and H₂ adsorption and thus the reactants on the Ni atoms can be activated more easily.[158]

2.4.2.3.6. La₂O₃ addition.

Phuoc *et al.* prepared a hydrotalcite-derived high loading Ni-Al₂O₃ catalyst and modified it by La. The La modified catalyst achieved a more relevant activity enhancement at low temperature and high space velocity (480 L g⁻¹ h⁻¹, CO₂/H₂/N₂ = 1/4/1 v/v), high CH₄ productivity (101 L_{CH₄} g_{Ni}⁻¹ h⁻¹) and stability. Despite the high Ni loadings, patches of La₂O₃ in Al₂O₃ contributed to the CO₂ associative activation.[111] Mihet *et al.* prepared Ni/La₂O₃-SiO₂ by successive impregnation of silica matrix, showing a good catalytic performance for CO₂ methanation. The La₂O₃ addition was shown to increase the Ni dispersion and provide more moderate strength basic sites, which was beneficial to the H₂ and CO₂ activation.[159]

2.4.2.3.7. Addition to Zeolite.

The utilization of zeolites as supports for the CO₂ methanation catalysts preparation was thoroughly reviewed by Bacariza *et al.*[160] and so this will be only briefly mentioned here, focusing only on doping effects. Zeolites are crystalline microporous aluminosilicate minerals, accommodating a wide variety of cations. The general formula M_xAl_xSi_{1-x}O₂·yH₂O where M is either a metal ion (Na⁺, K⁺, Ca²⁺, Mg²⁺) or H⁺. The Si/Al ratio is adjustable, and these positive ions are rather loosely held and can readily be exchanged for others in a contact solution. The metal ions and one of Si and Al could be regarded as

dopant, and literally, the different kinds of metal ions and Si/Al ratio have influence on the performance of zeolite-supported catalysts.

Bacariza *et al.* prepared a series of HUSY zeolite supported Ni catalysts and studied the effect of different compensating cations.[161] The results showed that the order of improvement of the catalytic performances is $\text{Cs}^+ > \text{Na}^+ > \text{Li}^+ > \text{H}^+$ for the monovalent cations and $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+}$ for the divalent. The compensating monovalent cations did not influence the reducibility and Ni particle size. Therefore, the different catalytic performance for the samples with different monovalent cation was attributed to the enhancement of the CO_2 adsorption capacity and framework basicity of the zeolites. For divalent cations, apart from the enhancement of CO_2 adsorption and activation, Mg^{2+} also decreased the Ni particle size, leading to a better performance compared to Ca^{2+} and Ba^{2+} .

Regarding the effect of the Si/Al ratio, Bacariza *et al.* found that the catalytic performances were improved by increasing the Si/Al ratio of USY zeolites whatever the compensating cation.[162] Higher Si/Al ratios led to more hydrophobic materials, while zeolites basicity was considerably higher for lower Si/Al ratios. That is, the hydrophobicity of sample is also a key parameter to explain the performance enhancements considering H_2O may play an inhibitory role in the reaction.

Table 2.4. Summary of the effect of different addition to non-reducible supports.

addition	support	role	function
TiO ₂ addition	Al ₂ O ₃	strong interaction between Ru and the rutile-TiO ₂ support	smaller particle size
	SiO ₂		increase the reducibility of Co
ZrO ₂	Al ₂ O ₃	weak the interaction	increase the

addition		between Ni and Al ₂ O ₃	reducibility NiO
		introduce oxygen vacancy	promote the CO ₂ dissociation
	MCM-41	strengthen the interaction between Zr and Ni	
Mn addition	Al ₂ O ₃		enhance formate pathway
		Mn ³⁺ /Mn ²⁺ redox pairs	enhance H spillover
Ca addition	Al ₂ O ₃	weak the interaction between NiO and Al ₂ O ₃	increase the reducibility of Ni
La ₂ O ₃ addition	Al ₂ O ₃		increase the Ni dispersion
			more medium basic site

2.4.3. Effect of preparation method on CO₂ methanation catalysts

Among the many methods to prepare supported metal catalysts, impregnation is the simplest and most widespread method. Impregnation can be classified into wet impregnation (WI) and dry or incipient wetness impregnation (DI), the difference of which is the amount of precursor solution. The former uses an amount of the precursor solution in large excess of the pore volume of the support, yielding a thin slurry, while the latter restrains the solution amount to about what is needed to fill the pore volume. Some limitations exist in the process of catalyst preparation using those two impregnation methods. For the WI, the impregnated support needs to be filtered out. Not all the precursors could be retained by the support, which means part of the precursor still be left in the excess liquid and causes waste. Obviously, WI could not control the loading precisely. Alternatively, the solvent excess is eliminated by evaporation, solving the problem of the control on the active species loading (all the metal precursor remains

on the support). In this case, for highly porous supports, an accumulation of the active phase on the external surface is usually obtained as only a small fraction of the active elements are loaded into the pores. With the DI, after drying of the wet paste, all the ions from the metal precursor will be retained on the support. Catalysts prepared by impregnation methods do not usually favor the production of small particles (high dispersion). During the drying process, the lack of induced interaction between the precursor and the support may allow mobility of the precursor. As drying ensues, the precursor agglomerate together on the external surface of the support with the loss of the solvent. To prepare the catalyst with better performance, the impregnation method with modification and some other preparation methods are listed below.

As we will report in the following Chapters, there is room for improvement in CO₂ methanation catalysts preparation, and some of the original preparation methods we will disclose do allow boosting performance. To set the scene and have useful comparisons points, the various methods that can be used to prepare CO₂ methanation catalysts are briefly reviewed below.

2.4.3.1. Pretreatment

Thermal treatment under suitable atmosphere could be an effective approach to regulate the SMSI. Lin *et al.* treated nickel nitrate impregnated CeO₂ sample in oxidative (air), reductive (H₂), and inert (N₂) atmosphere and reported that higher CO₂ conversion was achieved over Ni/CeO₂ activated in H₂. [163] The incorporation of Ni nanoparticles into CeO₂ occurs under the air treatment with subsequent reduction, forming relatively strong MSI but decreasing availability of active surface. Under N₂ treatment and reduction, Ni nanoparticles agglomerated into large strips with a layer morphology over CeO₂ support. Direct activation of Ni²⁺ ions on ceria in H₂ atmosphere serves to generate appropriate metal-support interaction that favors the formation of highly dispersed Ni nanoparticles, higher density of surface oxygen vacancies and larger amounts of weak basic sites. This

accounts for the higher capacity for H₂ and CO₂ adsorption/activation, and thus enhanced methanation performance. Li *et al.* also found that the NH₃-treatment and H₂-treatment of an anatase TiO₂ support enhance remarkably the activity of Ni, which is due to the fact that the prereduction of the support generates a large amount of Ti³⁺ in the bulk, suppressing the formation of the titania overlayer and leading to more Ni species accessible to the reactants (Fig. 4b).[164]

2.4.3.2. Precursors

The nature of the metal precursors used in the catalyst preparation can have a marked influence on the dispersion. Wen *et al.* prepared a series of Ni/SiO₂ catalysts with different nickel salt precursors by an impregnation method.[165] The decomposition and transformation of the anion of the nickel precursors could prominently affect the properties of the Ni-M (M represented the type of nickel salt precursors) catalysts. For the Ni-AA (acetylacetonate) catalyst, the strong coordination and interaction between CH₃COCHCOCH₃⁻ cations and surface silanol group over the SiO₂ support led to high NiO dispersion. Besides, the size of the CH₃COCHCOCH₃⁻ anion is bigger than those of the other counterions (Cl⁻ < NO₃⁻ < SO₄⁴⁻ < CH₃COO⁻ < CH₃COCHCOCH₃⁻), which might help to further promote the dispersion of nickel species on support due to the shielding effect of the CH₃COCHCOCH₃⁻ anion. Furthermore, SMSI was identified based on the higher reduction peak for Ni-AA catalyst. Those two factors make Ni-AA perform with the highest activity and stability among these catalysts.

2.4.3.3. Ammonia evaporation method.

To avoid the agglomeration during the drying process after impregnation, increasing the interaction between metal precursor and support is a feasible way. Hongmanorom *et al.* prepared a kind of Ni/SBA-15 catalyst via ammonia evaporation method.[58] Ni-phyllsilicate structure was formed via ammonia evaporation method and offered strong Ni to silica interaction. Thus, highly dispersed and

small Ni particles embedded in the channels of SBA-15 after reduction at 800 °C could be obtained, leading to a superior catalytic performance in CO₂ methanation as compared to catalysts prepared via wet impregnation method. Ni/CeO₂ was also prepared by ammonia evaporation method. CeO₂ support was firstly prepared using ordered mesoporous silica SBA-15 as a hard template, and Ni nanoparticles were then loaded into CeO₂ by strong electrostatic adsorption in ammonia solution. The high dispersion of small Ni nanoparticles was responsible for the excellent low-temperature CO₂ methanation performance.

2.4.3.4. Acid-assisted incipient wetness impregnation method

Adding organic acid has been reported to be one effective strategy to improve the dispersion of metal ions and thereby catalytic activity. Li *et al.* investigated the effects of various organic acids (propionic acid, malonic acid, succinic acid, adipic acid, l-malic acid, l-tartaric acid, n-hexylic acid, citric acid, l-alanine and l-lysine) on the preparation of cobalt catalysts on zirconia support. [166] Among the acids examined, the best choice is the carboxylic acid with longer chain and more carboxyl groups and hydroxyl groups. The amino acids can also change the charge property of ZrO₂ surface and increase the metal dispersion through strong electrostatic adsorption. Li *et al.* also found that the addition of citric acid improved the Ni dispersion and CO₂ methanation of Ni/Y₂O₃ catalyst. The formation of a nickel citrate complex used as a Ni precursor facilitated the Ni dispersion on support and strengthened the Ni-Y₂O₃ interaction. Such intensified Ni-Y₂O₃ interaction in turn gave rise to more oxygen vacancies and CO₂ adsorption. With a constant Ni loading, the increasing citric acid mole ratio favored the formation of active metallic Ni sites and basic sites on the surface, which were combined to play a synergistic effect in boosting CO₂ methanation reactivity.[167]

2.4.3.5. Vacuum filtration method.

To have a better dispersion of supported metal species, it is important

to permeate the metal precursor into pore of support. To achieve this target, Fan *et al.* applied a simple vacuum filtration process after dispersing the metal precursor and support into the solvent.[18] Porous hexagonal boron nitride (pBN) supports (an ideal support material for thermocatalysts due to the high thermal stability and conductivity) was demonstrated to improve the utilization of Ru. For the Ru/pBN-F (F denoting the vacuum filtration process), Ru clusters with a size of ~ 0.5 nm were formed and were uniformly distributed on the surface of pBN. On the other hand, for the Ru/pBN-R (R denoting the rotary evaporation process), larger nanoparticles were formed, and nonuniformly dispersed over the surface of pBN, attributed to the inadequate contact between the Ru precursor and pBN. The vacuum filtration process could overcome the capillary force in the mesopores and favor the adequate contact between the Ru precursor and pBN.[168] Furthermore, vacuum filtration helped removing excess precursor that did not electrostatically adsorb on the surface and thus inhibit the uncontrolled and nonuniform particle growth.

2.4.3.6. Plasma decomposition method.

Typically, the thermal decomposition is applied to convert the metal precursor into the metal oxide after loading the metal precursor onto the support. However, uncontrolled sintering of particles may occur over the support as the result of the relatively high temperatures employed in this step. Proper decomposition method could also lead to the confined metal particles.

Rui *et al.* prepared a Ni/CeO₂ catalyst via decomposition of nickel nitrate hexahydrate by gas discharge plasma. The activity of the obtained catalyst shows a CO₂ conversion of 84.2 % at a high space velocity of 56000 h⁻¹, while it is only 34.7 % on the regular calcined catalyst. Meanwhile, the methane formation rate of 100.3 $\mu\text{mol gcat}^{-1} \text{s}^{-1}$ is achieved with methane selectivity of 99.5 %. Compared to the reported works, this methane formation rate reaches the highest level ever reported at the reaction temperatures below 300 °C. Based on the characterization, an interfacial structure where Ni atoms bind with O

atoms from ceria could be obtained by plasma decomposition. A strong metal-support interaction is caused and thus confines small nickel particles on the CeO₂ surface.

Zhang *et al.* reported the preparation of Ni/SiO₂ catalysts by impregnation method, followed by glow discharge plasma treatment. From the characterization results, the plasma treatment improved the dispersion of active components remarkably, when compared to a Ni/SiO₂ catalyst prepared by impregnation and conventional thermal decomposition method. Correspondingly, the conversion of CO₂ and the space time yield of CH₄ over the plasma-treated catalyst were higher.

2.4.3.7. Sol-gel method

Sol-gel chemistry has been widely used for the preparation of heterogeneous catalysts[169], and the role of the addition of organic additives including various surfactant, ethylenediaminetetraacetic acid (EDTA), polyvinylpyrrolidone (PVP), citric acid, and cyclodextrin (as either as pore-generating agents, or reactivity modifiers) was also investigated. A better dispersion of the metal precursors due to the interaction between organic matter and metal ions and the formation of metal-organic complexes can be obtained. These complexes can inhibit the aggregation process and generate smaller metal particles, and more metal-oxide interface through drying and calcining catalyst precursor is exposed. Moreover, during the synthesis processes of the catalysts, no toxic or precious chemicals and filtration or centrifugation are needed.

Furthermore, the formation of solid solution in fresh catalysts prepared by sol-gel method can be beneficial for forming metal nanoparticles with ultra-small sizes after activation. Ye *et al.* prepared a Ni/CeO₂ catalyst by a sol-gel method, in which more Ni²⁺-containing mixed oxide solid solution was identified and thus a much higher degree of dispersion was obtained compared with the catalyst synthesized by an impregnation method at the same nickel loading. CO₂ conversion could reach 80.5% even at a temperature as low as 250 °C under a high gas hourly space velocity of 40000 mL g⁻¹ h⁻¹.

2.4.3.8. Co-precipitation method

He *et al.* used a co-precipitation method to synthesize Ni-Al hydrotalcite derived catalyst, Ni-Al₂O₃-HT, the Ni nanoparticles of which are still highly dispersed with an average particle size of ca. 4 nm even at an ultra-high loading of 78 wt%. The as-prepared catalyst had an outstanding performance towards the CO₂ methanation reaction. The TOF of Ni-Al₂O₃-HT is almost 6 times than those of the Ni/Al₂O₃ catalysts prepared by an impregnation method at the same Ni loading.[55]

2.4.3.9. Electrospinning method

Different with the preparation method of decomposing the metal precursor after loading it, there is another way to prepare the supported catalyst. That is, metal particles are prepared firstly and then loaded on the support. This process allows the preparation of metal particles with well morphology. However, it is difficult to find a proper way to load the prepared metal particles on the support.

Hu *et al.* prepared a kind of Ni/CeO₂ catalyst by the co-electrospinning method. Ni nanoparticles (NPs) were synthesized by the hot-injection method firstly.[170] Subsequently, the NiNPs@CeO₂NF was prepared by the co-electrospinning method, which shows superior catalytic performance with CO₂ conversion of 82.3 % at the low temperature of 300 °C.

Loccufier *et al.* prepared a kind of Ru@MIL-101 functionalized silica nanofibrous veil for CO₂ methanation reaction.[20] Silica nanofibers were made according to a methodology that combines electrospinning with sol-gel chemistry. A straightforward dip-coating procedure of the carrier was used to obtain a Ru@MIL-101 functionalized silica nanofibrous veil, avoiding Ru clustering. The obtained catalytic membrane exhibited an apparent turnover frequency of 3257 h⁻¹ at 250 °C.

Table 2.5. Summary of the function of different preparation method.

method	role	function
ammonia evaporation method	increased metal-support interaction	highly dispersed and small Ni particles
acid-assisted incipient wetness impregnation method	change the charge property of support surface/form nickel-organic complex	highly dispersed Ni particles
sol-gel method	formation of metal-organic complexes	highly dispersed and small Ni particles
vacuum filtration process	overcome the capillary force in the mesopores and favor the adequate contact between the metal precursor and support/ remove excess precursor that did not electrostatically adsorb on the surface	inhibition of the uncontrolled and nonuniform particle growth/ highly dispersed and small Ni particles
plasma decomposition method	-	highly dispersed Ni particles
electrospinning method	-	load the prepared metal particles with well morphology on the support

Chapter 3 Research objectives and strategies

3.1. Research objectives

Chapter 2 reveals that various Ni-based catalysts have been continuously explored and compared to the reported works in the field searching for the most active catalyst in terms of selectivity, CO₂ conversion, and CH₄ yield in CO₂ methanation. In this process, several parameters influencing the catalytic performance have been identified, such as particle size and dispersion, SMSI, reducibility, basicity, and methanation pathway. Generally, those parameters could be modified by three ways, that is, adding promoter, choosing proper support, and discovering new preparation method. However, achieving a high methanation activity at low-temperature (especially below 250 °C) is still a great challenge. Furthermore, there is no unified view on the path that governs catalytic activity due to the influence of support and dopant in the different catalyst system.

Thus, this thesis attempts to contribute to deciphering the mechanism of CO₂ methanation on Ni-based catalysts, focusing on Ni itself. What we need to study is: (1) the form of adsorbed CO₂ over the catalyst surface, (2) the hydrogenation pathway of the adsorbed CO₂ in different form, (3) the rate determining step of the different pathway, (4) the possibility of different pathway proceeding in parallel.

Also, with the teachings of this better fundamental understanding of the working behavior of these catalysts, we aim to prepare new types of Ni-based catalysts with high activity.

3.2. Strategies

The starting point of our strategy is to prepare Ni/SiO₂ model catalysts, that will allow us to learn the details of the mechanism of CO₂ methanation focusing on Ni itself without the influence from dopant and support. In this perspective, knowing that the activity of Ni/SiO₂ is usually modest (as compared to Ni on other reducible supports), we decided to target catalysts with high Ni loading. However, metal-

support interaction in silica-based catalysts are weak and metal dispersion is usually very low, due to sintering. To alleviate this issue, we focused our attention on a peculiar sol-gel synthesis route, we the idea to ensure high Ni dispersion, even at high Ni loading. This model catalysts are then studied at the fundamental level, relying on advanced (including in situ) characterization techniques and on theoretical calculations (DFT) to understand the properties that govern the catalytic behavior of these model catalysts.

Based on the literature review presented above and based on our own results obtained with the Ni/SiO₂ catalysts, we considered it was promising to study doping strategies to boost catalytic performance. We chose to investigate Mn, Co, and Cu as dopants, because those metal has been widely studied as dopant in the literature. Again, the effect of these dopants on the catalytic behavior of the catalysts is rationalized by using a series of (in situ) characterization techniques to correlate the catalyst properties, the plausible reaction mechanisms, and the performance.

Finally, with the new knowledge acquired, we turned our attention to the development of an innovative catalyst that would putatively benefit from the most decisive features and exhibit high methanation activity. To that end, our strategy was to turn to ceria as the support, instead of silica. This choice is rationalized by the fact that CeO₂ is an interesting support due to the abundant surface oxygen vacancies and redox properties, which could facilitate the CO₂ activation. Also, inspired by the photocatalytic CO₂ methanation over g-C₃N₄ catalysts, we had the idea to use C₃N₄ as an additive in the preparation of the catalyst. The rationale behind this idea is C₃N₄ could provide extra active site for CO₂ activation.

Chapter 4 Experimental methodologies

This chapter starts with the details of catalyst characterizations, which are utilized in following thesis chapters. The preparation of catalysts is separately described in detail in the respective chapter.

4.1. Sample preparation

Three kinds of catalyst (high loading Ni/SiO₂, bimetallic Ni-M/SiO₂ prepared by sol-gel methods, and Ni/CeO₂-CN-OP prepared by one-pot method) will be disclosed and discussed in the manuscript. The corresponding sample preparation is described in the experimental summary of each chapter.

4.2. Catalyst characterization

4.2.1. Transmission electron microscopy (TEM)

TEM is used to identify the morphology properties of the sample. TEM measurements were operated with the help of Valentina Girelli and Ovidiu Ersen (the sample in Chapter 4), Sandra Casale and Capucine Sassoye (the sample in Chapter 5 and 6). TEM measurement of sample in Chapter 4 were operated on JEOL2100F microscope working at 200kV with a Cs corrector and equipped with a CCD camera and BF Gatan and HAADF Jeol detectors. TEM measurements of sample in Chapter 5 and 6 were performed using JEOL-2100 Plus (LaB6) equipped with an Oxford EDX detector. The software of Nano Measurer 1.2 was used to calculate particle sizes.

4.2.2. N₂ physisorption

N₂ physisorption is used to identify the textural properties of the sample. The N₂ adsorption-desorption analysis was carried out by a Tristar 3000 (Micromeritics, USA) instrument. The sample was degassed at 250 °C for 3 h to remove physical absorbed water and impurities on the surface before the measurement. The total pore volume (V_p) was calculated from the amount of nitrogen absorbed at a P/P_0 of 0.98 and the pore size distribution of each catalyst was drawn from the desorption branch with

the Barrett-Joyner-Halenda (BJH) method.

4.2.3. X-ray diffraction (XRD)

XRD is used to identify the crystal structure of the sample. XRD measurements were performed with a Bruker AXS-D8 Advance (Germany) diffractometer using Cu K α ($\gamma = 1.78 \text{ \AA}$) radiation at 35 kV and 40 mA.

4.2.4. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)

ICP-AES is used to identify the chemical elements of the sample. The weight percentages of Ni inside the catalysts were measured by ICP-AES on an ICAP 6500 from Thermo Scientific.

4.2.5. H₂ chemisorption

H₂ chemisorption is used to identify the metal dispersion combined with the results of ICP-AES. H₂ chemisorption at 30 °C was used to measure the Ni dispersion using ASAP 2010C apparatus from Micrometrics. Catalyst weight ca. 200 mg was loaded into a Pyrex tube, and subsequently degassed in He for 30 min. After evacuation, the sample was reduced at 500 °C (for the sample in Chapter 1 and 2) or 350 °C (for the sample in Chapter 3) in pure H₂ for 2 h followed by purging with He for 1 h and adsorption of H₂. Two isotherms were measured in the range of 0.13-60 kPa. The first isotherm accounts for reversible physisorption and irreversible chemisorption. The sample was evacuated at 30 °C to desorb reversibly adsorbed H₂. The second isotherm was then measured which accounts only for the reversibly adsorbed H₂. The subtraction of the linear part of the two isotherms gave the total amount of irreversibly chemisorbed H₂. The amount of surface Ni atoms was calculated from the amount of chemisorbed H₂ assuming that the chemisorption stoichiometry is H:Ni = 1.

4.2.6. X-ray photoelectron spectroscopy (XPS)

XPS is used to identify the surface composition and chemical state of the sample. XPS analyses were carried out at room temperature with an

SSI-X-probe (SSX 100/206) photoelectron spectrometer from Surface Science Instruments (USA), equipped with a monochromatized microfocus Al X-ray source (1486.6 eV). Samples were set on the sample holders by double face adhesive tape. Charging effect of the samples were eliminated by placing a nickel grid above the samples and using a flood gun set at 8 eV. The binding energy scale was calibrated on the Si 2p peak fixed at 103.5 eV (for the sample in Chapter 4 and 5) or on the C 1s peak fixed at 284.8 eV (for the sample in Chapter 6).[171]

4.2.7. H₂-temperature programmed reduction (H₂-TPR)

H₂-TPR is used to identify the reducibility of the sample. H₂-TPR measurements were performed on a Hiden CATLAB-PCS microreactor connected to a mass spectrometer equipped with a quadrupole separator. The samples (50 mg) were pretreated with high purity Ar at 250 °C and a flow rate of 30 mL/min for 0.5 h to remove water and other contaminants. When the samples were cooled down to room temperature, 5% H₂/Ar was introduced into the system at a flow rate of 30 mL/min. The MS signal and sample temperature were recorded while the temperature was increased to 900 °C at a heating rate of 10 °C/min.

4.2.8. CO₂-temperature programmed desorption (CO₂-TPD)

CO₂-TPD is used to identify the basicity of the sample. CO₂-TPD measurements were performed on a Hiden CATLAB-PCS microreactor connected to a mass spectrometer equipped with a quadrupole separator. 50 mg sample was reduced in-situ at 500 °C (for the sample in Chapter 1 and 2) or 350 °C (for the sample in Chapter 3) for 2 h in 5% H₂/Ar. After reduction, the gas was changed to Ar for 1 h to remove the adsorbed H₂. Then the sample was cooled down to 50 °C, and 15% CO₂/Ar was admitted for 1 h. The system was then purged by an Ar flow for 1 h at 50°C. Finally, the catalyst was heated up to 900 °C at a rate of 10 °C/min in a flow of Ar.

4.2.9. In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) -

In-situ DRIFTS is used to identify the active surface species. In-situ DRIFTS measurements were carried out on the Nicolet 6700 spectrometer.

In Chapter 4, for each DRIFTS measurement, the catalyst was mixed with KBr (1:5 mass ratio) and 0.03 g of this mix was loaded into the chamber and in-situ reduced at 500 °C for 1 h again in flowing H₂ and He. Then, the gas was changed to He to flush the sample for 30 min at 500 °C to remove residual H₂. Afterwards, the temperature was decreased to a certain temperature (450, 170, 120 or 30 °C, chosen according to the results of CO₂-TPD) and the background was recorded. Subsequently, CO₂ was flowed onto the sample for 1 h and then the gas was changed to He. Finally, the chamber was set to the desired temperature (30, 120, 170 or 450 °C) and the spectrum was recorded when reaching a steady state.

In Chapter 5, for each DRIFTS measurement, the catalyst was mixed with KBr (1:5 mass ratio) and 0.03 g of this mix was loaded into the chamber and in-situ reduced at 500 °C for 1 h by a 50% H₂/50% He (20 mL min⁻¹). Then, the gas was changed to He to flush the sample for 30 min at 500 °C to remove residual H₂. Afterwards, the temperature was decreased to 30 °C and then the background was recorded. Subsequently, a CO₂/H₂/He mixture gas (6.7% CO₂/26.8% H₂/66.5% He at a flow 15 mL min⁻¹) was introduced and the temperature was increased in a step mode from 100 to 400 °C with an increment of 50 °C, while the spectra were collected at each temperature when reaching a steady state.

In Chapter 6, for each DRIFTS measurement, the catalyst was loaded into the chamber and in-situ reduced at 350 °C for 1 h in flowing H₂ and He. Then, the gas was changed to He to flush the sample for 30 min at 350 °C to remove residual H₂. Afterwards, the temperature was decreased to 50 °C and the background was recorded. Subsequently, different gases were flowed. To observe the adsorbed CO₂ species and their desorption behavior, 3 mL/min CO₂ was flowed onto the sample for 1 h and then the gas was changed to He. To observe the CO₂

methanation process, a gas mixture consisting of 13.3% CO₂/53.2% H₂/He was flowed. To observe the consumption of surface CO₂ adsorbed species, the feed gas was switched to 61.5% H₂/He after exposing the loaded sample under the reaction gases (13.3% CO₂/53.2% H₂/He) at 300 °C for 1 h. Finally, the temperature was increased to a certain temperature, while the spectra were collected at each temperature when reaching a steady state.

4.2.10. Temperature programmed surface reaction (TPSR)

TPSR is used to elucidate the dynamical interaction. TPSR measurements were performed on a Hiden CATLAB-PCS microreactor connected to a mass spectrometer equipped with a quadrupole separator.

In Chapter 4 and 5, for the CO₂-TPSR test, 50 mg of catalyst was reduced in-situ at 500 °C for 2 h under a 5% H₂/Ar flow (20 mL/min) and then was purged in an Ar flow (20 mL/min) for 1 h. After cooling down to 50 °C under Ar (20 mL/min), a 20 mL/min flow of 15% CO₂/Ar was introduced to the reactor for 1 h and purged by Ar gas for 30 min. The TPSR profiles were recorded from 50 °C to 650 °C with a 5 °C/min heating rate when 5 mL/min of 5% H₂/Ar was flowed into the reactor. The signal of CH₄ and CO₂ was examined by MS with the m/z of 15 and 44.

In Chapter 5, for the formaldehyde-temperature programmed surface reaction (HCHO-TPSR) test, 50 mg of reduced catalyst was placed into the reactor and then the reactor was immersed in a HCHO solution (Sigma-Aldrich, 37 wt. % in H₂O, containing 10-15% methanol as stabilizer) for 1 h. After installing the reactor, 20 mL/min of Ar was introduced to the reactor for 30 min. The TPSR profiles were recorded from 30 °C to 250 °C with a 5 °C/min heating rate when 5 mL/min of 5% H₂/Ar was flowed into the reactor. The signal of HCHO and methanol was examined by MS with the m/z of 29 and 31.

4.2.11. Computational methods

All calculations were carried out by using the Dmol³ program in Materials Studio[172, 173]. Density functional theory calculations

within the generalized gradient approximation (GGA) and the Perdew–Burke–Ernzerhof (PBE) functional[174, 175] were carried out to study the mechanism of CO₂ methanation on Ni(1 1 1), which is considered as the most active and stable surface of Ni-based catalysts for CO₂ methanation[49, 176]. Double numerical plus polarization (DNP) basis sets were used[177], and all calculations were spin-unrestricted to account for the magnetic properties of Ni. A Fermi smearing of 0.05 Hartree was utilized. The vacuum between the slabs was set to span a range of 12 Å to ensure no significant interaction between the slabs. A 3 × 3 slab (five layer, see Fig. S2) was chosen to represent the Ni(1 1 1) surface for CO₂ methanation. The bottom three layers of the nickel slab were fixed, whereas all other atoms were allowed to relax. The convergence criteria for structure optimization and energy calculation were set to 1.0 × 10⁻⁶ eV/atom for SCF, 1.0 × 10⁻⁵ eV/atom for energy, 0.03 eV/Å for maximum force, and 1.0 × 10⁻³ Å for maximum displacement. Transition state (TS) search was performed at the same theoretical level with complete linear synchronous transit/quadratic synchronous transit (LST/QST) method.[178]

4.3. CO₂ methanation

The catalytic performance of the catalysts was measured in a continuous flow gas-phase microreactor, at atmospheric pressure. The scheme of setup is shown in Fig. 4.1. In a typical run, 50 mg of catalyst was placed in the reactor (i.d. 6 mm). Before reaction, the catalyst was reduced in situ. Afterwards, a mixture of CO₂ and H₂ balanced with He was introduced to the reactor. The catalytic tests were carried out in step mode in the 200 °C to 400 °C range. Each temperature was maintained for 88 min, allowing for 4 GC analyses. The gas exiting the reactor was analyzed on a gas chromatograph (Varian CP3800), equipped with Hayesep Q, Molsieve 5A, and CP-Sil-5CB columns. The separated gases were analyzed with a flame ionization detector (CH₄) and a thermal conductivity detector (CO and CO₂). All transfer lines were maintained at 125 °C to avoid water condensation. Conversion (X_{CO_2}) and selectivity (S_{CH_4}) were calculated according to the following

equations:

$$X_{CO_2} = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}}$$

$$S_{CH_4} = \frac{F_{CH_4,out}}{F_{CO_2,in} - F_{CO_2,out}}$$

where F is the molar flow rate. The turnover frequency (TOF) was calculated by the following equation:

$$TOF (s^{-1}) = \frac{\frac{X_{CO_2}}{V_m} \times F_{CO_2,in}}{\text{mole of surface Ni atoms}}$$

We verified experimentally there is no heat and mass transfer limitations in the tested conditions by varying the amount of catalyst and flow and changing the size of the catalyst pellets (see supplementary information, Fig. S1). To build the Arrhenius plots in the 210-290 °C temperature range, a high GHSV (336000 mL g⁻¹ h⁻¹) was applied, maintaining the CO₂ conversion is below 15%.

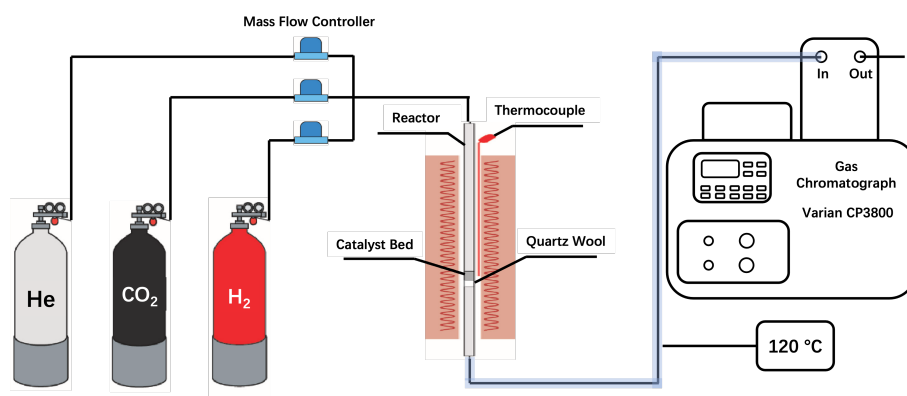


Fig. 4.1. The scheme of the setup for the performance test.

Chapter 5 CO₂ methanation with high-loading mesoporous Ni/SiO₂ catalysts: toward high specific activity and new mechanistic insights

The results presented in this chapter are published in:

CO₂ methanation with high-loading mesoporous Ni/SiO₂ catalysts: toward high specific activity and new mechanistic insights,

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In this chapter, we disclose the sol-gel preparation of high-loading mesoporous Ni/SiO₂ catalysts. (HR)-TEM, XRD, N₂ physisorption, and H₂ chemisorption show that small Ni particles (<5 nm) are obtained, even at loading up to 38 wt%. The best catalyst reached a specific activity of 10.2 $\mu\text{mol}_{\text{CH}_4} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$ at 250 °C (TOF = 0.0155 s⁻¹; almost 3 times higher than a reference catalyst prepared by impregnation). Being based on inert silica, these catalysts are ideal model materials to elucidate the reaction mechanism on nickel. Combining CO₂-TPD, in-situ CO₂-DRIFTS, and TPSR with DFT calculations, we show that CO₂ methanation follows mostly the RWGS+CO-hydrogenation and the formate pathways, the former being dominant at low temperature.

5.1. Introduction

Ni can be finely dispersed in the form of nanoparticles on various oxide supports (SiO₂, Al₂O₃, TiO₂, CeO₂, ZrO₂) to form active methanation catalysts.[8, 164, 179, 180] Different strategies have been implemented to improve the activity at low temperature, such as doping with a second metal[83, 180, 181], tuning the metal-support interaction[164], controlling the metal nanoparticles size and shape[49, 182, 183], etc. Those methods mainly focus on improving the intrinsic activity of the catalyst, by tuning the properties of the active sites (e.g., improve the reducibility of NiO, enhance CO₂ activation). Apart from this, increasing the *amount* of active sites is also a direct and effective way to boost the specific activity of a catalyst. Using a support with high specific area, such as molecular sieves, mesoporous oxides, MOFs, etc. can help obtaining catalysts with small nickel particles (high dispersion).[25, 184, 185] However, the optimal Ni loading generally does not exceed 20%, as the aggregation of nickel nanoparticles is observed with the further addition of Ni.[25, 74, 154]

Sol-gel methods are primed to prepare composites with tailored textural and chemical properties, and has been widely used in catalyst preparation.[186] For example, Lin *et al.* prepared a Ni-based catalyst (7.9 wt.%) supported on a mesoporous Al₂O₃-ZrO₂ support synthesized

by a single-step epoxide-driven sol-gel method, which presented a high catalytic activity ($19 \mu\text{mol g}^{-1} \text{s}^{-1}$ at 300 °C) and CH₄ selectivity (99.3 %) with excellent stability.[154] Ye *et al.* reported on a nanostructured Ni/CeO₂ catalyst (16.75 wt.%) prepared by a facile sol-gel method, the activity of which ($21.1 \mu\text{mol g}^{-1} \text{s}^{-1}$, 300 °C) was up to 48 times higher than the benchmark Ni/CeO₂ catalysts prepared by state-of-the-art impregnation method.[8] But the optimal Ni loading of those catalysts is still limited to relatively low values (10-20 wt.%). Recently, Yang *et al.* reported a sol-gel strategy using ethylene glycol, zinc nitrate, and tetraethyl orthosilicate as precursors to prepare ZnO/SiO₂, in which the loading of well-dispersed ZnO nanograins reached up to 57%.[187]

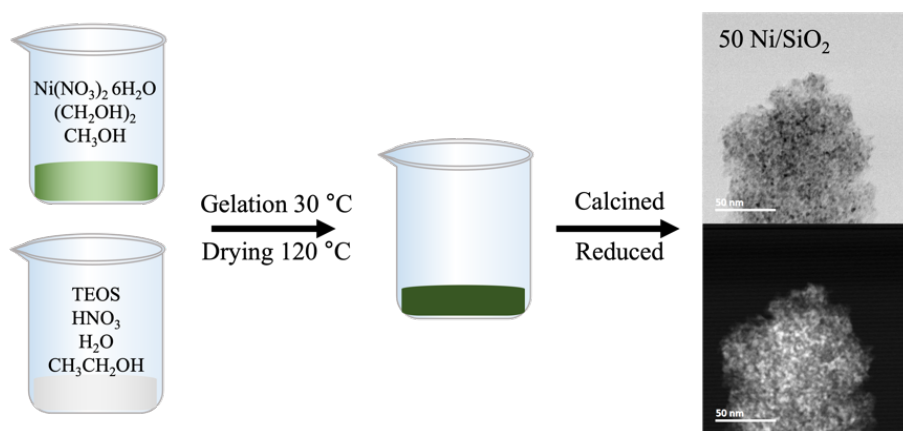
This report prompted us to explore the sol-gel preparation of high-loading and high dispersion Ni/SiO₂ catalysts, reasoning that high loading Ni with small particle and high dispersion can provide more active site for CO₂ methanation. With these new catalysts in hands, and using a combination of experimental and computational data, we also address a long-standing debate on the reaction mechanism. In fact, many experimental and theoretical studies have been conducted to elucidate the possible pathways leading to methane (i.e. the “formate route” and the “CO route”[49, 188]) but such discussions are usually focused on doped active phases and/or on the role of metal-support interactions in creating oxygen vacancies. Here, with small Ni nanoparticles embedded in an inert and stable silica matrix, we can decipher the mechanism as it is occurring on Ni. Our data allowed establishing that formate, carbonyl, and C species from the adsorption and activation of CO₂ participate in the catalysis in three pathways, among which the RWGS+CO hydrogenation pathway has the rate determine step with the lowest energy barrier and is dominated at low reaction temperature.

5.2. Experimental summary

5.2.1. Catalyst preparation

A series of mesoporous Ni/SiO₂ catalysts with different Ni loading were synthesized by a sol-gel method (Scheme 5.1). Typically, 0.6 mL anhydrous ethanol (EtOH), 0.8 mL distilled H₂O, and 1.9 mL HNO₃ (4M) were added to 5.6 mL tetraethyl orthosilicate (TEOS) and stirred for 1 h to obtain a clear SiO₂ sol. The required amount of nickel nitrate hexahydrate was dissolved in ethylene glycol (EG) and methanol ($V_{\text{EG}}:V_{\text{methanol}} = 3:2$) was added to obtain a 2 M nickel nitrate solution. The solution was then added to the SiO₂ sol and stirred for another 1 h. The obtained slurry was aged at 30 °C for 12 h and dried at 120 °C for another 12 h to form a gel. The dried gel was calcined in air at 300 °C (1 °C/min) for 2 h, and then at 500 °C (1 °C/min) for an additional 2 h. The calcined sample are denoted as “n NiO/SiO₂”, where n represents the theoretical amount of NiO in wt%. The calcined catalyst was reduced in situ in the reactor (see below) under a H₂/He flow, and the corresponding samples were denoted “n Ni/SiO₂”. To examine the role of EG, Ni/SiO₂-ME was also prepared in the same way using only methanol as solvent, respectively.

As a benchmark, we prepared 50 Ni/SiO₂-IM by an impregnation method. 5.84 g Ni(NO₃)₂·6H₂O was added to 20 mL distilled water, and then the solution was mixed with 1.5 g SiO₂ (purchased from Sigma-Aldrich, CAS number: 112926-00-8, pore volume: 1.15 cm³/g, 1.5 Å), followed by vigorously stirring at 80 °C until water was completely evaporated. The obtained solid was dried at 120 °C for 12 h and calcined in the same way as the Ni/SiO₂ sol-gel catalysts series.



Scheme 5.1. Schematic description of the preparation of Ni/SiO₂ catalysts by the ethylene glycol-assisted sol-gel method. On the right: Bright Field (BF) STEM and High Angle Annular Dark Field (HAADF) STEM micrographs showing an amorphous disordered silica matrix in which Ni nanoparticles are embedded.

5.3. Results and discussion

5.3.1. Structural and morphological characterization.

Textural properties of the NiO/SiO₂ with different Ni loading were examined by nitrogen adsorption-desorption analyses. Isotherms are presented in Fig. 5.1 and the detailed physicochemical characteristics of NiO/SiO₂ are shown in Table 5.1. The specific surface area of the catalysts with 30 and 40 wt.% of nominal NiO loading is as high as ~520 m².g⁻¹. The specific surface area tends to decrease with the further increase of Ni loading, but at 60 wt.% nominal NiO loading, it still reaches as high as 345 m².g⁻¹. All samples exhibit type IV adsorption isotherms with an H1-type hysteresis loop (Fig. 5.1a), indicating the presence of mesopores.[189] With increasing Ni content, the total pore volume (V_p) and the average pore diameter increases firstly and then decreases for the 60 NiO/SiO₂, and 50 NiO/SiO₂ is the most porous. Furthermore, the micropore volume (V_{Mi}) decreases when the Ni loading increases, while the mesopore volume (V_{Me}) shows a similar

trend as total pore volume. The impregnated catalyst (50 NiO/SiO₂-IM) has a smaller specific surface area, as compared to the corresponding catalyst made by sol-gel and larger pores.

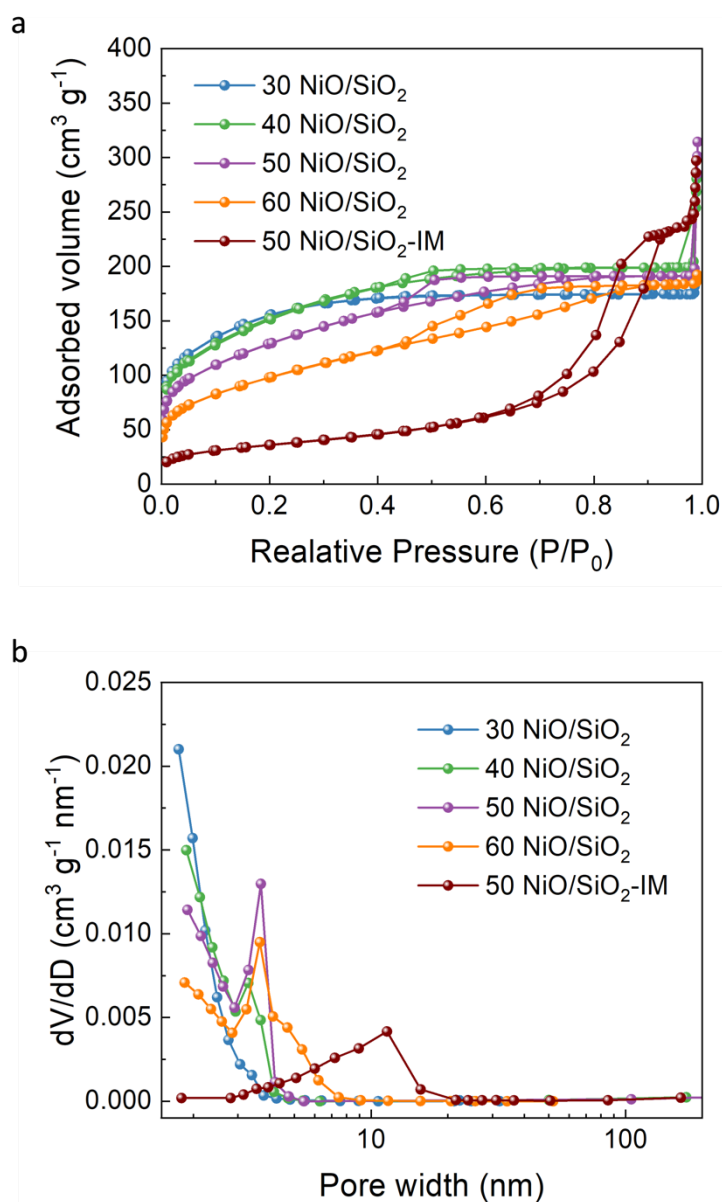


Fig. 5.1. (a) N₂ adsorption-desorption isotherms and (b) BJH pore size distributions of NiO/SiO₂ catalysts.

The morphology and nanostructures of calcined and reduced catalysts are displayed in Fig. 5.2 and Fig. S3. TEM shows that nickel in 50 NiO/SiO₂ is uniformly distributed in the form of small nanoparticles, while large aggregates of nickel are observed in the impregnated samples (50 NiO/SiO₂-IM). Upon reduction, 50 Ni/SiO₂ maintains a uniform distribution of nanoparticles with an average size of 3.7 nm (Fig. 5.2c and 5.2d). The lattice spacing of 0.201 nm matches with that of (111) lattice planes of Ni (Fig. 5.2f). In contrast, Ni particles in 50 Ni/SiO₂-IM appear strongly agglomerated (Fig. 5.2h and 5.2i) and the Ni particle size reaches as high as 46 nm in size. Consistently, the dispersion – measured by H₂ chemisorption – was much higher for 50 Ni/SiO₂ (11%) than for 50 Ni/SiO₂-IM (6.1%). Similar to 50 NiO/SiO₂, small and uniformly distributed NiO and Ni particles are observed in 30 Ni/SiO₂ and 40 Ni/SiO₂ (Fig. S3a-S3d). However, aggregation is observed for the 60 NiO/SiO₂ and 60 Ni/SiO₂ (Fig. S3e and S3f). In the Ni/SiO₂ series, Ni dispersion linearly decreases with increasing Ni loading. It reaches 13.8%, 12.9% and 10.1% respectively for 30, 40 and 60 Ni/SiO₂ (Table 5.1).

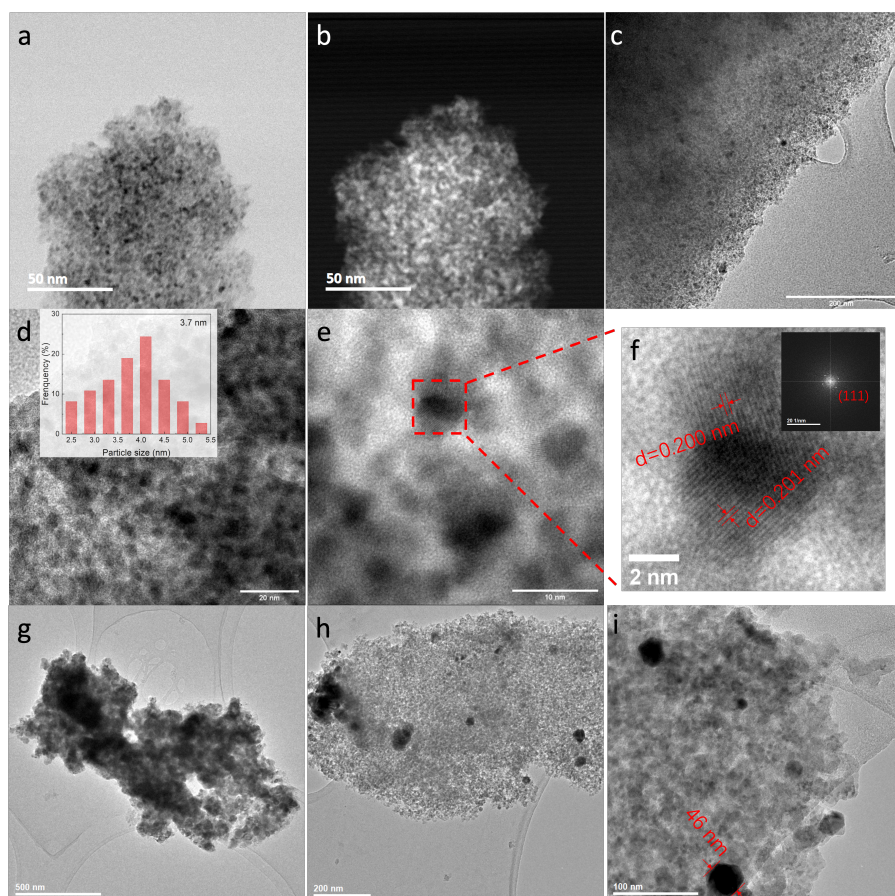


Fig. 5.2. (a) BF-STEM image and (b) HAADF-STEM image of the 50 NiO/SiO₂, (c, d) TEM images and (e, f) HR-TEM images, of the 50 Ni/SiO₂ catalyst (inset of (d) is the Ni particles size distribution; inset of (f) being its FFT pattern); (g) TEM image of the 50 NiO/SiO₂-IM, (h, i) TEM images of the 50 Ni/SiO₂-IM.

Table 5.1. Physicochemical characteristics of the NiO/SiO₂ and their TOF values.

Sample	S _{BET} (m ² /g)	V _p (cm ³ /g)	V _{Micro} (cm ³ /g)	V _{Meso} (cm ³ /g)	D _p (nm)	Ni content ^a reduced (%)	Ni disperison ^b reduced (%)	Ni particle size ^c reduced (nm)	TOF (s ⁻¹ , 250 °C)
SiO ₂	648	0.43	0.32	0.11	2.3	-	-	-	-
30 Ni/SiO ₂	520	0.28	0.25	0.03	2.1	23	13.8	2.3	0.0128
40 Ni/SiO ₂	527	0.43	0.21	0.19	3.2	31	12.9	2.8	0.0141
50 Ni/SiO ₂	455	0.49	0.15	0.3	4.2	38	11	4.6	0.0155
60 Ni/SiO ₂	345	0.3	0.08	0.18	3.4	45	10.1	7.1	0.0136
50 Ni/SiO ₂ -IM	126	0.46	-	0.46	14.2	38	6.1	41.0	0.0056

^a Determined by ICP-AES measurement.^b Determined by H₂ chemisorption.^c Obtained from Scherrer equation.

5.3.2. Characterization of the Ni phase.

The XRD patterns of the calcined samples (Fig. 5.3a) show the diffraction peaks corresponding to the crystal structure of NiO (PDF 65-2901). These characteristic reflection peaks are located at 2θ around 37.3°, 43.3°, 62.9°, 75.2°, and 78.7°, attributed due to the diffractions from the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes of NiO, respectively. The XRD patterns of reduced catalysts (Fig. 5.3b) show metallic Ni reflections (PDF 04-0850) at $2\theta = 44.5^\circ$ (1 1 1), 51.8° (2 0 0), and 76.3° (2 2 0). Furthermore, small peaks at $2\theta \approx 30^\circ$ and 65° attributed to NiO could also be observed, which can be attributed to the reoxidation of the reduced catalyst upon handling. Indeed, an in-situ XRD for the 50 Ni/SiO₂ catalyst (Fig. S4) confirmed that NiO species was fully reduced to Ni metallic after treated in H₂ for 2 h at 500 °C. The intensity of NiO diffraction peaks increases with the NiO content in calcined NiO/SiO₂ catalysts, and a similar trend is shown for the metallic Ni in the reduced Ni/SiO₂ catalysts, indicating that higher Ni loading resulted in the formation of larger crystallites, as presented in Table 5.1. The crystallite size of 50 Ni/SiO₂ estimated by the Scherrer formula is around 4.6 nm, which is consistent with the TEM results. The NiO/SiO₂-IM shows sharper and more intense NiO peaks and the Ni/SiO₂-IM has stronger Ni peaks, which suggests the metal crystallites size is much bigger prepared by IM as compared to sol-gel method and is also consistent with TEM observations. In this case, the crystallite size is estimated at 41 nm.

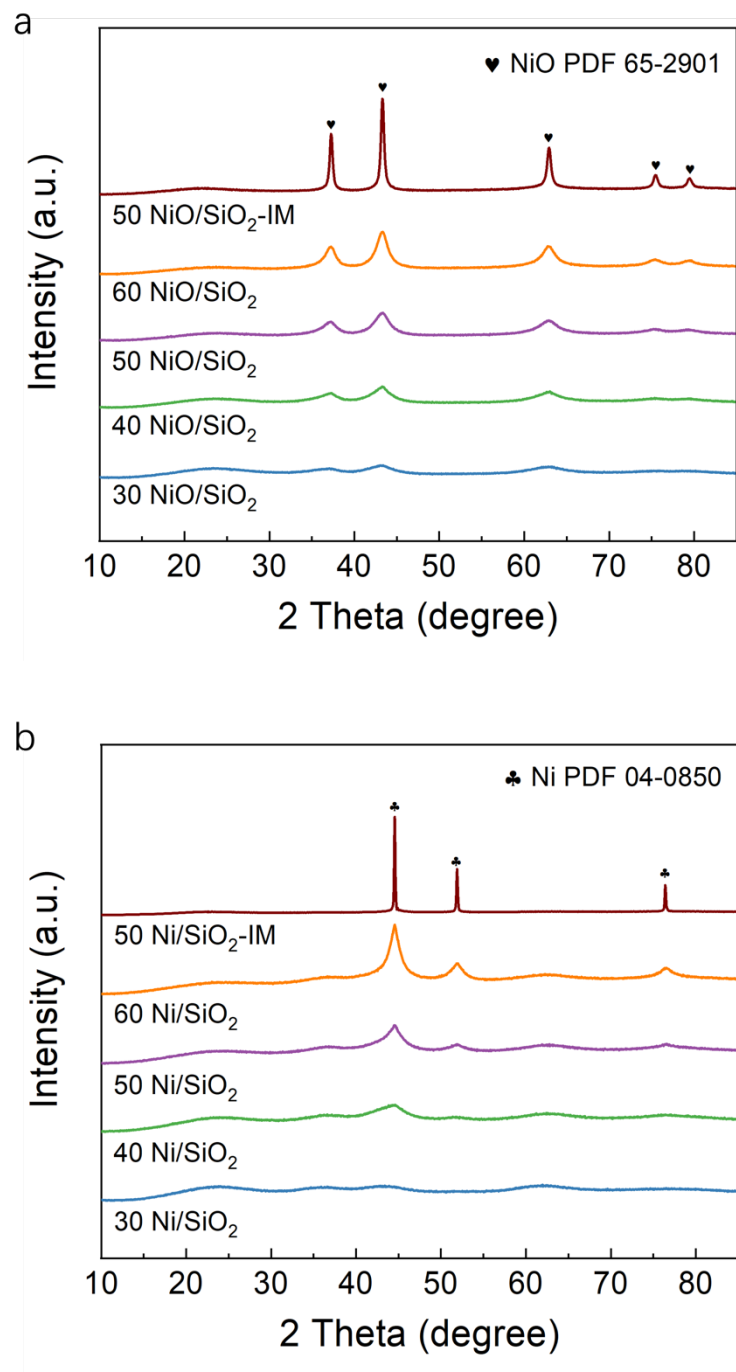


Fig. 5.3. The XRD patterns of (a) calcined and (b) reduced catalysts.

From the above, it appears that the ethylene glycol-assisted sol-gel route employed here allowed preparing high-loading Ni-SiO₂ catalysts with a high dispersion of small Ni nanoparticles. To highlight the beneficial effect of ethylene glycol, we also prepared 50 Ni/SiO₂-Me by sol-gel method with only methanol (no EG) being added during the synthesis of nickel nitrite solution. The Ni particle size of 50 Ni/SiO₂-Me (XRD pattern shown in Fig. S5a) calculated from Scherrer equation is ca. 16.3 nm, which is much bigger than that of 50 Ni/SiO₂ (4.6 nm). According to the literature, EG inhibits the agglomeration of metal species, as the metal nitrate reacts with EG through a redox reaction during the gel process to form stable carboxylate complexes.[187] The latter has a high decomposition temperature, so the sintering of the metal oxide is effectively inhibited. Furthermore, the textural properties are strongly affected by the presence/absence of EG (N₂ physisorption isotherms for 50 Ni/SiO₂-Me are presented in Fig. S5b). Specific surface area and pore volume of 50 Ni/SiO₂-Me only reach 378 m²/g and 0.16 cm³/g (to be compared with 455 m²/g and 0.49 cm³/g for 50 Ni/SiO₂), indicating that EG plays a significant role as a texturing agent.

XPS was also carried out to determine the surface composition and chemical state of the catalysts. The high resolution Ni 2p_{3/2} spectra of calcined catalysts (Fig. 5.4a and Fig. S6) exhibit a peak at 855.3 eV corresponding to Ni²⁺ and a shake-up satellite peak at 861.3 eV[190]. The XPS of the reduced sample (Fig. 4a) clearly show the co-existence of Ni²⁺ and metallic Ni⁰ (peak at BE $\approx$ 852.4 eV). This appears inconsistent with the XRD results (showing only the metallic Ni phase in the reduced catalysts) but can be explained by surface passivation.[191] Two types of oxygen species can be detected by deconvoluting the O 1s peak (Fig. 5.4b and Fig. S6). The peak with BE at around 529.9 eV was ascribed to the surface lattice oxygen of NiO, whereas the second peak at 532.8 eV was attributed to Si-O-Si and surface adsorbed oxygen.[8, 192] Expectedly, for the calcined catalysts, Ni/O_{Ni} is approximately equal to 1. For the reduced catalysts, Ni/O_{Ni} increases markedly, consistent with the reduction of the NiO particles. This increase is more marked for higher Ni loading (Table S1), which

indicates a more complete reduction (lower tendency to undergo surface passivation) of the larger NiO particle size.

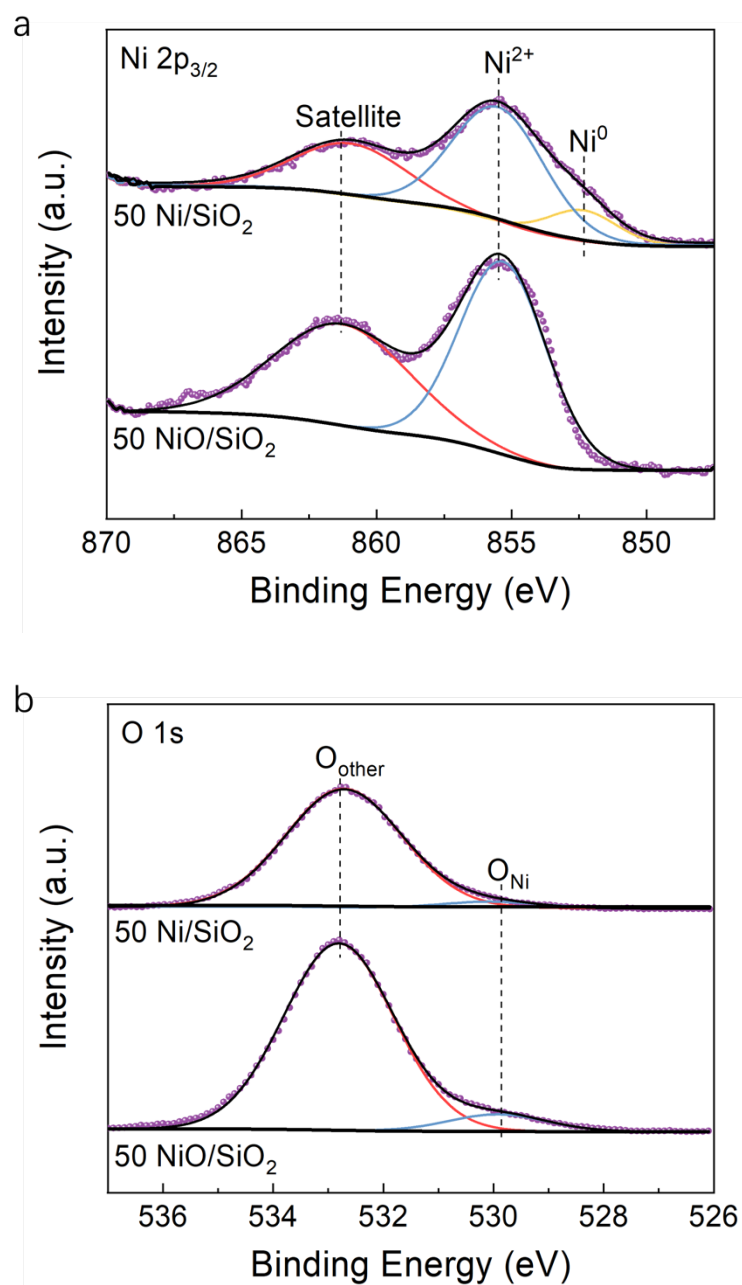


Fig. 5.4. XPS spectra of Ni 2p_{3/2} (a) and O 1s (b) for the 50 NiO/SiO₂ (calcined) and the 50 Ni/SiO₂ (reduced).

The reduction behavior of catalysts was investigated using H₂-TPR measurements, as shown in Fig. 5.5. Two reduction peaks are observed at about 370 °C and 530 °C, which can be ascribed to the reduction of highly dispersed NiO species moderately and strongly interacting with the support.[164] Here, the percentage of NiO reduced at lower temperature increases with the Ni loading (39, 48, 59, 64 % respectively for 30, 40, 50, and 60 Ni/SiO₂), which indicates that the proportion of strongly interacting NiO species decreases when the Ni loading increases.

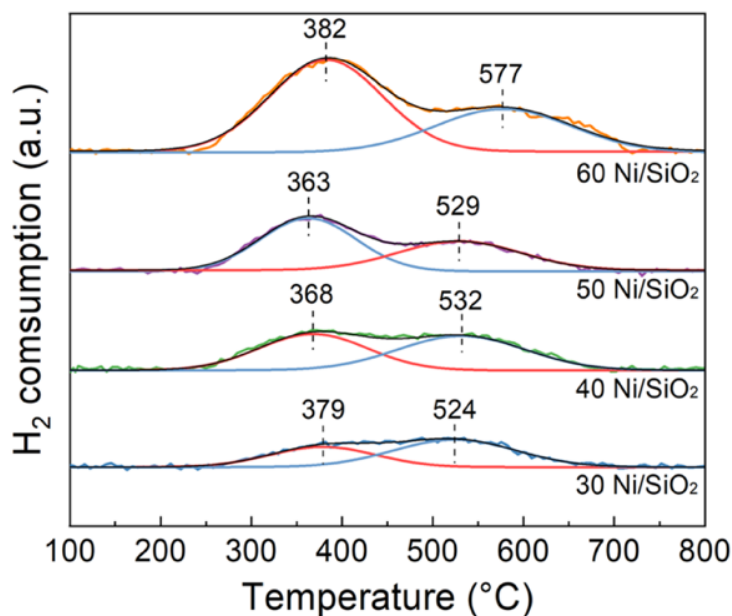


Fig. 5.5. H₂-TPR profiles of the NiO/SiO₂ catalysts.

5.3.3. CO₂ methanation.

The catalytic performance of the materials was tested in the 200-400 °C range under 1.0 bar at a GHSV of 24,000 mL·g⁻¹·h⁻¹ (based on the total

flow). Fig. 5.6 shows that all samples exhibit already some methanation activity at 200 °C. Then activity increases when reaction temperature increases and tends to level off close to the theoretical equilibrium at 350 °C and 400 °C. At each reaction temperature, activity increases when the Ni loading increases from 23 to 38 wt.%. At 45 wt.%, activity appears to drop, consistent with the poorer Ni dispersion discussed above. A maximal CO₂ conversion of 84% with 96.5% CH₄ selectivity is obtained at 350 °C for the 50 Ni/SiO₂. 50 Ni/SiO₂ catalyst was also tested with the GHSV of 24,000 mL·g⁻¹·h⁻¹ at 300 °C for 50 h (Fig. S7) and showed excellent stability, maintaining CO₂ conversion and CH₄ selectivity above 76 % and 98 %, respectively. 50 Ni/SiO₂ catalyst is much more active than the 50 Ni/SiO₂-IM prepared by the more classical impregnation technique. For example, at 250 °C (where conversion is still far from the thermodynamic equilibrium), the catalyst prepared by sol-gel is about 4 times more active than the impregnated one. TOF values (considering the conversion, Ni loading and Ni dispersion) are also calculated and presented in Table 5.1. At 250 °C, 50 Ni/SiO₂ (0.0155 s⁻¹) is 2.8 times more active than 50 Ni/SiO₂-IM (0.0056 s⁻¹).

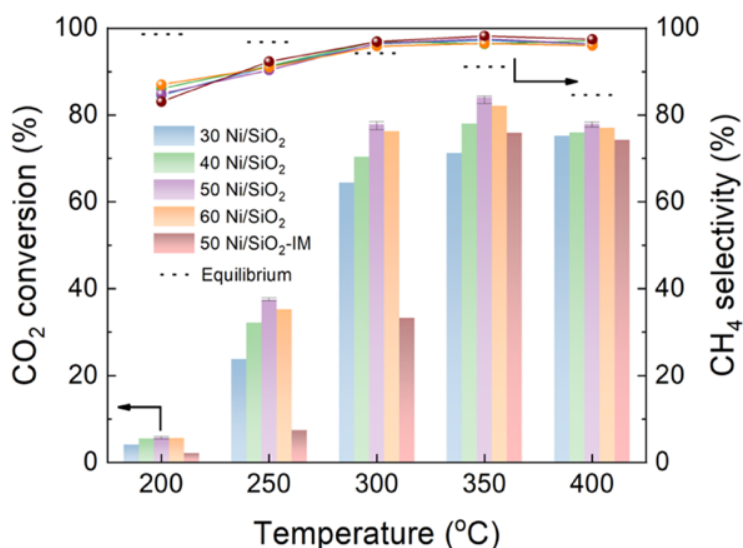


Fig. 5.6. CO₂ conversion and CH₄ selectivity over the Ni/SiO₂

Also, we have collected published data corresponding to Ni and SiO₂-based catalysts tested in similar conditions (space velocity, pressure, temperature, gas composition) and translated them into specific activity ($\mu\text{mol}_{\text{CH}_4} \text{g}_{\text{cat}}^{-1} \text{s}^{-1}$) considering only experimental data points that have been obtained far enough from the thermodynamic equilibrium, i.e. < 40% conversion. Fig. 5.7 shows that our sol-gel based catalyst outcompetes all other reported catalysts. This high specific activity is obviously to be related to the high Ni loading in our samples. If we normalize the performance by the Ni loading, our catalysts are lower than some of the others, showing that a better use of Ni is possible (see also the comparison of TOF values in Table S2). However, high specific activity is important from an engineering point of view, as it governs capital and operational expenditures for the methanation plant. It should be reminded that such high loadings were not accessible with previously reported preparation methods, as the performance dropped dramatically when pushing the loading above 10 or 15 wt.%, as a result of Ni aggregation and sintering (very poor dispersion). With the sol-gel method presented here, the loading can be increased above 20 wt.% and as high as 38 wt.% while maintaining high Ni dispersion and increasing the catalytic activity. It is only when reaching 45 wt.% loading that the dispersion decreases markedly and that the specific activity starts to drop.

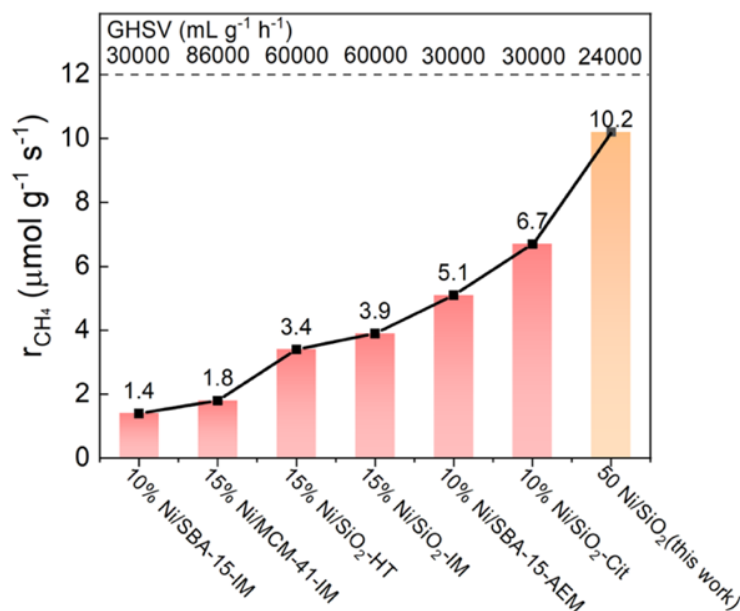


Fig. 5.7. The specific activity of 50 Ni/SiO₂ at 250 °C compared to other reported Ni/SiO₂ catalysts (10% Ni/SBA-15-IM prepared by impregnation method[58], 15% Ni/MCM-41-IM prepared by impregnation method[193], 15 Ni/SiO₂-HT prepared by hydrothermal method[194], 15 Ni/SiO₂-IM prepared by impregnation method[195], 10% Ni/SBA-15-IM prepared by ammonia evaporation method[58], 10% Ni/SiO₂-Cit prepared by combustion-impregnation method[196])

To have a better understanding of the catalytic behavior of these materials, we built the Arrhenius plot by carrying out the reaction with 50 Ni/SiO₂ between 210 and 290 °C (Fig. 5.8). The CO₂ conversion is maintained below 15% (kinetic regime, far from thermodynamic equilibrium) at a high GHSV of 336000 ml g⁻¹ h⁻¹ to measure the intrinsic activity. Surprisingly, instead of one straight line, we observed a break in the Arrhenius plot, indicating that the apparent activation energy was markedly different below and above ~250 °C (82 kJ mol⁻¹ and 99 kJ mol⁻¹ respectively). This feature is usually attributed to competing reactions or reaction mechanisms.[197] In the next section, we discuss the possible implications of such findings by inspecting the

mechanism from an experimental and computational perspective.

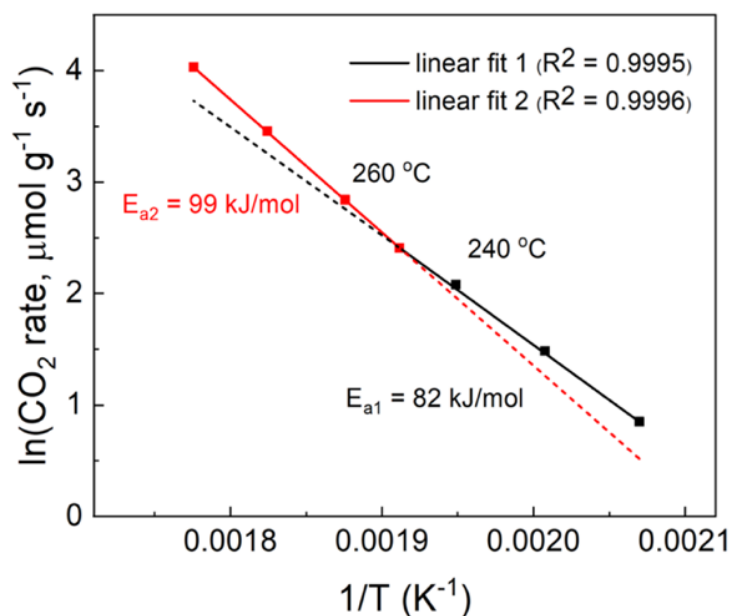


Fig. 5.8. Arrhenius plot of the 50 Ni/SiO₂.

5.3.4. Mechanism study.

Three reaction mechanisms have been proposed to describe the catalytic hydrogenation of CO₂: (i) the formate pathway, (ii) the reverse water gas shift (RWGS)+CO-hydrogenation pathway, and (iii) the C-O bond cleavage pathway.[49, 188, 198, 199] In the formate route, CO₂ is molecularly chemisorbed to form carbonate intermediates, which decompose to formate species and react with H₂ to produce methane. In the CO route, the CO₂ molecules undergoes a dissociative chemisorption, yielding a surface carbonyl and an oxygen atom that both react with H₂ afterwards. In the C-O bond cleavage pathway, the yielded carbonyl from the CO₂ dissociation can further dissociate to form carbon which then reacts with H₂.

Many theoretical and experimental studies have been conducted to

study the mechanism of CO₂ methanation on Ni-based catalysts.[68, 75, 200, 201] However, there is no unified view on the path that governs catalytic activity. For Ni/CeO₂ catalysts, for example, the formate pathway and the RWGS-CO hydrogenation pathway were shown to occur in parallel, the latter mechanism being dominant, especially at low temperature.[191] On the contrary, on Ni/ZrO₂ and Ni/(Mg,Al)O_x catalysts, the formate pathway was identified as the most plausible.[200, 201] Obviously, the support can have a great influence on the CO₂ methanation mechanism. Furthermore, using DFT simulation, Ren *et al.* claimed that the C-O bond cleavage pathway should prevail on Ni catalysts.[68] Clearly, there is a need to further inspect conflicting experimental observations and theoretical calculations. Here, we use a combination of temperature programmed surface reaction (TPSR) experiments and density functional theory (DFT) simulation in an attempt to decipher the different possible mechanisms at play in the relevant reaction temperature ranges.

CO₂-TPD tests were firstly performed to assess the CO₂ adsorption ability of the catalysts. As shown in Fig. 5.9a, the total CO₂ adsorption amount increases with the Ni loading. Furthermore, there is almost no CO₂ detected for the pure SiO₂ in the CO₂-TPD process (Fig. S9), confirming that CO₂ adsorption occurs on the surface of Ni. Three distinct desorption events can be observed, corresponding to three kinds of adsorbed CO₂ species. DRIFTS coupled with CO₂ adsorption and desorption sheds light on the nature of these species (Fig. 5.9b). 50 Ni/SiO₂ was saturated by CO₂ and then flushed under He atmosphere at 30 °C before recording IR spectra. The spectrum features the clear signatures of bidentate carbonate (1665, 1484 cm⁻¹), bicarbonate (1622 cm⁻¹), monodentate carbonate (1521 cm⁻¹), and polydentate carbonate (1402 cm⁻¹).[49, 200] As the temperature is increased to 120 °C, the band for bicarbonate disappears, and a new band for multi-bonded carbonyl (1693 cm⁻¹)[202-204] appears but is removed at 450 °C. Meanwhile, the band for monodentate carbonate decreases at 120 °C and disappears at 170 °C. To sum up, bicarbonate and monodentate carbonate species were desorbed at 120 and 170 °C, and the CO from

the dissociation of CO₂ was desorbed at 450 °C.

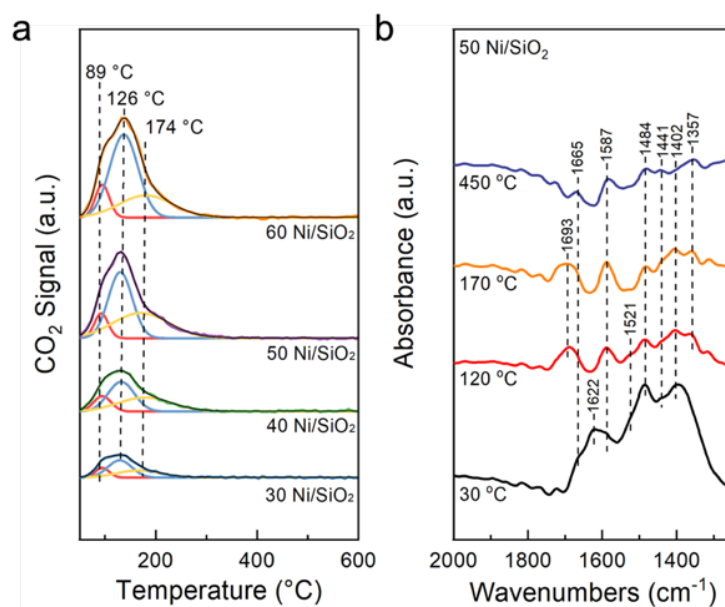


Fig. 5.9. (a) CO₂-TPD of profiles of the NiO/SiO₂ catalysts, (b) in-situ CO₂ desorption DRIFTS of the 50 Ni/SiO₂.

After having identified the nature of the adsorbed species and their stability over the catalysts, a set of CO₂-TPSR tests was designed to elucidate how these species dynamically interacts with the Ni/SiO₂ catalyst in the presence of H₂. Specifically, CO₂-TPSR experiment was performed by adsorbing CO₂ at 30 °C followed with the purge process in Ar under different temperature, and then using a flow of 5% H₂ during the temperature ramp. Based on the fact that bicarbonate, monodentate carbonate and carbonyl species could be desorbed at 120 °C, 170 °C and 450 °C respectively (see CO₂-TPD and DRIFTS), we set three purge temperature slightly higher (140 °C, 200 °C or 500 °C) to provoke the desorption of targeted adsorbed CO₂ species. From the CO₂-TPSR results (Fig. 5.10a-5.10c), we can observe CH₄ formed from ca. 150 °C, and the CH₄ production profile is modified when altering the purge temperature. As expected, the total amount of CH₄ produced decreases when the purge temperature increases. After

deconvoluting the CH₄ production profile, three distinct peaks centered at about 210 °C, 270 °C and 375 °C can be identified (denoted as P₂₁₀, P₂₇₀, and P₃₇₅). We hypothesize that these three methane production peaks may indicate different routes for CO₂ methanation starting from different adsorbed species.

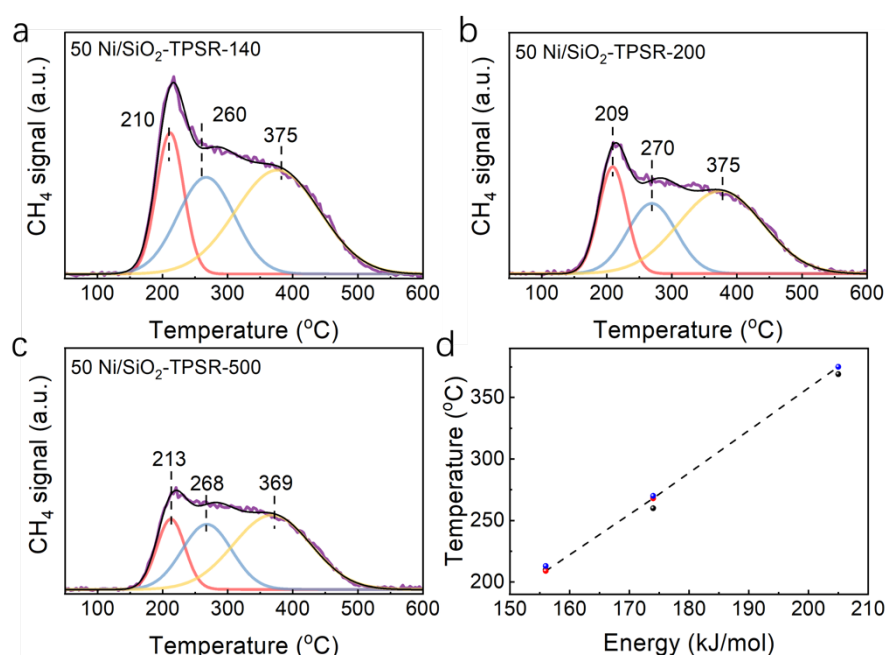


Fig. 5.10. (a-c) TPSR of 50 Ni/SiO₂ with different purge temperature; (d) Relationship between the energy barrier of RDS for each pathway obtained from DFT and the temperature of CH₄ formation peak.

The amount and percentage of CH₄ formed during TPSR for the different peaks are listed in Table S3. Comparing Fig. 5.10a (purge temperature: 140 °C) with Fig. 5.10b (purge temperature: 200 °C), a marked decrease of the P₂₇₀ could be observed (while the other peaks are marginally modified). Since monodentate carbonate are the species that can be evacuated from the surface when the purge temperature increases from 140 °C to 200 °C, it can be inferred that the CH₄ from the P₂₇₀ is related to the hydrogenation of monodentate carbonate. Since monodentate carbonate can be hydrogenated to CH₄ via the formate

pathway with the monodentate formate as an intermediate[75], we propose that the P₂₇₀ can be attributed to CH₄ formed via the formate pathway. Furthermore, an obvious decrease of the P₂₁₀ is observed when comparing Fig. 5.10c (purge temperature: 500 °C) with Fig. 5.10b (purge temperature: 200 °C). Considering the fact that carbonyl species are desorbed when the purge temperature increases from 200 °C to 500 °C, the CH₄ from the P₂₁₀ can be related to the hydrogenation of carbonyl. The carbonyl species can be hydrogenated to CH₄ via the RWGS+CO hydrogenation pathway.[191] Therefore, we propose the P₂₁₀ can be attributed to the CH₄ formed via the RWGS+CO hydrogenation pathway.

DFT simulation was conducted to further investigate the possible reaction paths from CO₂ to CH₄. Although the metal-support interaction is a widely recognized effect in heterogeneous catalysis, using SiO₂, as an inert and stable support, could eliminate the impacts of oxygen vacancy and other factors (such as reduction-induced encapsulation) introduced by the support on the reaction.[205, 206] Furthermore, based on the characterization, CO₂ adsorbed occurs solely on the surface of Ni, which allows us to simplify the structure of the catalysts to Ni, as typically needed in DFT studies.[207-209]

The reaction energy pathways for the hydrogenation of CO₂ into CH₄ over a model Ni (111) surface are given in Fig. 5.11. We find that the most endothermic step of RWGS+CO-hydrogenation pathway is the formation of methoxy (*OCH₃) at 156 kJ/mol, whereas for the formate pathway and C-O bond cleavage pathway, it is respectively the formation of the formate intermediate (*OCHO) at 174 kJ/mol and the formation of CH₄ from *CH₃ at 205 kJ/mol. Those three calculated energies are different but are in the same range, which means the corresponding pathway can potentially proceed in parallel. Our results show that the CO₂ methanation via RWGS+CO-hydrogenation pathway is lower in energy than that via formate pathway and C-O bond cleavage pathway; hence, RWGS+CO-hydrogenation pathway is more feasible and dominant at low temperature, in agreement with the TPSR results.

Interestingly, we found a linear relationship between the temperatures of the three CH₄ formation peaks (TPSR) and the energy barrier of the RDS for each pathway obtained from DFT (Fig. 5.10d). Reasoning that P₂₁₀ and P₂₇₀ correspond to the CH₄ formed from the RWGS+CO and the formate pathways respectively, we propose that the P₃₇₅ peak corresponds to methane production occurring via the C-O bond cleavage pathway. This can be consisted with the AP XPS data deputed by Heine *et al.* [59], but it is suggested that further efforts are needed to provide direct experimental evidence for that pathway at high temperature.

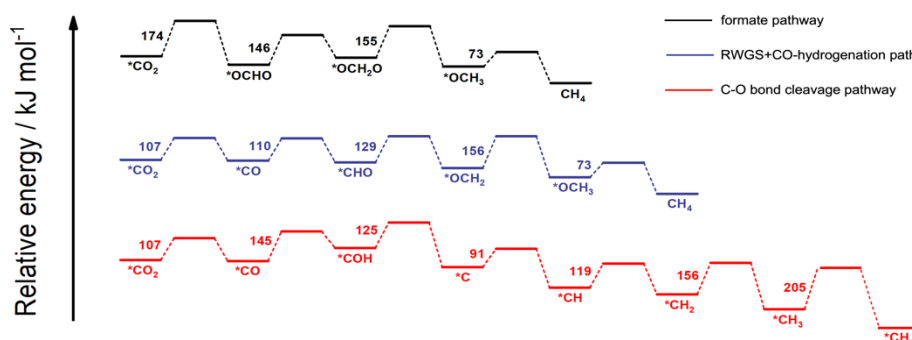


Fig. 5.11. Relative potential energy surfaces for CO₂ methanation in formate pathway, RWGS+CO-hydrogenation pathway and C-O bond cleavage pathway.

Overall, combining the experimental and theoretical methods, we identify that on the surface of the small Ni particles found in the high-loading Ni/SiO₂ catalysts, adsorbed CO₂ can be hydrogenated to CH₄ via three pathways. Monodentate carbonate can be hydrogenated to CH₄ in the formate pathway. Carbonyl from the dissociation of CO₂ and C from the further dissociation of CO on the catalyst surface are hydrogenated to CH₄ in RWGS+CO hydrogenation pathway and C-O bond cleavage pathway respectively. In the conditions of the continuous catalytic reaction, the co-existence and possible interplay of different mechanisms may explain why the Arrhenius plots features a broken line, with more than one activation energy. In particular, the inflection points (at ~ 250 °C) in the Arrhenius plots is between 210 °C and 270 °C (the

temperature of first and second peak of deconvoluted TPSR curve), and the E_a below 250 °C is lower than the E_a over 250 °C, which suggests that the RWGS+CO hydrogenation pathway with lowest energy barrier is dominant below 250 °C. Theoretically, there should be another inflection points in the Arrhenius plots between 270 °C and 380 °C, but our study only includes data between 210 °C and 290 °C (in our set-up, it is difficult to reduce the CO₂ conversion to <15% when the reaction temperature is over 300 °C).

5.4. Conclusion

In summary, this study leads to two main conclusions. First, it is possible to prepare Ni/SiO₂ catalysts with high nickel loading, while maintaining high dispersion. Mesoporous Ni/SiO₂ catalysts were prepared using a simple sol-gel method. These catalysts exhibited high specific surface area (in the 350-530 m²/g range), open texture and a high Ni dispersion (e.g., 11% for 38 wt.% Ni/SiO₂ catalyst) of small Ni nanoparticles (~4.6 nm). Consistently, these mesoporous Ni/SiO₂ catalysts displayed record specific activity (10.2 μmol g⁻¹ s⁻¹ at 250 °C), clearly outperforming other SiO₂ supported Ni-based catalysts.

Secondly, we provide insights into the CO₂ methanation mechanism that takes place on these catalysts. Combining theoretical and experimental methods, the occurrence of the three different CH₄ formation pathways can be confirmed. Carbonyl from the dissociation of CO₂ is hydrogenated to CH₄ in the RWGS+CO hydrogenation pathway, which is dominant at low temperature (< 250 °C) due to its lowest energy barrier compared to the other two pathways. The formate pathway, correlated with the monodentate carbonate surface species, could proceed in parallel. C from the further dissociation of CO on the catalyst surface is hydrogenated to CH₄ in the C-O bond cleavage pathway.

Chapter 6 Deciphering the role of dopant (Mn, Co, and Cu) in the CO₂ methanation reaction over Ni/SiO₂ catalysts prepared by sol-gel chemistry

The results presented in this chapter are submitted and under review; a preprint is available:

CO₂ methanation: deciphering the role of dopants (Mn, Co, and Cu) in Ni/SiO₂ catalysts prepared by sol-gel chemistry

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In this chapter, a series of model bimetallic catalysts were prepared by sol-gel chemistry to study the effect of dopant on the catalytic performance. Compared to Ni/SiO₂ catalyst, the Mn-doped and Co-doped catalysts showed a higher methanation activity, with the former showing better performance below 250 °C and the latter showing better performance over 300 °C. On the contrary, the Cu-promoted catalyst showed a lower CO₂ conversion with a lower CH₄ selectivity in the whole temperature range. A comprehensive characterization study (TEM, XRD, XPS, H₂-TPR, CO₂-TPD, in situ DRIFTS, and TPSR analyses) suggests that the effect of promoters is not directly related to improvement of dispersion, reducibility, or basicity. Instead, we show that the promoters orient the reaction mechanism and favor the conversion of key intermediates. Mn addition has the highest promoting effect on the hydrogenation of formaldehyde intermediate (*OCH₂) to methoxy intermediate (*OCH₃), i.e. the rate determining step of the “RWGS+CO hydrogenation” pathway which is shown to predominate at low reaction temperature. Co addition facilitates the formation of formate species, i.e. the rate determining step of the formate pathway which is also active at high reaction temperature. Cu addition has a negative effect on the rate determining step of those two pathways, resulting a lower performance of Ni-Cu/SiO₂.

6.1. Introduction

Among the numerous ways to increase the catalytic performance, the effect of promoter has been extensively studied. According to the research, the promoter could alter the dispersion of active components, the reducibility, the surface basicity and even the reaction pathways.[104, 113, 141, 210] However, the results are still controversial, which could result from different support. Wu *et al.* reported that the Ni-Mn/Al₂O₃-ZrO₂ catalyst exhibited the best catalytic activity in comparison to other addition (Fe, Co and Cr).[105] On the contrary, Xu *et al.* found that the Co-doped catalysts exhibited much higher activity than the Mn, Fe, and Cu-doped catalysts in the

Ni/Ce_{0.8}Zr_{0.2}O₂ system.[211] Therefore, the effect of promoter on the Ni-based catalyst with an inert support requires further clarification.

Herein, a series of Ni-M/SiO₂ (M = Mn, Co, Cu) bimetal catalysts were prepared by sol-gel method and employed for CO₂ methanation. We found that Mn addition improved the CO₂ methanation activity of the Ni/SiO₂ catalyst at relatively low temperature (below 250 °C), and Co addition improved the CO₂ methanation activity of the Ni/SiO₂ catalyst at relatively high temperature (over 300 °C). The doping effect on the structure of the obtained catalyst was well elucidated. Moreover, the CO₂ methanation mechanism was investigated by in situ diffuse reflectance infrared spectroscopy (DRIFT) spectroscopy and temperature-programmed surface reaction (TPSR).

6.2. Experimental summary

6.2.1. Catalyst preparation

The bimetallic Ni-M/SiO₂ (M = Mn, Co, and Cu) and a monometallic Ni/SiO₂ were both prepared by a sol-gel method. Typically, anhydrous ethanol (EtOH), distilled H₂O, and HNO₃ were added to tetraethyl orthosilicate (TEOS) at a molar ratio of 3:1.8:0.03:1 and stirred for 1 h to obtain a clear SiO₂ sol. The required amount of Ni(NO₃)₂·6H₂O and transition metals (Mn, Co, and Cu) nitrates were dissolved in ethylene glycol (EG) and methanol ($V_{EG}:V_{\text{methanol}} = 3:2$), and the solution was maintained at 2 M of metal salts (Ni + dopant). The solution was then added to the SiO₂ sol and stirred for another 1 h. The obtained slurry was aged at 30 °C for 12 h and dried at 120 °C for another 12 h to form a gel. The dried gel was calcined in air at 300 °C (1 °C/min) for 2 h, and then at 500 °C (1 °C/min) for an additional 2 h. The mass fraction of nickel loading was fixed at 20% for all the catalysts and the theoretical molar ratio for Ni/M (M = Mn, Co, and Cu) was fixed at 4. The calcined sample were denoted as “Ni-M/SiO₂”. The calcined catalyst was reduced in situ in the reactor under a H₂/He flow (see below), and the corresponding samples were denoted “Ni-M/SiO₂-

r”.

6.3. Results and discussion.

6.3.1. Catalytic performance.

The CO₂ methanation performance of Ni/SiO₂ and bimetallic Ni-M/SiO₂ catalysts was evaluated in the 200-400 °C temperature range, with a GHSV of 24000 mL g⁻¹ h⁻¹. CO₂ conversion and CH₄ selectivity are shown in Fig. 6.1. In terms of CH₄ selectivity, Ni/SiO₂-r catalyst is over 90% at the reaction temperature over 250 °C. Mn and Co addition have no obvious influence on the CH₄ selectivity, whereas Cu addition leads to more CO generated over Ni-Cu/SiO₂-r catalyst via the reverse water gas shift (RWGS) reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$), resulting in CH₄ selectivity lower than 90%. In terms of CO₂ conversion, both Mn and Co addition improved the CO₂ conversion in the whole temperature range. Notably, Mn addition had a more pronounced effect at lower temperature (≤ 250 °C), while Co addition had a more pronounced effect at higher temperature (≥ 300 °C). On the contrary, Cu addition consistently has a negative effect on the catalytic activity, CO₂ conversion in the 200-400 °C temperature range for Ni-Cu/SiO₂ is lower than that for Ni/SiO₂.

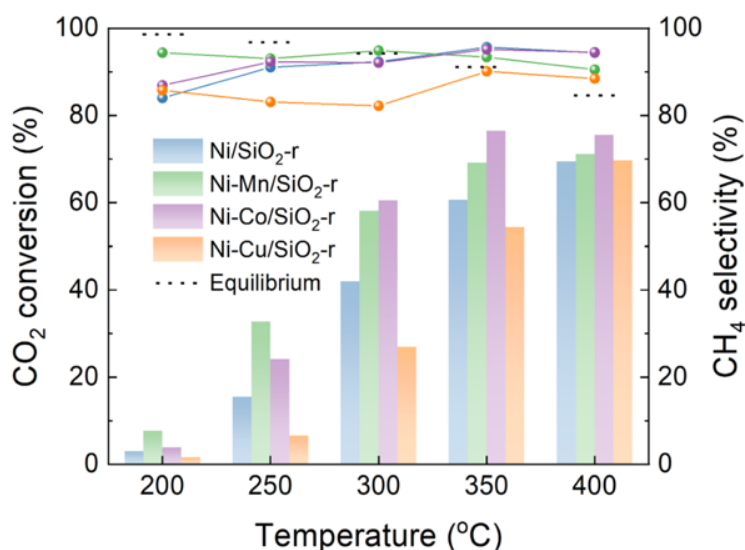


Fig. 6.1. CO₂ methanation performance in terms of CO₂ conversion and CH₄ selectivity as a function of temperature.

6.3.2. Catalyst characterization.

The catalyst morphology and nanostructure were explored by TEM, and high-resolution TEM (HRTEM) techniques. As shown in Fig. 6.2a-d, uniformly dispersed particles could be observed for all reduced catalysts. The average particle size of Ni/SiO₂-r, Ni-Mn/SiO₂-r, Ni-Co/SiO₂-r, and Ni-Cu/SiO₂-r is 3.3, 4.7, 3.8 and 3.5 nm, respectively (listed in Table 5.1). The clear lattice fringe distances observed on Ni/SiO₂-r is 0.203 nm, corresponding to the Ni (111) plane.[75] On Ni-Mn/SiO₂-r and Ni-Cu/SiO₂-r, the Ni (111) plane could also be confirmed. On the contrary, on Ni-Co/SiO₂-r, the interplanar spacing is 0.216 nm, which is assigned to the NiCo (1-11) plane and indicates the formation of NiCo alloy.[212] Furthermore, Mn₃O₄ (312) plane over Ni-Mn/SiO₂-r, CoO (200) plane over Ni-Co/SiO₂-r and Cu (111) plane over Ni-Cu/SiO₂-r are confirmed by the observation of a 0.174 nm, 0.236 nm, and 0.218 nm lattice fringe distance, respectively.[213-215]

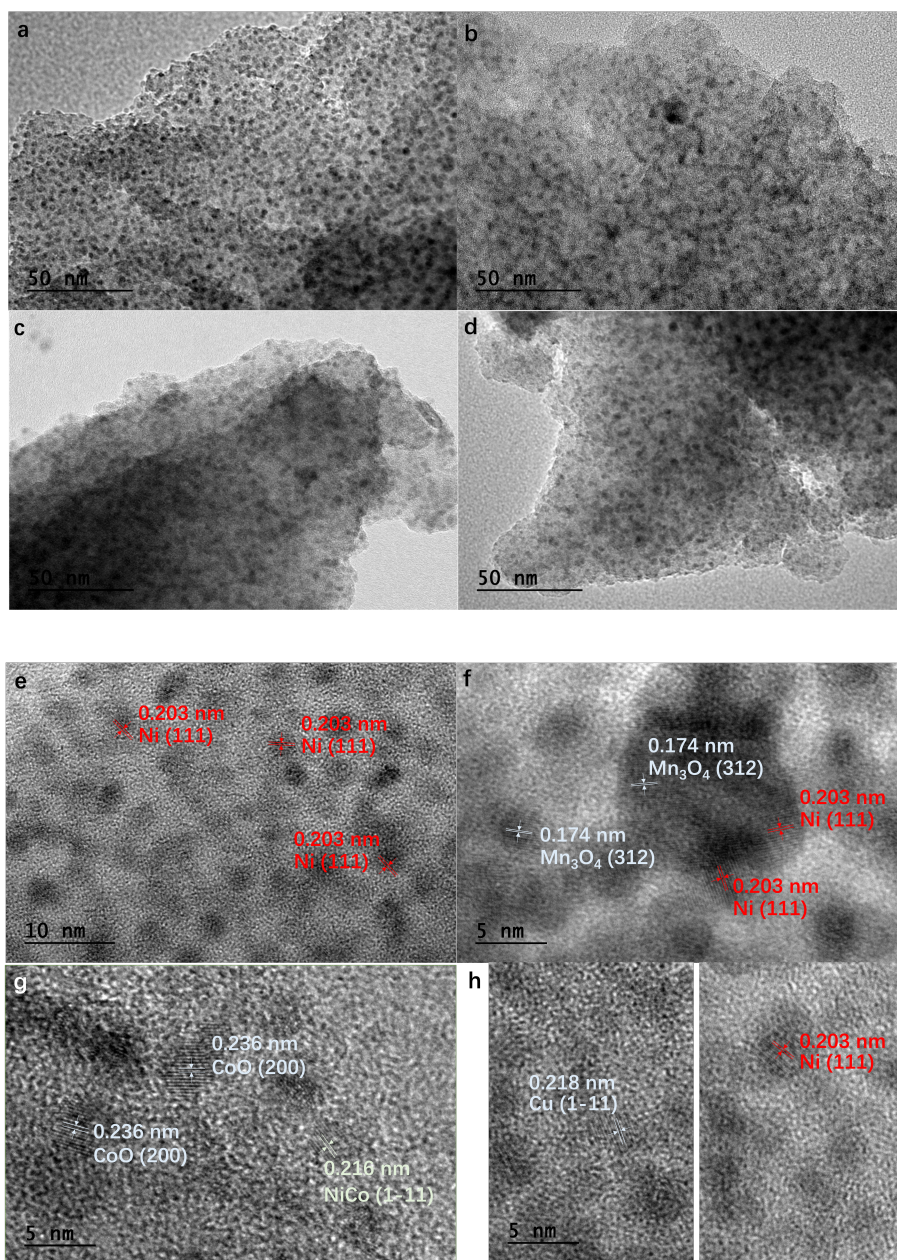


Fig. 6.2. TEM images of reduced (a, e) Ni/SiO₂-r, (b, f) Ni-Mn/SiO₂-r, (c, g) Ni-Co/SiO₂-r, and (d, h) Ni-Cu/SiO₂-r catalysts.

The catalysts textural properties were measured by N₂ physisorption. As shown in Fig. S10, the catalysts all exhibited type IV adsorption

isotherms with a H1-type hysteresis loop, which is characteristic of mesoporous materials[216]. Their average pore diameter is always in the same range of 2.1-2.4 nm (Table 6.1). Specific surface area and total pore volume reach as high as ~510 m²/g and 0.15 cm³/g respectively, for all samples.

The catalyst crystalline structure was determined by XRD (Fig. 6.3). All samples exhibited a broad diffraction signal centered at $2\theta \sim 23^\circ$, which is ascribed to the amorphous silica.[207] For the calcined samples, two weak and broad diffraction peaks at 37.1° and 43.2° can be assigned to the (111) and (200) planes of NiO.[75] After being reduced under H₂, no obvious diffraction peaks are detected in the reduced samples, suggesting that the expectedly formed Ni particles are small. Consistently, a high Ni dispersion value (15.8%) was determined by H₂ chemisorption measurement for Ni/SiO₂. For metal-doped catalysts, the dispersion remains in the same range, yet slightly lower (listed in Table 6.1), which points to slightly larger particles.

Table. 6.1. Physical Properties of the prepared catalysts.

Sample	S _{BET} (m ² /g)	V _p (cm ³ /g)	D _p (nm)	Ni content ^a (%)	Dopant content ^a (%)	Ni dispersion ^b (%)	Ni particle size ^c (nm)
Ni/SiO ₂	510	0.15	2.1	18.9	-	15.8	3.3
Ni-Mn/SiO ₂	539	0.19	2.4	18.3	5.1	12.4	4.7
Ni-Co/SiO ₂	564	0.16	2.2	18.2	4.7	13.4	3.8
Ni-Cu/SiO ₂	566	0.14	2.2	18.7	4.6	14.1	3.5

^a Determined by ICP-AES measurement.^b Determined by H₂ chemisorption.^c Obtained from the TEM results.

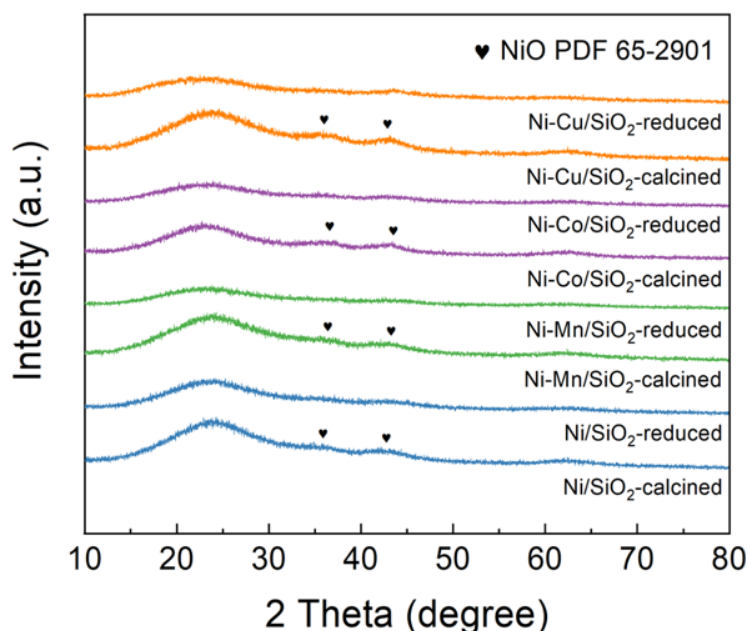


Fig. 6.3. XRD patterns of the calcined and reduced catalysts.

The reduction behavior of calcined catalysts was investigated using H₂-TPR measurements (Fig. 6.4). Two H₂ consumption peaks centered at 373 °C and 565 °C were fitted for Ni/SiO₂ catalysts, which correspond to the reduction of Ni²⁺ to metallic Ni⁰, with the contribution at higher temperature associated to NiO particles in stronger interaction with the SiO₂ matrix. Mn, Co, and Cu addition was found to facilitate the reduction of Ni species as the corresponding reduction peaks shifted to lower temperatures compared to pristine Ni/SiO₂ catalysts. Additional peaks are observed at 740 °C for Ni-Co/SiO₂ and at 257 °C for Ni-Cu/SiO₂, assigned to the reduction of cobalt oxide and copper oxide, respectively.[89, 217, 218] A distinct reduction of Mn oxide was not observed (possibly overlapped with the reduction of Ni oxide).

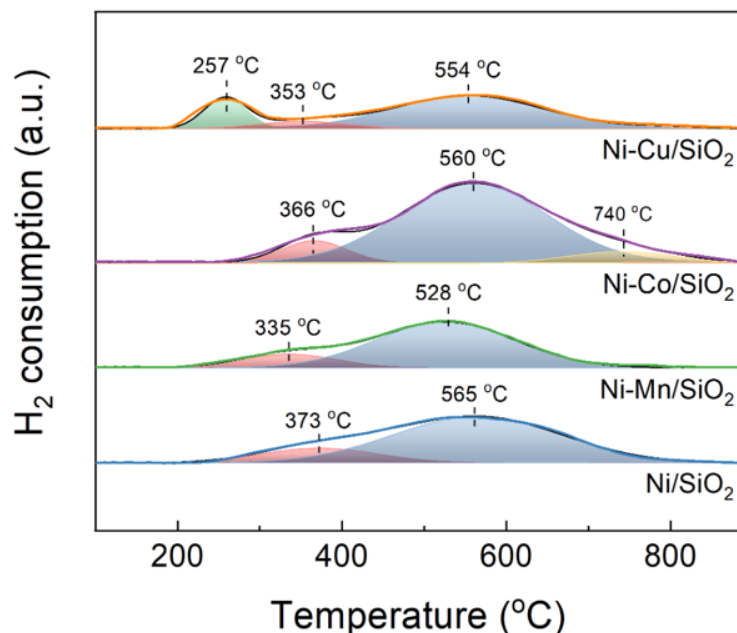


Fig. 6.4. H₂-TPR profiles of the prepared catalysts.

The chemical state and surface compositions of the reduced catalysts were determined by XPS. As shown in the high-resolution Ni 2p_{3/2} spectra (Fig. 6.5a), the peak at 852.6 eV observed on all reduced catalysts confirms the presence of metallic Ni.[219] Furthermore, the peak at 855.7 eV with a broad satellite at 861.7 eV is associated to the presence of NiO, which can be explained by the re-oxidation of small Ni nanoparticles surface, in ambient air.[191] The chemical state of the promoters (Mn, Co, and Cu) was also analyzed (Fig. 6.5b). The spectrum of Mn 2p_{3/2} in Ni-Mn/SiO₂-r can be deconvoluted into three peaks with binding energies of 644.7 eV, 641.3 eV, and 639.8 eV attributed to Mn⁴⁺, Mn³⁺ and Mn²⁺, respectively.[220, 221] In the high-resolution spectrum of Co 2p_{3/2} of Ni-Co/SiO₂-r, the peak at 782.1 eV accompanied by a broad satellite peak at 786.8 eV are attributed to surface Co²⁺ species, and the weak shoulder peak at around 776.9 eV can be linked to the presence of Co⁰ species.[222] Thus, while showing somewhat more reduced Mn 2p_{3/2} and Co 2p_{3/2} peaks than in the

calcined catalysts (Ni-Mn/SiO₂ and Ni-Co/SiO₂, see Fig. S11), the reduced catalysts still show a majority of oxidized doping agents (Mn⁴⁺ and Mn³⁺ on the one hand and Co²⁺ on the other hand). This is consistent with the absence of a distinct reduction peak in H₂-TPR. On the contrary, the Cu 2p_{3/2} spectrum from Ni-Cu/SiO₂-r shows only one peak attributed to Cu⁰ species, at around 933.0 eV.[223] Thus, the partly oxidized Cu found in Ni-Cu/SiO₂ (Fig. S11) is fully converted to metallic Cu upon reduction, which is consistent with the obvious reduction peak for the Ni-Cu/SiO₂ catalyst in H₂-TPR.

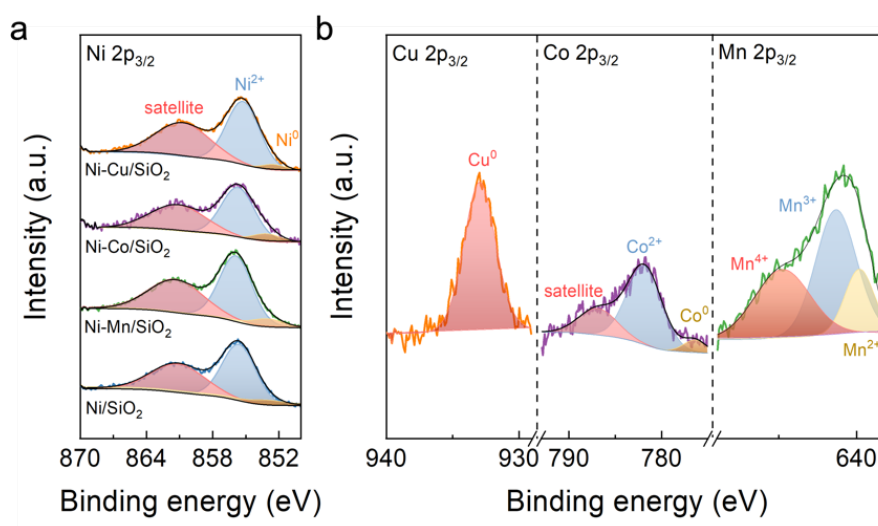


Fig. 6.5. XPS spectra of (a) Ni 2p_{3/2}, (b) Mn 2p_{3/2}, Co 2p_{3/2}, and Cu 2p_{3/2} over the prepared catalysts.

CO₂-TPD experiments were performed to characterize the surface basicity (Fig. 6.6). CO₂ desorption events – characterized by their intensity and temperature – can reveal the amount and strength of different CO₂ adsorption sites. The peak appearing at around 100 °C is attributed to physisorbed CO₂. [224, 225] Furthermore, we can observe three more distinct desorption events at higher temperature (ca. 150 °C, ca. 205 °C, and over 550 °C), which are corresponded to three kinds of adsorbed CO₂ species over the weak, medium and strong basic site and exist in the form of bicarbonate, monodentate carbonate and bidentate

carbonate.[75] A series of works indicated that the catalytic activity can be promoted by increasing the number of weak and medium basic sites but is not correlated with the strong basic sites (which are thought to suppress further hydrogenation).[80, 226] The amount of CO₂ adsorption at weak and medium basic sites is listed in Table 6.2. It can be seen that Ni-Cu/SiO₂-r possesses higher weak and medium basicity than Ni/SiO₂-r, while Ni-Mn/SiO₂-r and Ni-Co/SiO₂-r possess much lower weak and medium basicity than Ni/SiO₂-r.

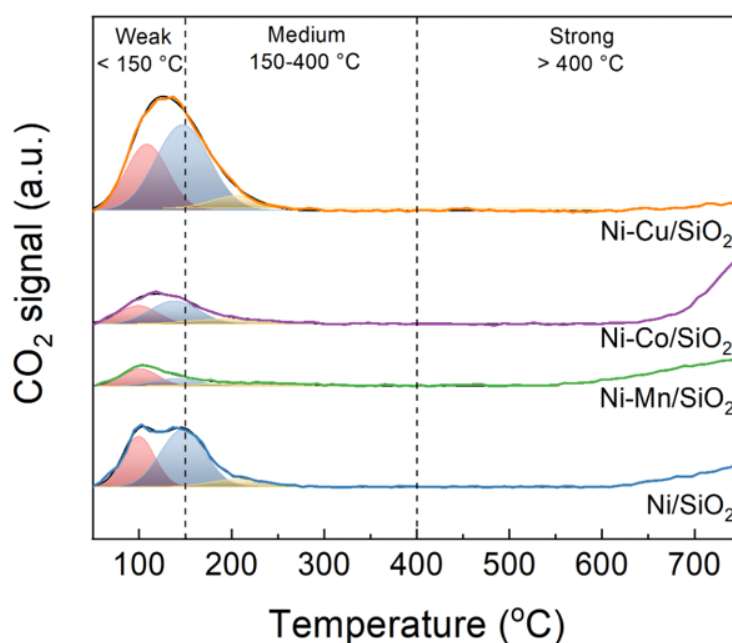


Fig. 6.6. CO₂-TPD profiles of the prepared catalysts.

Table 6.2. The CO₂-TPD analyses of the reduced catalysts.

	Weak basicity	Medium basicity
Ni/SiO ₂ -r	3.29	0.55
Ni-Mn/SiO ₂ -r	0.45	0.35
Ni-Co/SiO ₂ -r	1.45	0.54
Ni-Cu/SiO ₂ -r	5.97	0.82

Dispersion, reducibility and basicity are the key factors usually proposed to govern catalytic performance.[227] Herein, the addition of Cu (compared with pristine Ni/SiO₂) was shown to lead to (i) similar dispersion (H₂ chemisorption) , (ii) increased reducibility (H₂-TPR), and (iii) increased basicity (CO₂-TPD). All three factors should be favorable and should point to higher catalytic performance. Yet, Ni-Cu/SiO₂ exhibited the lowest activity. The addition of Mn and Co resulted in similar dispersion and increased reducibility (compared with pristine Ni/SiO₂) but decreased basicity. However, a higher catalytic performance was obtained for the Ni-Mn/SiO₂ and Ni-Co/SiO₂. Overall, in this catalyst system, there must be another factor playing a key role on the methanation activity. To understand this apparent discrepancy, we have to investigate the reaction mechanism.

6.3.3. Investigation of the CO₂ Methanation Mechanism by in situ DRIFTS and TPSR Experiment.

In general, the possible CO₂ methanation reaction pathways can be divided into three categories: the formate pathway, the RWGS+CO-hydrogenation pathway and the direct C–O bond cleavage pathway.[227] In this study, in-situ DRIFTS and TPSR experiments were carried out in a reacting mixture of CO₂/H₂, in an attempt to identify the surface species that form during reaction and thereby enhance our understanding of the possible CO₂ methanation pathways over the studied catalysts.

Fig. 6.7 shows the DRIFT spectra recorded in CO₂ methanation conditions over the four catalysts, from 100 °C to 400 °C. For Ni/SiO₂-r (Fig. 6.7a), two main species are visible at 100 °C, namely carbonate and carbonyl species. In detail, monodentate carbonate (1512 cm⁻¹), bidentate carbonate (1462 cm⁻¹) and bicarbonate (1388 cm⁻¹) can be observed.[200] The presence of these carbonates as the CO₂-derived surface species is consistent with CO₂-TPD results. As the temperature increases, the bands of those carbonate species become less intense, and the peak attributed to bicarbonate disappears totally at 250 °C. Meanwhile, the vibration modes of monodentate formates (1330 cm⁻¹)

and bidentate formates (1369 cm⁻¹)[75] appear with high intensity at 150 °C and 250 °C respectively. It has been reported that monodentate formates and bidentate formates can be derived from the hydrogenation of monodentate carbonates and bidentate carbonates.[226] In addition to carbonate and formate species, the bands for 2-fold carbonyl species (1947 cm⁻¹) and 3-fold carbonyl species (1833 cm⁻¹)[75] can be clearly seen from 100 °C. These carbonyl species adsorbed on Ni sites are thought to originate from the dissociative adsorption of CO₂. [228] It seems possible that the adsorbed carbonyl species can further react with the adsorbed H atoms on Ni sites to produce formyl (*HCO) species, as indicated by the band at 1747 cm⁻¹[229], and the formyl species can be subsequently hydrogenated towards CH₄. Furthermore, formaldehyde species (1123 cm⁻¹) and methoxy species (1044 cm⁻¹) also appear as intermediate.[229, 230]

For bimetallic Ni-M/SiO₂-r catalysts (Fig. 6.7b-6.7d), carbonate and carbonyl species can be observed with higher intensity (Ni-Mn/SiO₂-r, Ni-Co/SiO₂-r) or lower intensity (Ni-Cu/SiO₂-r) as compared to those over Ni/SiO₂-r. Furthermore, the peak intensity of formate species (ca. 1312 cm⁻¹ and 1355 cm⁻¹) and formaldehyde species (ca. 1123 cm⁻¹) shows clear difference for those four catalysts. Specifically, the peak intensity of the formate intermediate increases following the sequence of Ni-Cu/SiO₂-r < Ni/SiO₂-r < Ni-Mn/SiO₂-r < Ni-Co/SiO₂-r (Fig. 6.8a), while the peak intensity of formaldehyde intermediate increases following the sequence of Ni-Mn/SiO₂-r < Ni-Co/SiO₂-r < Ni/SiO₂-r < Ni-Cu/SiO₂-r (Fig. 6.8b).

As shown in our previous work[231], monodentate carbonate species can be hydrogenated to CH₄ via the formate pathway, in which the formate formation is the rate determining step. Carbonyl species derived from the dissociation of CO₂ on the catalyst surface is hydrogenated to CH₄ via the RWGS+CO hydrogenation pathway, in which the rate determining step is the formation of methoxy from formaldehyde.[39] In this context, DRIFTS results suggest that the formation of formate could be facilitated by Mn and Co addition, as

indicated by the higher peak intensity of formate over Ni-Co/SiO₂-r and Ni-Mn/SiO₂-r compared with Ni/SiO₂-r (Ni-Co/SiO₂-r > Ni-Mn/SiO₂-r > Ni/SiO₂-r). That is, Mn and Co addition could enhance the formate pathway, and Co addition exhibits a more positive effect on this pathway.

Mn and Co addition appear to facilitate the formation of methoxy from formaldehyde as suggested by the lower peak intensity of formaldehyde over Ni-Mn/SiO₂-r and Ni-Co/SiO₂-r compared with Ni/SiO₂-r (Ni-Mn/SiO₂-r < Ni-Co/SiO₂-r < Ni/SiO₂-r). Correspondingly, Mn and Co addition enhance the RWGS+CO hydrogenation pathway, with the former showing stronger enhancement effect. To confirm the effect of dopants on the transformation of formaldehyde, we performed HCHO-TPSR experiments. In Fig. 6.9a, the curve of $m/z = 29$ represents the desorption of formaldehyde, and the curve of $m/z = 31$ represents the desorption of methanol (methanol is added as stabilizer in the HCHO solution). Each of these curves only have one desorption peak. The curve of $m/z = 15$, however, shows two distinct desorption peaks. $m/z = 15$ could represent both methanol and methane. Considering the same trend between the first peak of the $m/z = 15$ curve and the $m/z = 31$ curve (methanol), the first peak of the $m/z = 15$ curve is attributed to the desorption of methanol. Thus, the formation of CH₄ is revealed by the second peak of the $m/z = 15$ curve. Similar curves are observed for the three bimetallic catalysts (Fig. S12), and the curves of $m/z = 15$ of the four catalysts are shown in Fig. 6.9b. The Ni/SiO₂-r, Ni-Mn/SiO₂-r, Ni-Co/SiO₂-r, and Ni-Cu/SiO₂-r catalyst exhibit CH₄ formation breakthroughs at 167 °C, 160 °C, 162 °C, and 181 °C and reaches maximum at 206 °C, 197 °C, 201 °C, and 240 °C. The breakthrough and maximum of CH₄ production at lower temperatures demonstrate that Ni-Mn/SiO₂-r and Ni-Co/SiO₂-r are intrinsically more active than Ni/SiO₂-r for the hydrogenation of formaldehyde to CH₄, and Mn addition show a better effect than Co addition. On the contrary, Cu addition inhibits the hydrogenation of formaldehyde to CH₄.

The rate determine step of RWGS+CO hydrogenation pathway has a

lower energy barrier compared with that of formate pathway.[231] The stronger promotion effect of Mn on the hydrogenation of formaldehyde to CH₄ (the rate determine step of RWGS+CO hydrogenation pathway) is revealed by the highest activity of Ni-Mn/SiO₂-r at lower temperature (≤ 250 °C). When the reaction temperature is higher than 300 °C, Ni-Co/SiO₂-r catalyst has the highest activity because Co promotes the formation of formate species (the rate determine step of formate pathway) to the utmost extent. On the contrary, Cu addition inhibits the formation of formate and the transformation of formaldehyde to methoxy, and thus the performance of Ni-Cu/SiO₂-r catalyst decreases compared to Ni/SiO₂-r catalyst.

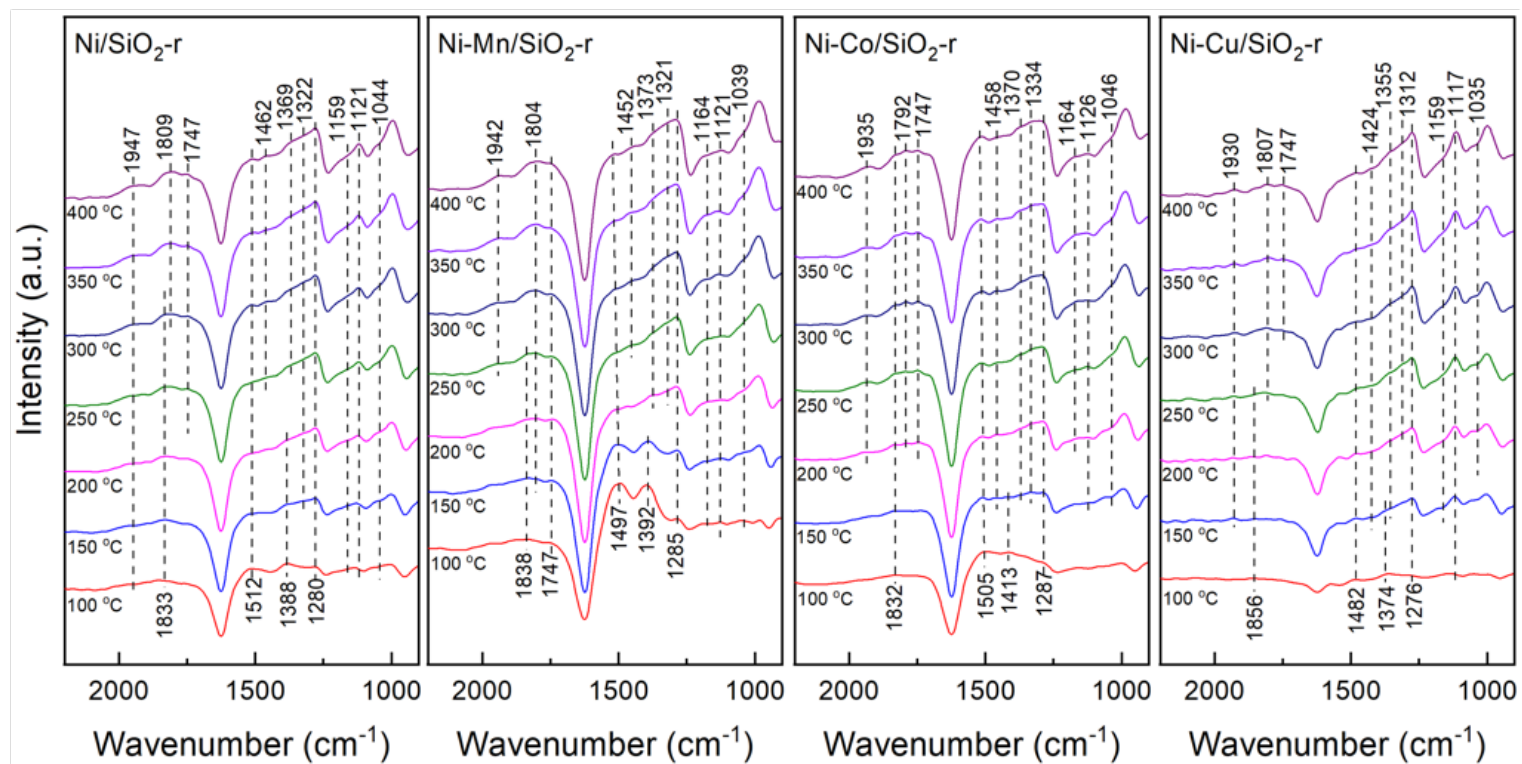


Fig. 6.7. CO₂ methanation DRIFTS experiments on (a) Ni/SiO₂, (b) Ni-Mn/SiO₂, (c) Ni-Co/SiO₂, and (d) Ni-Cu/SiO₂ catalysts.

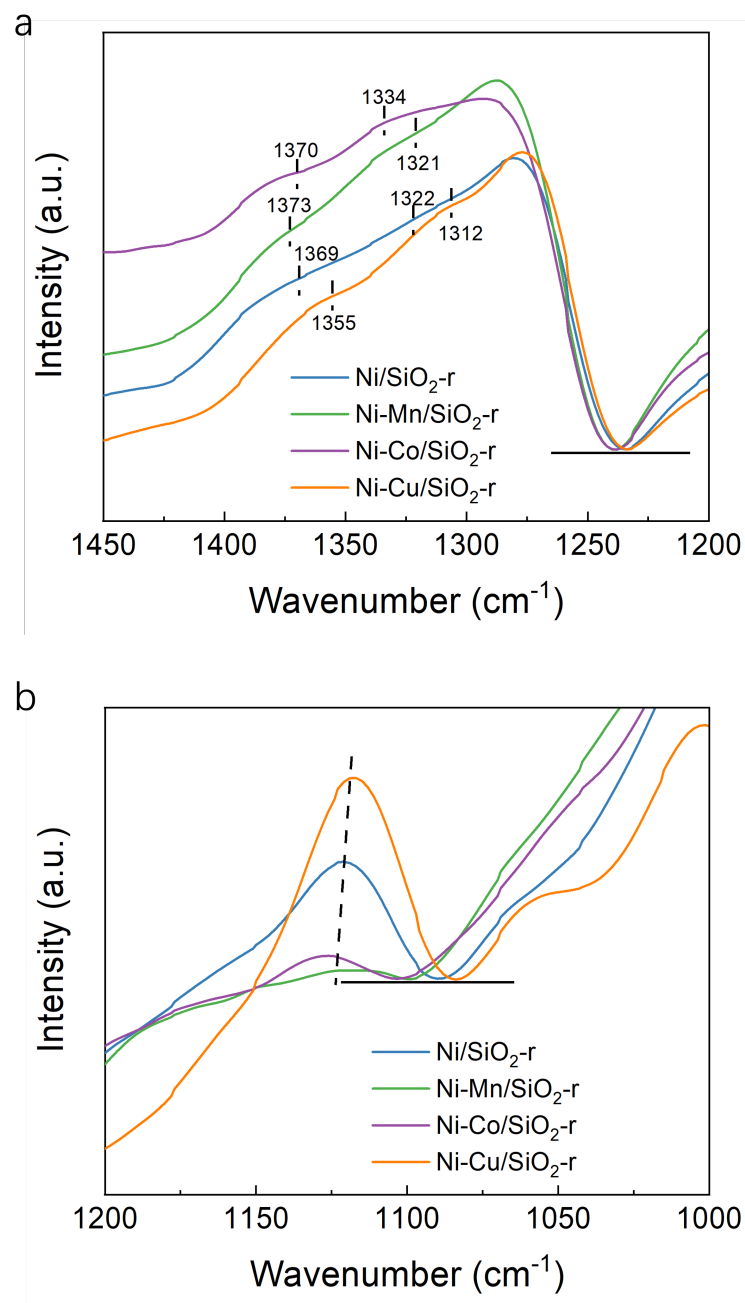


Fig. 6.8. Comparison of peak intensity of (a) formate intermediate and (b) formaldehyde intermediate.

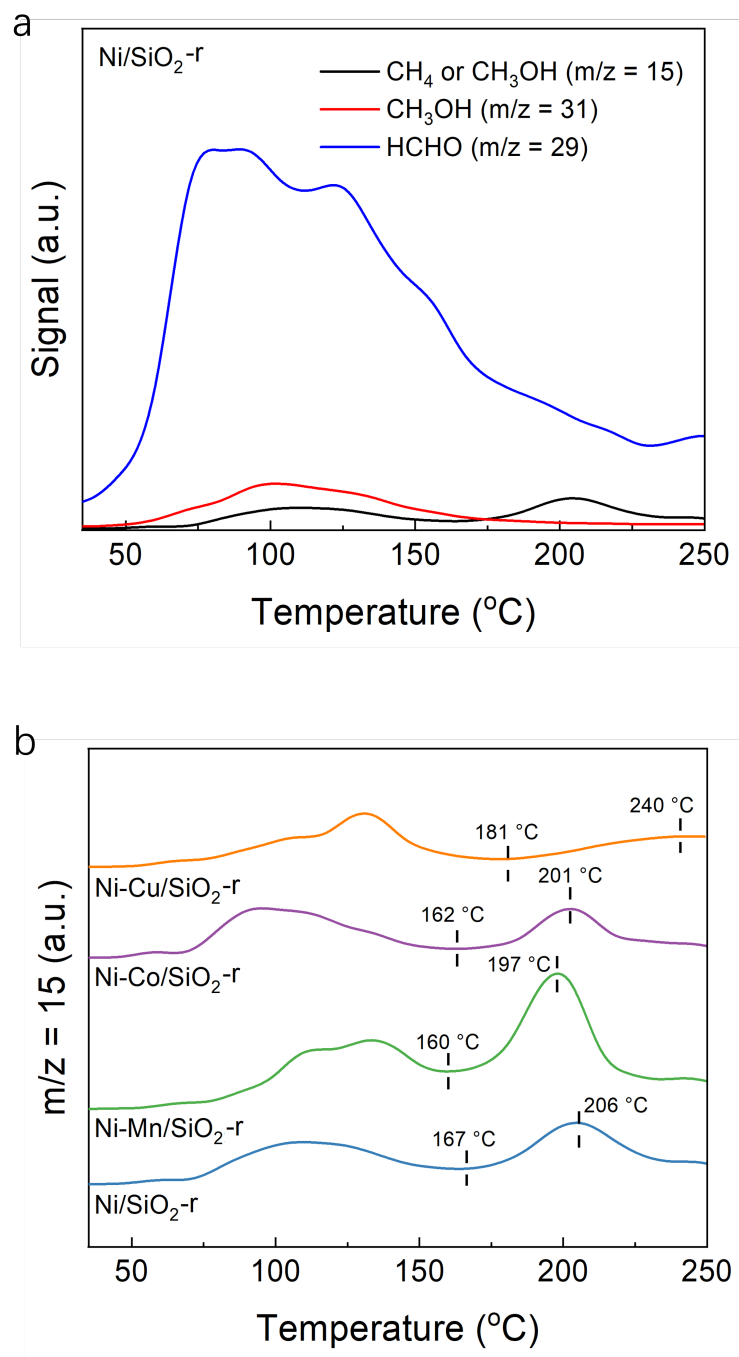


Fig. 6.9. (a) HCHO-TPSR over Ni/SiO₂. (b) HCHO-TPSR over the

prepared catalysts.

CO₂+H₂ TPSR tests were also carried out to explore how CO₂ molecules dynamically interact with the catalysts surface during CH₄ production. Specifically, CO₂ was firstly adsorbed and then maintained under a H₂ atmosphere while increasing the temperature. As shown in Fig. 6.10, the total amount of CH₄ formed over the prepared catalysts decreases in the order of Ni-Cu/SiO₂-r > Ni /SiO₂-r > Ni-Co/SiO₂-r > Ni-Mn/SiO₂-r, which is consistent with the amount of adsorbed CO₂ measured in CO₂-TPD experiments. After deconvoluting the profiles, three CH₄ formation peaks can be identified for all the prepared catalysts. Based on a previous mechanistic study[231], we propose to assign peaks α , β , and γ to the CH₄ formed via the RWGS+CO hydrogenation pathway, formate pathway, and C-O cleavage pathway, respectively. For Ni-Mn/SiO₂, the α peak shifts to lower temperature, indicating again that Mn addition facilitates the CH₄ formation via the RWGS+CO hydrogenation pathway. For Ni-Co/SiO₂, the α peak is unaffected but the β peak shifts to lower temperature, indicating Co addition facilitates the CH₄ formation via the formate pathway. On the contrary, both the α and the β peaks shift to higher temperatures for Ni-Cu/SiO₂, indicating the Cu addition inhibits the CH₄ formation via the RWGS+CO hydrogenation and formate pathway.

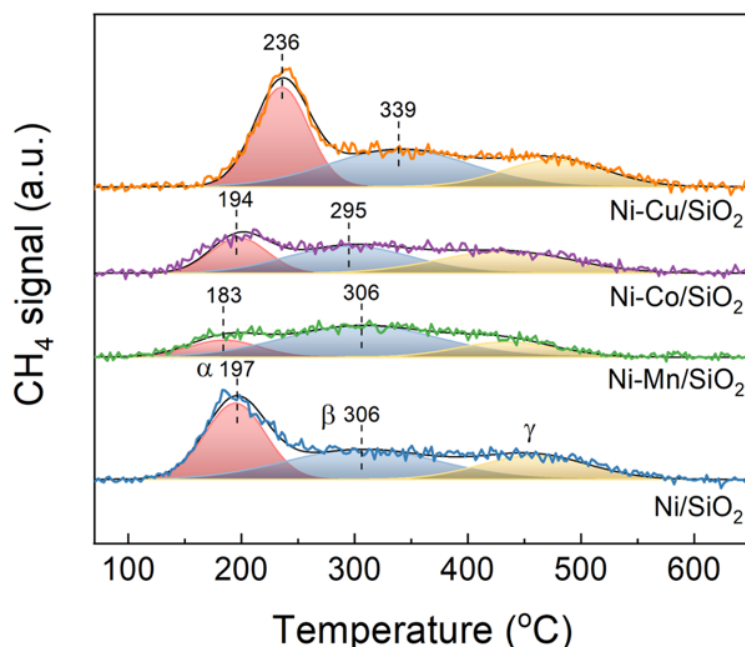


Fig. 6.10. TPSR over the prepared catalysts.

Based on the results of in-situ DRIFTS and TPSR, the promotion effect of Mn and Co addition can be visualized. RWGS+CO hydrogenation pathway is dominant at low temperature. Mn addition facilitates the RWGS+CO hydrogenation pathway to the greatest extent, which leads to the highest activity of Ni-Mn/SiO₂ at lower temperature. The formate pathway can proceed in parallel but appears more important at higher temperature. Co addition has the highest promotion effect on the formate pathway, which leads to the highest activity of Ni-Co/SiO₂ at higher temperature.

6.4. Conclusion

In summary, a series of bimetallic Ni-M/SiO₂ mesoporous catalysts (M = Mn, Co, and Cu) were successfully synthesized by sol-gel method and used for the CO₂ methanation reaction. Ni-Mn/SiO₂ and Ni-Co/SiO₂ shows higher activity, while Ni-Cu/SiO₂ shows lower activity

than the pristine, unpromoted, Ni/SiO₂-r catalyst. The effect of doping on dispersion, reducibility and basicity do not seem to explain the activity trends. Instead, doping appears to affect the methanation mechanism, and this is shown to play the most critical role to determining the catalytic performance. Both the RWGS+CO hydrogenation pathway and the formate pathway are identified, with the former being dominant at lower temperature (below 250 °C). Cu addition inhibits those two pathways and results in a lower catalytic activity of Ni-Cu/SiO₂ compared with Ni/SiO₂. RWGS+CO hydrogenation pathway could be promoted to the greatest extent by the Mn addition, and formate pathway could be enhanced to the greatest extent by the Co addition. Correspondingly, Ni-Mn/SiO₂ and Ni-Co/SiO₂ shows the highest performance at lower and higher temperature, respectively.

Chapter 7 Enhanced low-Temperature CO₂ methanation performance over Ni/CeO₂ catalysts prepared by facile one pot method with the addition of carbon nitride

In this chapter, a Ni/CeO₂-CN-OP catalyst was prepared by one-pot method assisted with the C₃N₄. The activity of the obtained catalyst showed a significantly high CO₂ conversion (82.6%) and a CH₄ productivity of up to 178 mmol g_{cat}⁻¹ h⁻¹ with a higher CH₄ selectivity (99.4%) even at a temperature as low as 250 °C. As evidenced from surface analysis results (Raman, XPS, and CO₂-TPD), the assistance of C₃N₄ and the one-pot preparation method increased the number of surface oxygen vacancies and medium basic sites. In situ DRIFTS revealed that CO₂ methanation on Ni/CeO₂ catalysts followed RWGS+CO hydrogenation pathway and the formate pathway, with the former being dominant at low temperatures. The copromotion of those two pathways by the higher amount of oxygen vacancy and medium basic site of Ni/CeO₂-CN-OP was responsible for its outstanding low temperature methanation performance.

7.1. Introduction

According to the results of Chapter 4 and 5, CO₂ methanation mainly follows the formate pathway and the RWGS+CO hydrogenation pathway. Instead of mutually independence, these two pathways may occur in parallel. The formate pathway involves the stepwise hydrogenation of adsorbed CO₂ species into CH₄ with the formate from the hydrogenation of carbonate as an important intermediate. In this pathway, tailoring the catalyst basicity is thought to be a key strategy for tuning the CO₂ adsorption behavior. Monodentate carbonate originates from the adsorption of CO₂ on medium basic site, and medium basicity is widely accepted as optimal for CO₂ methanation.[75] Pan *et al.* combined CO₂-TPD and in-situ FTIR analyses and proposed that intermediate species formed on the medium basic sites of Ni/Ce_{0.5}Zr_{0.5}O₂ could be converted to methane more quickly than those on the weak basic sites. Additionally, they reported that the strong basic sites of Ni/Al₂O₃ could hinder further hydrogenation of carbonate intermediates.[226]

The RWGS+CO hydrogenation pathway involves the dissociation of

CO₂ to CO, followed by the hydrogenation of CO to CH₄. According to the literature, facilitating the CO₂ activation is a promising way to increase the catalytic performance.[36, 104] Different strategies have been developed in an attempt to promote this process. First, selecting proper support. Among the numerous candidates, CeO₂ is an interesting one as support due to the abundant surface oxygen vacancies and redox properties.[64, 232, 233] Additionally, the morphology of CeO₂ with different preferentially exposed crystal facet has been found to be a critical factor in CO₂ methanation, which is attributed to the difference of oxygen vacancy formation energy over different facets.[191] Second, selecting a suitable preparation method. For example, Jia *et al.* reported the enhanced activity of Ni/ZrO₂ prepared by plasma decomposition method for CO₂ methanation.[49] The plasma decomposition caused the formation of Ni-ZrO₂ interfacial sites with more oxygen vacancies, which played crucial roles in CO₂ activation and methanation. Third, adding promoters. For example, Vrijburg *et al.* demonstrated the addition of Mn could increase the activity of Ni/TiO₂ catalyst. The improved activity originated from the decoration of Ni nanoparticles by highly dispersed MnO, on which more facile CO₂ activation could proceeded more effectively.[104]

Based on this and on the understanding of the CO₂ mechanism that we have acquired in the previous chapters, we reasoned that Ni-CeO₂-based formulations would be a good starting point to develop a highly active catalyst. Here, we aimed at enhancing the formation of oxygen vacancies and of surface basic sites. To that end, we developed a one-pot method involving the addition of carbon nitride (C₃N₄). The resulting catalyst (“Ni/CeO₂-CN-OP”) indeed was shown to reach high activity for CO₂ methanation. This performance is rationalized with the help of in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and temperature programmed surface reaction (TPSR).

7.2. Experimental summary

7.2.1. Catalyst preparation

Synthesis of carbon nitride. C₃N₄ was prepared by heating dicyandiamide (about 10 g) in a crucible with a cover to 550 °C for 2 h at a ramp rate of 5 °C/min in a muffle furnace. After letting it cool down to room temperature naturally, the obtained yellow product was recovered and ground into powder and designated as CN.

Synthesis of pristine CeO₂ support. CeO₂ support was obtained by calcining the Ce(NO₃)₃·6H₂O in a crucible with a cover to 550 °C for 4 h at a ramp rate of 5 °C/min in a muffle furnace.

Synthesis of CeO₂(CN) support. 2.2706 g of Ce(NO₃)₃·6H₂O was dissolved in 40 mL water. After stirring for 1 h, 1 g C₃N₄ powder was added into the solution and continuously stirred at room temperature for 4 h. The mixture was evaporated in the water bath at 70 °C under vigorous stirring and then further dried at 70 °C overnight. The obtained solids was calcined in a crucible with a cover at 550 °C for 4 h with a ramp rate of 5 °C/min.

Synthesis of Ni/CeO₂-CN-OP catalyst. Ni/CeO₂-CN-OP catalyst was prepared in a one-pot method. Typically, 2.2706 g of Ce(NO₃)₃·6H₂O and 1.1014 g Ni(NO₃)₂·6H₂O were dissolved in 40 mL water. After stirring for 1 h, 2 g C₃N₄ powder was added into the solution and continuously stirred at room temperature for 4 h. The mixture was evaporated in the water bath at 70 °C under vigorous stirring and then further dried at 70 °C overnight. The obtained solids were calcined in a crucible with a cover at 550 °C for 4 h with a ramp rate of 5 °C/min. After the calcination, around 700 mg sample could be collected after the calcination. As a benchmark, Ni/CeO₂-OP catalyst was prepared in the same way as Ni/CeO₂-CN-OP without adding the CN in the preparation process.

For comparison, Ni/CeO₂-IM and Ni/CeO₂(CN)-IM were synthesized with conventional impregnation method. The CeO₂ or CeO₂(CN) support was impregnated with an aqueous solution of Ni(NO₃)₂·6H₂O. After stirring for 1 h, the mixture was evaporated in the water bath at

70 °C under vigorous stirring and then further dried at 70 °C overnight. The obtained solids were calcined in the same method used for calcining Ni/CeO₂-CN-OP. The final obtained catalysts are denoted Ni/CeO₂-IM and Ni/CeO₂(CN)-IM, respectively.

7.3. Results and discussion

7.3.1. Textural, structural, and morphological Studies.

Textural properties of the supports and reduced catalysts were measured by N₂ physisorption (Fig. 7.1 and Fig. S13). The detailed textural parameters were listed in Table 6.1. The profile of CeO₂ (Fig. S13a) displays a type IV isotherms, indicating the existence of mesoporous structure.[234] The apparent H2 type hysteresis loop is associated to capillary condensation taking place in the particles with neck bottle-shaped pores.[235] The surface area, pore volume, and average pore diameter of CeO₂ are 68 m² g⁻¹, 0.22 cm³ g⁻¹, and 10.9 nm, respectively. As C₃N₄ was added during the preparation of CeO₂(CN), the type IV isotherms with H2 hysteresis loop remains basically unchanged (Fig. S13a). Compared with CeO₂, the surface area, pore volume, and average pore diameter of CeO₂(CN) increase to 79 m² g⁻¹, 0.29 cm³ g⁻¹, and 13.2 nm, which is due to removal of C₃N₄ during the calcination process. The supported Ni decreases those three parameters of both the Ni/CeO₂-IM and Ni/CeO₂(CN)-IM catalysts compared with the corresponding supports. For the catalysts prepared by one-pot method, the profile of Ni/CeO₂-OP also displays the type IV isotherms with H2 type hysteresis loop (Fig. 7.1a). Differently, mesoporous Ni/CeO₂-CN-OP catalyst shows H3 type hysteresis loop, characteristic of plate-type particles with slit-shaped pores.[167] The average pore diameter of Ni/CeO₂-OP and Ni/CeO₂-CN-OP is in the same range of 8.5-8.9 nm, while the latter shows a broader distribution of pore diameter (Fig. 7.1b). Ni/CeO₂-CN-OP exhibits smaller BET surface area (50 m² g⁻¹) and total pore volume (0.11 cm³ g⁻¹) than Ni/CeO₂-OP (89 m² g⁻¹, 0.23 cm³ g⁻¹).

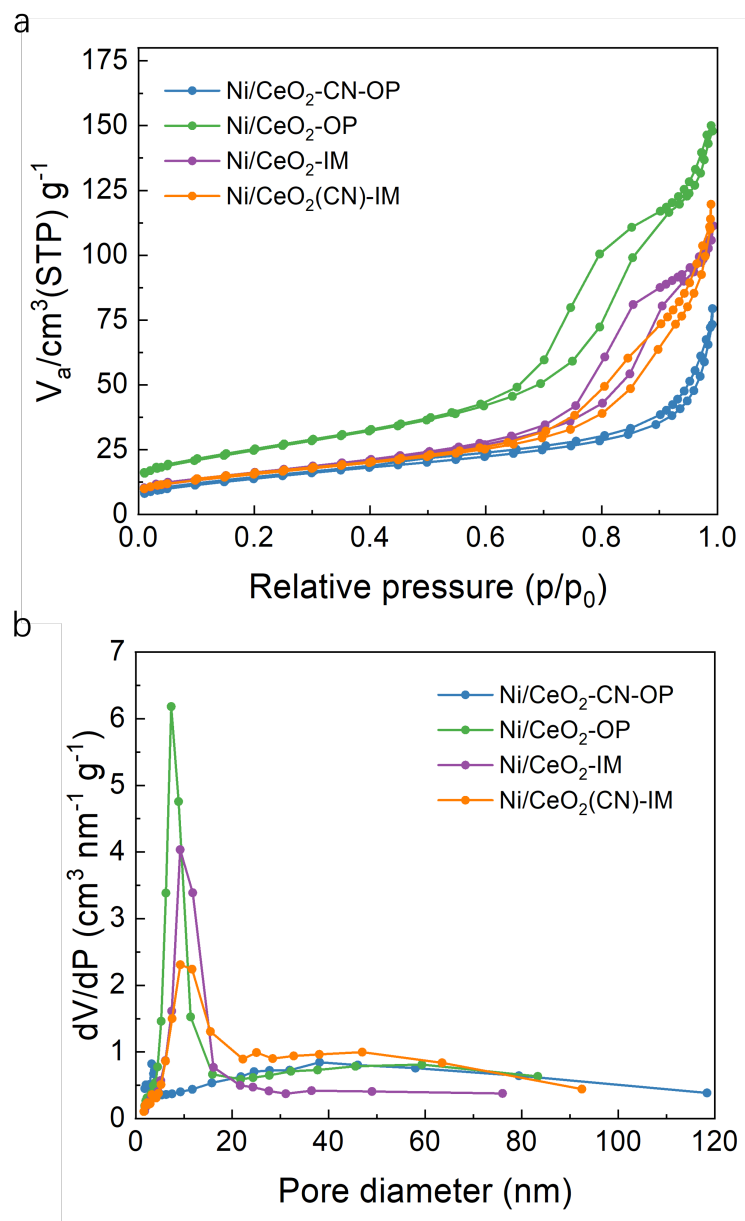


Fig. 7.1. (a) N₂ adsorption-desorption isotherms and (b) pore size distributions of the reduced Ni/CeO₂ catalysts.

Table. 7.1 Physical properties and Ni dispersion values of the CeO₂ supports and Ni/CeO₂ catalysts. Ni dispersion of Ni/CeO₂ catalysts and their TOF values.

	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)	Ni (wt %) ^a	Ni particle size (nm) ^b	D _{Ni} (%) ^c	TOF (s ⁻¹) ^d
CeO ₂	68	0.22	10.9	-	-	-	-
CeO ₂ (CN)	79	0.29	13.2	-	-	-	-
Ni/CeO ₂ -CN-OP	50	0.11	8.9	18.2	8.2	9.4	0.047
Ni/CeO ₂ -OP	89	0.23	8.5	18.0	28.8	7.1	0.038
Ni/CeO ₂ -IM	56	0.16	9.5	20.9	28.6	5.5	0.031
Ni/CeO ₂ (CN)-IM	55	0.19	12.1	19.8	26.0	8.5	0.033

^a Determined by ICP-MS.

^b Calculated from the Scherrer equation based on the Ni(111) diffraction peak.

^c Calculated from the H₂ chemisorption results.

^d TOF of CO₂ conversion at 225 °C.

XRD measurement was performed to identify the crystal structure of the supports and reduced catalysts. For all bare CeO₂ support (Fig. S14) and Ni/CeO₂ catalysts (Fig. 7.2), the main diffraction peaks at 28.6, 33.1, 47.5, 56.4, 59.1, 69.4, 76.7 and 79.1° can be attributed to the (111), (200), (220), (311), (222), (400), (331) and (420) planes of CeO₂ in fluorite structure (PDF 34-0394).[236] Moreover, the diffraction peaks at 44.5 and 51.8° originate from the (111) and (200) plane in the Ni⁰ cubic structure (PDF 04-0850).[237] This Ni⁰ peak becomes wider in the order Ni/CeO₂-IM $\approx$ Ni/CeO₂-OP < Ni/CeO₂(CN)-IM < Ni/CeO₂-CN-OP, suggesting the smaller Ni particles on the Ni/CeO₂-CN-OP surface. From the Scherrer equation based on the Ni(111) diffraction peak, the Ni crystallite size of Ni/CeO₂-CN-OP (8.2 nm) is much smaller than the other three catalysts (around 28 nm, listed in Table 7.1).

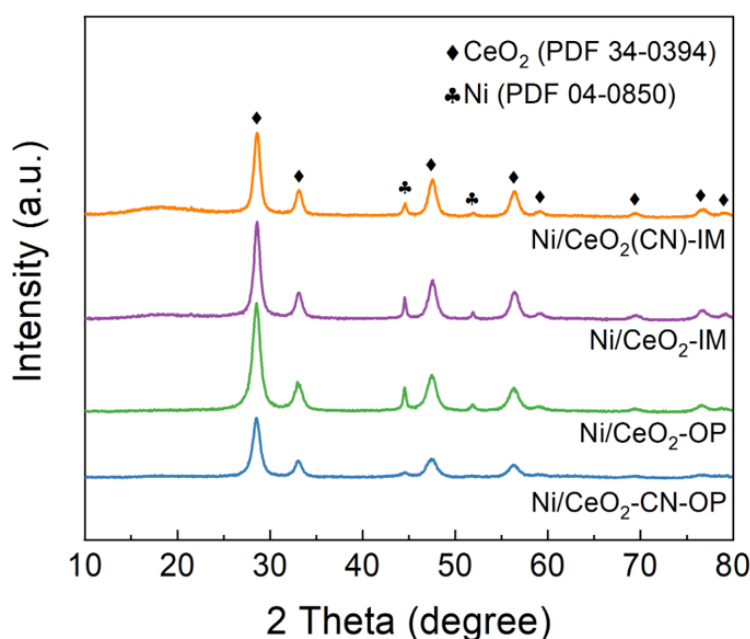
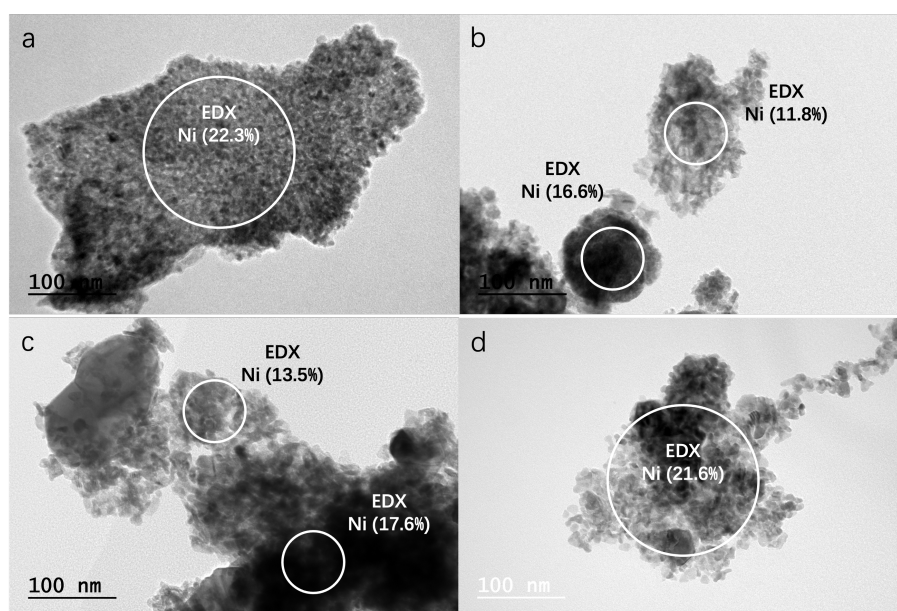


Fig. 7.2. XRD patterns of the Ni/CeO₂ catalysts.

The morphologies of Ni/CeO₂ were investigated using (HR)TEM. As shown in Fig. 7.3a-3d, Ni/CeO₂-CN-OP exhibits smaller particles compared with Ni/CeO₂-OP, Ni/CeO₂-IM and Ni/CeO₂-CN-IM.

However, the small difference in the contrast between Ni and CeO₂ makes it difficult to discern them.[238, 239] EDX analysis (inset Fig. 7.3a-3d) confirmed the presence of nickel. Furthermore, much more serious agglomeration over Ni/CeO₂-OP and Ni/CeO₂-IM can be observed compared with Ni/CeO₂-CN-OP. The Ni dispersion is also identified by H₂ chemisorption. From the results of H₂ chemisorption, there is no chemisorbed H₂ for the CeO₂ support, indicating the only site for H₂ chemisorption is Ni. Higher Ni dispersion (9.4%) in Ni/CeO₂-CN-OP compared with that in Ni/CeO₂-OP (7.1%) and Ni/CeO₂-IM (5.5%) is confirmed, as presented in Table 1. The Ni/CeO₂-CN-IM has a similar dispersion of 8.5% to Ni/CeO₂-CN-OP. The lattice fringes of the metal nanoparticles are also visible in HRTEM images. In Fig. 7.3e-3h, the clear lattice fringe distances are 0.19, 0.27 and 0.31 nm, corresponding to the CeO₂ (110), CeO₂ (100) and CeO₂ (111) planes, respectively. The first two suggest the presence of CeO₂ {110} and {111} planes, respectively.



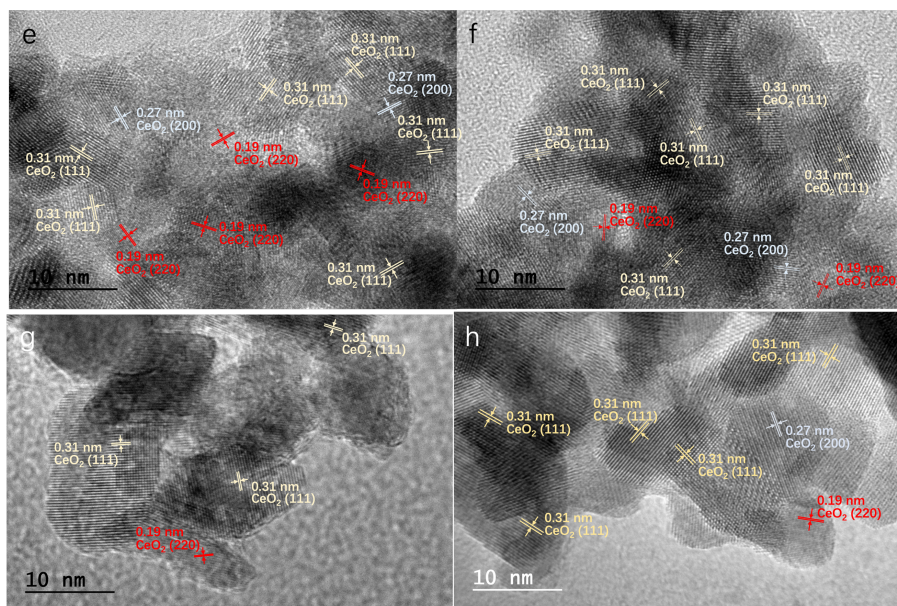


Fig. 7.3. TEM images of reduced (a) Ni/CeO₂-CN-OP, (b) Ni/CeO₂-OP, (c) Ni/CeO₂-IM, and (d) Ni/CeO₂-CN-IM. HRTEM images of (e) Ni/CeO₂-CN-OP, (f) Ni/CeO₂-OP, (g) Ni/CeO₂-IM, and (h) Ni/CeO₂-CN-IM.

7.3.2. Reducibility studies.

The reducibility of the Ni/CeO₂ catalysts and the corresponding supports was investigated using H₂-TPR measurements, as shown in Fig. 6.4 and Fig. S3. For CeO₂ supports (Fig. S15), small reduction peaks at 400-600 °C and 700-900 °C can be attributed to the reduction of surface capping oxygen and bulk lattice oxygen of CeO₂, respectively.[240] For all the Ni/CeO₂ catalysts, two major H₂ consumption peaks, labeled as β and δ , can be distinguished (Fig. 7.4). The β peaks centered in the temperature range of 310-370 °C can be attributed to reduction of NiO species moderately (β_1 , 310-330 °C) and strongly (β_2 , 360-410 °C) interacting with CeO₂. [75] Obviously, the proportion of NiO strongly interacting with CeO₂ for the catalysts prepared by one-pot method is much higher than that for the catalysts prepared by impregnation method, and the addition of C₃N₄ further increases this proportion. That is, one-pot preparation method and the

addition of C₃N₄ could enhance the metal-support interaction. The δ peak located at around 750 °C shows the reduction of crystalline CeO₂ from Ce⁴⁺ to Ce³⁺. In addition to those two major peaks, for the Ni/CeO₂(CN)-IM, Ni/CeO₂-OP and Ni/CeO₂-CN-OP catalysts, a new reduction peak (labeled as α) at lower temperature (190-230 °C) is detected. According to the literature, this peak is ascribed to the reduction of adsorbed oxygen species, which is from the Ni-O-Ce interfacial sites and can be easily removed by hydrogen.[229, 241] There is no α reduction peak for Ni/CeO₂-IM and Ni/CeO₂-CN-OP has larger α peak than Ni/CeO₂-OP and Ni/CeO₂(CN)-IM, which indicate that C₃N₄ addition and one-pot preparation method could facilitate the formation of Ni-O-Ce solid solution. The Ni/CeO₂-CN-OP catalyst also shows an extra peak at 440 °C (labeled as γ), which is related to the surface reduction of CeO₂ by spillover hydrogen at the Ni-CeO₂ interface.[242]

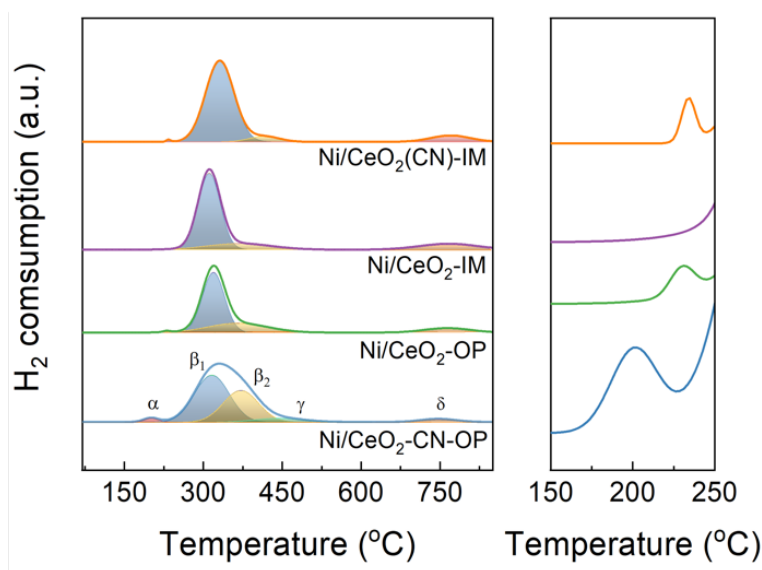


Fig. 7.4. H₂-TPR profiles of the Ni/CeO₂ catalysts.

7.3.3. Basicity studies.

CO₂-TPD measurement was performed to evaluate the basicity of the

Ni/CeO₂ catalysts. The CO₂ desorption curve (Fig. 7.5a) is fitted and divided into three temperature regions based on basicity strength including <150 °C, 150-400 °C and 400-700 °C, which are ascribed to weak, medium, and strong basic site, separately.[227] A series of works indicated that increasing the amount of medium basic site could promote the methanation performance, while the strong basic sites did not play a positive role in enhancing methanation activity due to the suppression of further hydrogenation. For comparison, Table 7.2 presents the amount of desorbed CO₂. It can be seen that the Ni/CeO₂-CN-OP has the lowest weak basicity. On the contrary, medium and strong basic site are the predominant basic site over Ni/CeO₂-CN-OP, and the amount of medium and strong basic site is higher than the other three catalysts.

The adsorbed CO₂ species were further investigated using the in-situ DRIFTS characterization. As shown in Fig. 7.5b, after being saturated by CO₂ and then flushed under He atmosphere at 50 °C for 30 min, the recorded spectra of Ni/CeO₂-CN-OP and Ni/CeO₂-IM both displays clear signature of bicarbonate (1482, 1295 cm⁻¹), monodentate carbonate (1582 cm⁻¹), and bidentate carbonate (1398 cm⁻¹).[200, 243, 244] For Ni/CeO₂-CN-OP and Ni/CeO₂-IM, the peaks assigned to bicarbonate species decrease progressively and could be removed totally below 200 °C. For the monodentate carbonate species, increasing the temperature also leads to a gradual decrease in peak intensity on Ni/CeO₂-CN-OP and Ni/CeO₂-IM. When the temperature increases to 300 °C, the peak for monodentate carbonate on Ni/CeO₂-CN-OP disappears completely. By contrast, there is still a small shoulder peak for monodentate carbonate on Ni/CeO₂-IM until the temperature increases to 350 °C. The intensity of bidentate carbonate peak remains almost unchanged below 350 °C. Meanwhile, polydentate carbonate species (1454 cm⁻¹)[245] occurs above 100 °C on Ni/CeO₂-CN-OP and Ni/CeO₂-IM and extra peaks attributed to carbonyl and monodentate formate species are formed on Ni/CeO₂-CN-OP.

Based on the results of CO₂-TPD and in-situ DRIFTS, the amount and

nature of the adsorbed CO₂ species are identified. Specifically, CO₂ can adsorb on weak basic site and form bicarbonate, which could be removed from the catalyst surface below 200 °C. Meanwhile, CO₂ adsorption on medium basic sites results in the formation of monodentate carbonates, the amount of which decreases in the order Ni/CeO₂-CN-OP > Ni/CeO₂(CN)-IM > Ni/CeO₂-OP > Ni/CeO₂-IM as presented in Table 6.2.

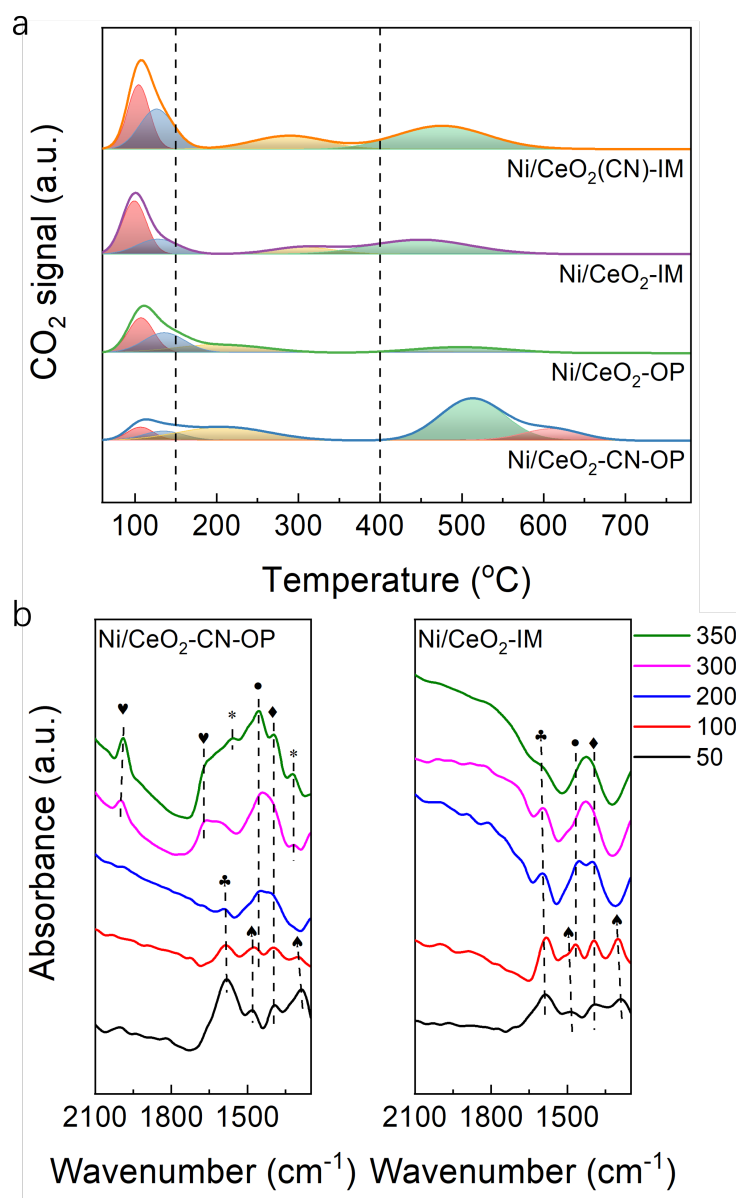


Fig. 7.5. (a) CO₂-TPD spectra of Ni/CeO₂ catalyst; (b) in-situ CO₂ desorption DRIFTS of the Ni/CeO₂-CN-OP and Ni/CeO₂-IM catalyst. Symbol definition: bicarbonate (♠), monodentate carbonate (♣), bidentate carbonate (♦), monodentate formate (*), polydentate carbonate (•), carbonyl (♥).

Table 7.2. CO₂-TPD analysis of the Ni/CeO₂ catalysts.

sample	CO ₂ desorption ($\mu\text{mol CO}_2 \text{ g}_{\text{cat}}^{-1}$)		
	weak ($< 150\text{ }^{\circ}\text{C}$)	medium ($150\text{--}400\text{ }^{\circ}\text{C}$)	strong ($> 400\text{ }^{\circ}\text{C}$)
Ni/CeO ₂ -CN-OP	7.4	24.9	67.9
Ni/CeO ₂ -OP	14.9	11.5	16.3
Ni/CeO ₂ -IM	12.4	8.9	28.7
Ni/CeO ₂ (CN)-IM	27.7	19.1	42.1

7.3.4. Characterizations for oxygen vacancies.

Oxygen vacancy is one of the essential defects on cerium-based catalysts for CO₂ methanation due to the fact that it could promote the activation of CO₂ and CO.[233, 246] The formation and concentration of oxygen vacancies were evinced and estimated from Raman spectra and XPS. The observed Raman features of the CeO₂ supports (Fig. S16) at 462 and 598 cm⁻¹ are assigned to the vibration model of octahedral local symmetry from the CeO₂ lattice (F_{2g}) and defect-induced mode (D), respectively.[247] The ratio of the intensity for the D band and F_{2g} band is calculated to evaluate oxygen vacancy concentration. The ratio increases from 0.035 of CeO₂ to 0.045 of CeO₂(CN), which means that the addition of C₃N₄ would increase the amount of oxygen vacancy. The Raman features of the Ni/CeO₂ samples are displayed in Fig. 7.6a. After the loading of Ni and reduction, a significant increase in the I_D/I_{F2g} value occurs (Fig. 7.6b) as a result of Ni incorporation into CeO₂ lattice. The I_D/I_{F2g} value of Ni/CeO₂-CN-OP (~0.59) is much higher than that of Ni/CeO₂-OP (~0.39), Ni/CeO₂-IM (~0.35) and Ni/CeO₂(CN)-IM (0.43), demonstrating more oxygen vacancies generated on Ni/CeO₂-CN-OP. Furthermore, an evidently lower Raman shift of F_{2g} band for Ni/CeO₂-CN-OP, Ni/CeO₂-OP and Ni/CeO₂(CN)-IM is observed. This shift indicates the lower symmetry of Ce–O bond in Ni/CeO₂-CN-OP, Ni/CeO₂-OP and Ni/CeO₂(CN)-IM and can be explained by the formation of Ni_xCe_{1-x}O_{2-δ} solid solution according to the H₂-TPR

results.[248, 249]

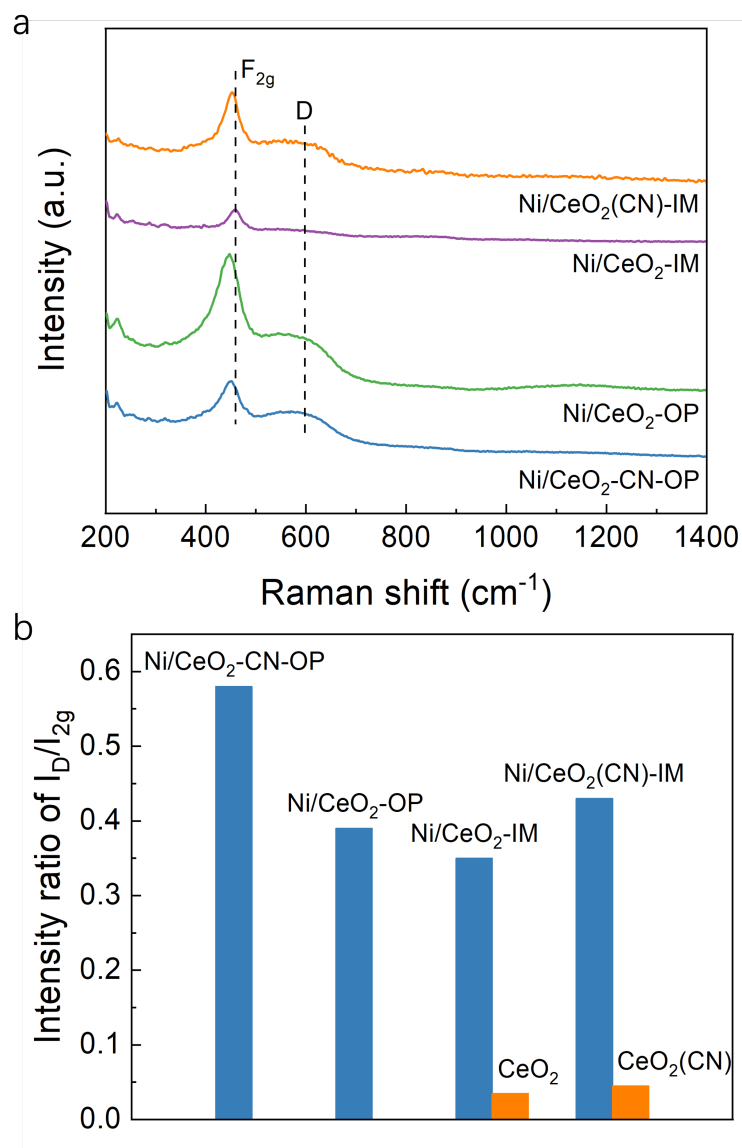
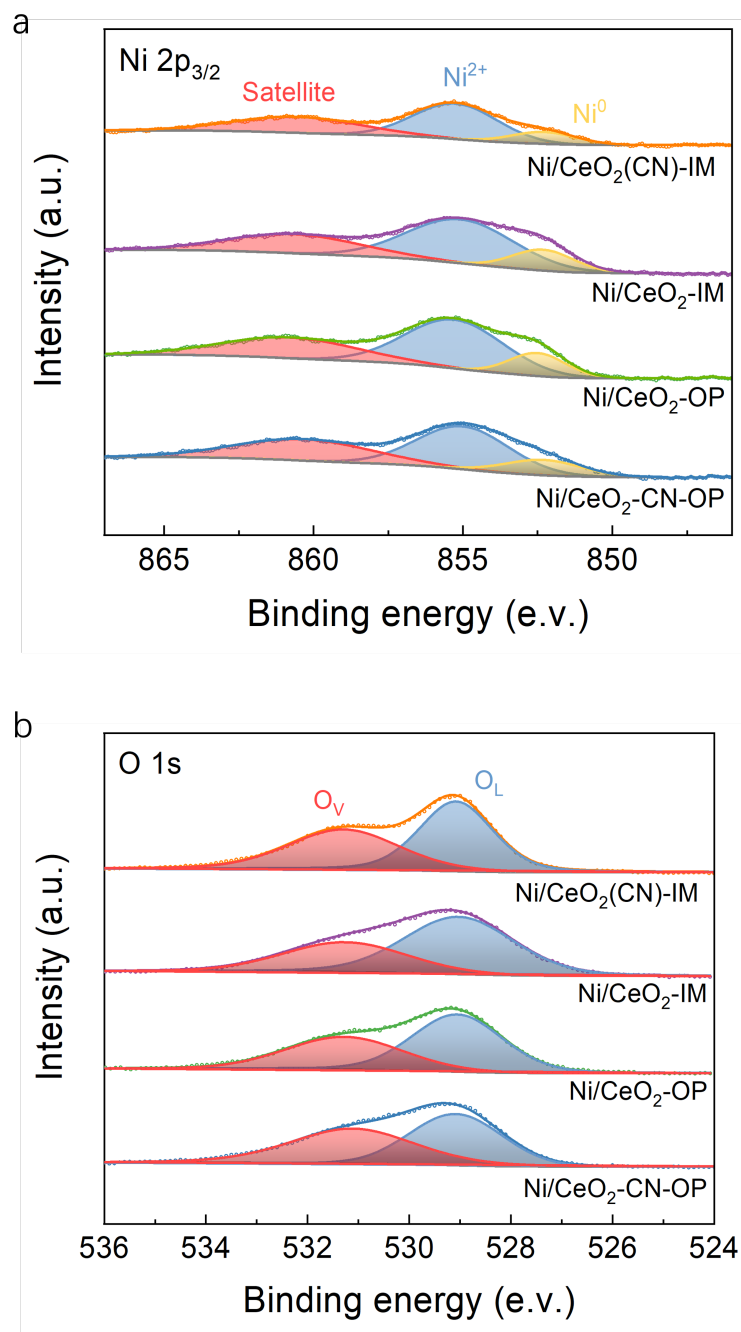


Fig. 7.6. Raman spectra of the Ni/CeO₂ catalysts.

The information on surface elemental composition and the chemical state over the Ni/CeO₂ catalysts were also determined by XPS analysis. As shown in the Ni 2p_{3/2} spectra (Fig. 7.7a), coexistence of Ni⁰ (at 852.5 eV) and Ni²⁺ (at 855.2 eV and satellite at 860.6 eV) can be found for all

catalysts.[61] The existence of Ni²⁺ is attributed to the quick oxidation of active Ni in air.[229] The difference of surface Ni⁰ percentage over these catalysts is small as displayed in Table 3. In the XPS spectra of O 1s (Fig. 7.7b), two deconvoluted peaks at 529.3 eV and 531.3 eV belonging to lattice oxygen (O_L) and oxygen vacancy (O_V) can be observed for all catalysts.[170] The relative concentration of oxygen vacancy can be reflected by the ratio of O_V/(O_L + O_V), as shown in Table 3. The relative concentration of oxygen vacancy decreases in the order: Ni/CeO₂-CN-OP > Ni/CeO₂(CN)-IM > Ni/CeO₂-OP > Ni/CeO₂-IM, which is in good line with the results of Raman. The Ce 3d spectra are shown in Fig. 7.7c. The pairs of spin-orbit coupling (3d_{5/2} and 3d_{3/2}) are labeled as u and v, respectively. The peaks at 916.2 eV (u'''), 906.8 eV (u''), 900.5 eV (u), 897.7 eV (v'''), 888.4 eV (v''), and 882.1 eV (v''') correspond to surface Ce⁴⁺ species, and the remaining four peaks at 902.3 eV (u'), 898.7 eV (u₀), 884.3 eV (v'), and 880.7 eV (v₀) are assigned to surface Ce³⁺ species.[250] According to the electrostatic balance mechanism, the ratio of Ce³⁺/(Ce⁴⁺ + Ce³⁺) could also reflect the content of oxygen vacancies. However, the difference in the ratio of Ce³⁺/(Ce⁴⁺ + Ce³⁺) between those four catalysts (shown in Table 7.3) is smaller than that in the ratio of O_V/(O_L + O_V). This discrepancy may be explained by the fact that the oxygen vacancy is more abundant in the surface because oxygen vacancy is enriched at interfacial sites between Ni and CeO₂, which leads to the much more significant difference in the ratio of O_V/(O_L + O_V).[75, 241]



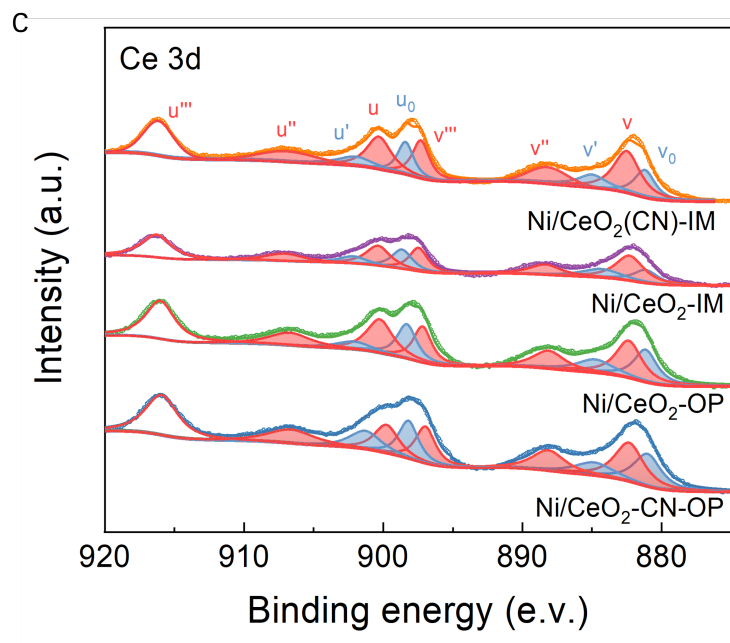


Fig. 7.7. XPS spectra of the Ni/CeO₂ catalysts: (a) Ni 2p_{3/2}, (b) O 1s, (c) Ce 3d.

Table 7.3. Surface information over the Ni/CeO₂ catalysts.

	Ni ⁰ / (Ni ⁰ + Ni ²⁺)	O _V / (O _V + O _L)	Ce ³⁺ / (Ce ³⁺ + Ce ⁴⁺)
Ni/CeO ₂ -CN-OP	14.4%	50.8%	26.5%
Ni/CeO ₂ -OP	14.5%	41.8%	25.1%
Ni/CeO ₂ -IM	15.0%	36.2%	24.3%
Ni/CeO ₂ (CN)-IM	13.4%	46.7%	26.1%

What factors lead to the difference in oxygen vacancy concentration over those prepared catalysts? From the HRTEM of the prepared catalysts (Fig. 7.2e-2h), more CeO₂ (110) facet could be observed over the surface of Ni/CeO₂-CN-OP compared with the other three catalysts. According to the literature, the oxygen vacancy formation energies are 2.28, 1.49, and 1.18 eV over the CeO₂ (111), (100), and (110) facet, respectively.[251] It is reasonable that Ni/CeO₂-CN-OP with more

CeO₂ (110) facet possesses higher amount of oxygen vacancy. However, HRTEM represents only a small part of the sample, it could not be used to quantify the different facet of the support. In order to distinguish surface Ce species between CeO₂ facets and obtain their concentrations, TMP-³¹P NMR test was performed. TMP-³¹P NMR is only useful for the bare CeO₂ support, thus we just performed this for CeO₂ support with and without assisted C₃N₄. Farahnaz *et al.* reported that ³¹P chemical shift ($\delta^{31}\text{P}$) is -46 ppm on CeO₂ (110) facet obtained by DFT calculations.[252] In Fig. 7.8a, a $\delta^{31}\text{P}$ of -44.8 ppm, closer to -46 ppm, can be observed for the CeO₂-CN support, indicating that the CeO₂-CN support majorly exposes (110) facets. The $\delta^{31}\text{P}$ depends on the surface electron density. Higher electron density could lead to a weaker interaction with TMP-Ce adducts and a more negative $\delta^{31}\text{P}$.[253] The surface Ce has the higher electron density on (100) facet than that on (110) facet.[254] Therefore, the more negative $\delta^{31}\text{P}$ for the CeO₂ support (-51.9 ppm) compared with the CeO₂-CN support (-44.8 ppm) should point to the more (100) facet on the CeO₂ support. The degree of electron sharing between the P atom of TMP and the surface Ce cation determines the electron density of ³¹P nuclei and hence its magnetic susceptibility under ³¹P NMR, which means the adsorption energy (E_{ad}) of TMP on CeO₂ facets should have a linear relationship with $\delta^{31}\text{P}$. E_{ad} of free TMP and E_{ad} of TMP on two CeO₂ facets are 0 eV, -0.81 eV for (110) facet, and -0.38 for (100) facet[255] and exhibit a linear relationship ($R^2 = 0.974$) with $\delta^{31}\text{P}$ of the corresponding facet (Fig. 7.8b), which confirm the correspondence of $\delta^{31}\text{P}$ (-51.9 ppm) and CeO₂ (100) facet.

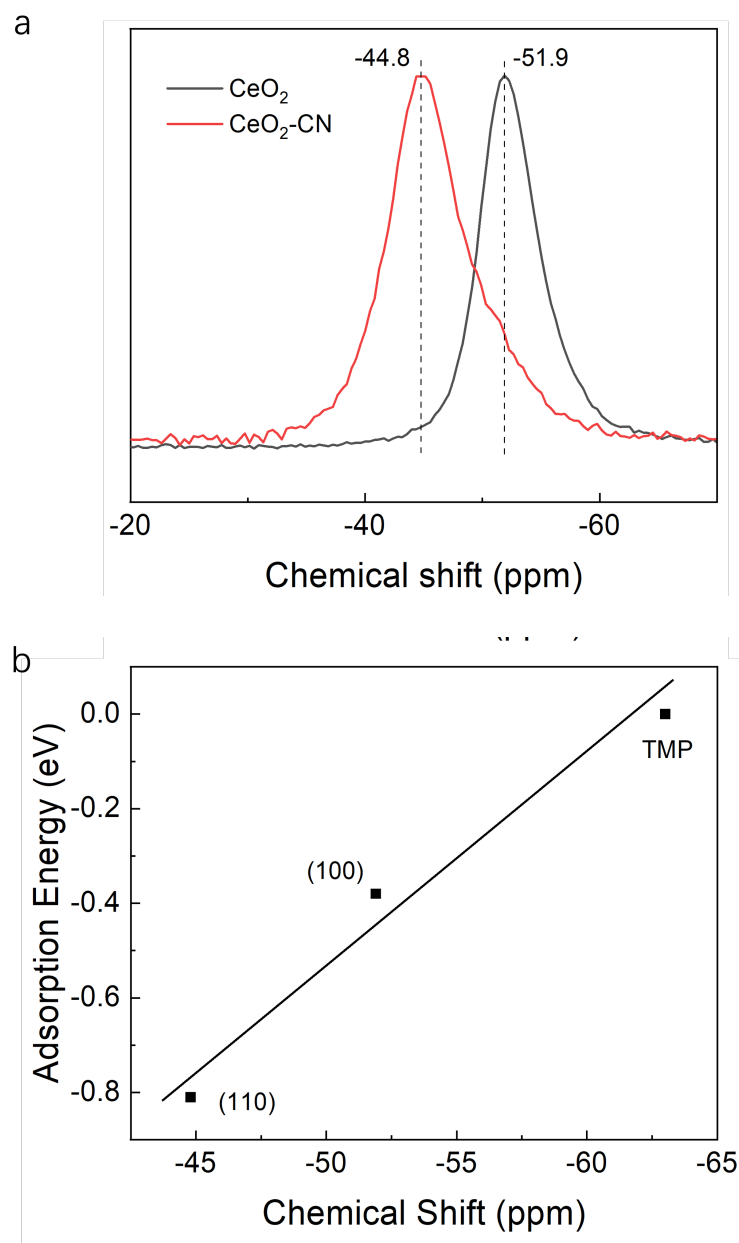


Fig. 7.8. (a) TMP-³¹P NMR spectra of CeO₂ and CeO₂-CN; (b) (d) Linear regression plot using experimental $\delta^{31}\text{P}$ and calculated E_{ad} of CeO₂ facets. Note that $\delta^{31}\text{P}$ for a pure TMP molecule is -63 ppm (i.e., adsorption energy = 0 eV).

Based on the Raman, XPS, and TMP-³¹P NMR test, the addition of carbon nitride during the preparation process could lead to the major exposure of CeO₂ (110) facet with the lower oxygen vacancy formation energies, thus providing the higher concentration of oxygen vacancy.

7.3.5. Catalytic performance for CO₂ methanation.

The CO₂ methanation performance was evaluated over Ni/CeO₂ catalysts in the temperature range between 200 and 325 °C with the GHSV of 36000 mL g⁻¹ h⁻¹, and the results are shown in Fig. 7.9a. In term of CH₄ selectivity, all catalysts attain almost 100 % at reaction temperature below 275°C. At higher temperature, Ni/CeO₂-CN-OP, Ni/CeO₂-OP and Ni/CeO₂(CN)-IM catalyst still maintain the CH₄ selectivity above 99 %, whereas a little byproduct CO is generated over Ni/CeO₂-IM catalyst via the reverse water gas shift (RWGS) reaction, resulting in 97 % CH₄ selectivity. In term of CO₂ conversion, the activity of Ni/CeO₂-CN-OP is higher than that of the other three catalysts in the whole testing temperature range. Especially, at 250 °C, the CO₂ conversion for Ni/CeO₂-CN-OP achieves 82.6%. A comparison of catalytic activity over those recently reported catalysts is presented in Table S4. To our delight, the catalytic activity over Ni/CeO₂-CN-OP at low temperature (250 °C), is comparable to the state-of-the-art methanation catalysts in the previous report. Generally, the TOF value is calculated to appraise the intrinsic activity of catalysts. As shown in Table 6.1, the TOF value of CO₂ conversion over Ni/CeO₂-CN-OP at 225 °C is up to 0.047 s⁻¹, which is 1.24 times, 1.52 times and 1.42 times higher than those over Ni/CeO₂-OP (0.038 s⁻¹), Ni/CeO₂-IM (0.031 s⁻¹), and Ni/CeO₂(CN)-IM (0.033 s⁻¹) respectively.

A prerequisite for the industrial application of a proper catalyst is the high durability. The stability of Ni/CeO₂-CN-OP was tested with the GHSV of 36000 mL g⁻¹ h⁻¹ at 250 °C for 72 h, as shown in Fig. 7.9b. Ni/CeO₂-CN-OP could maintain CO₂ conversion and selectivity above 80% and 99%, respectively. The reusability of the Ni/CeO₂-CN-OP was also tested. After the first cycle test at 250 °C for 2 h, the reactor is cooled down to room temperature under He atmosphere and then heated

to 250 °C again to test its performance. The results show the CO₂ conversion was maintained at 82%, which is same with the CO₂ conversion in first cycle, indicating a good reusability of the Ni/CeO₂-CN-OP

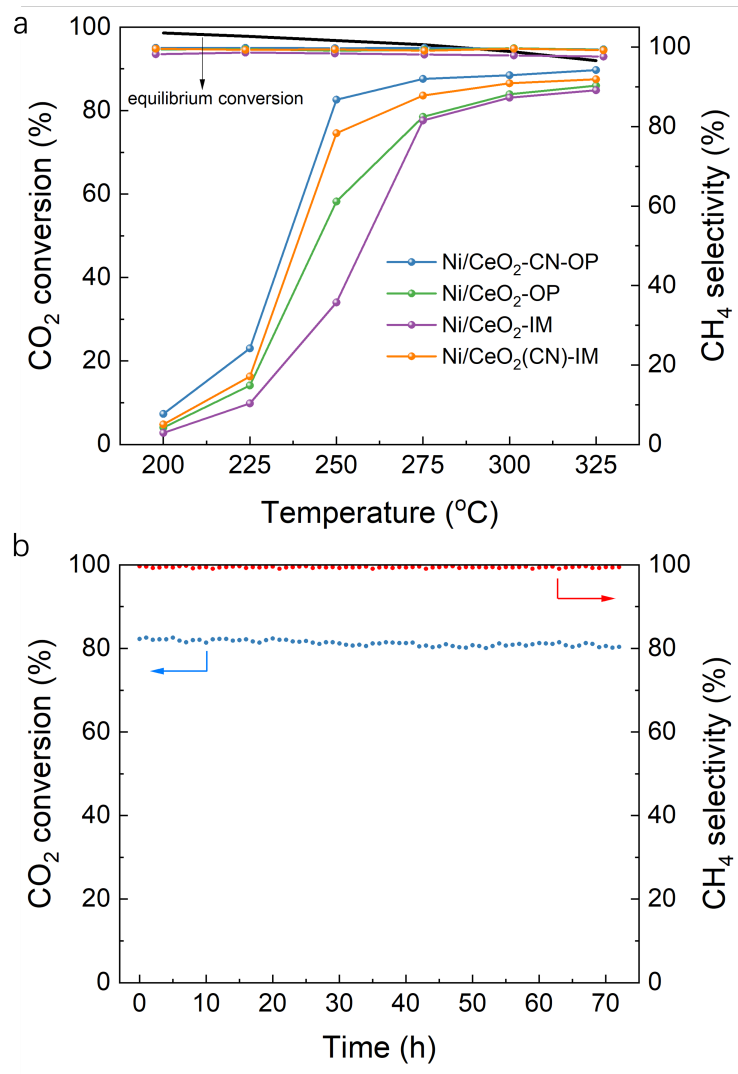


Fig. 7.9. (a) CO₂ methanation performance in terms of CO₂ conversion and CH₄ selectivity as a function of temperature. (b) CO₂ conversion and CH₄ selectivity at 250 °C against time on stream over

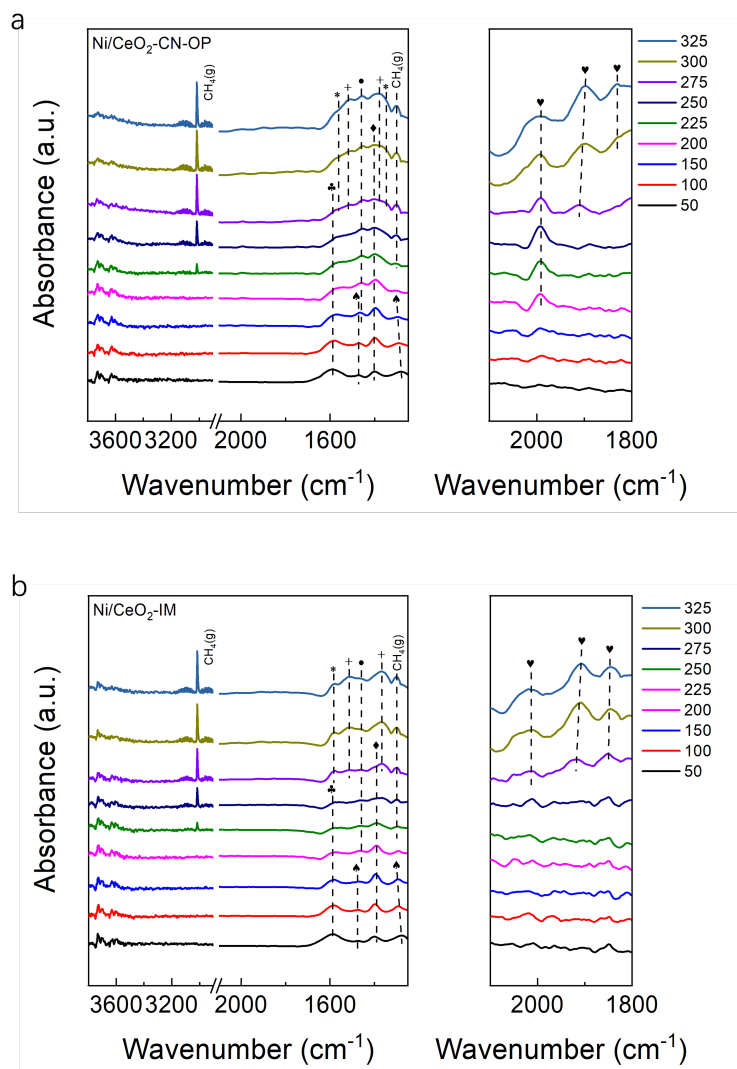
Ni/CeO₂-CN-OP.

7.3.6. Methanation mechanism investigation.

In general, the proposed CO₂ methanation mechanism can be categorized into RWGS+CO hydrogenation pathway and formate pathway. The former pathway involves the dissociation of CO₂ to CO and the hydrogenation of formed CO to CH₄. The latter pathway involves the stepwise hydrogenation of adsorbed CO₂ species into CH₄ without creating any CO species. Here, in-situ DRIFTS were performed under reaction conditions to provide information on the surface intermediates and reaction mechanism.

The DRIFTS spectra with the introduction of CO₂ and H₂ on Ni/CeO₂-CN-OP and Ni/CeO₂-IM as a function of temperature are shown in Fig. 7.10a and 7.10b. For Ni/CeO₂-CN-OP (Fig. 6.10a), as the reaction begin at 50 °C, appreciable peaks assigned to bicarbonate (1477, 1283 cm⁻¹), monodentate carbonate (1587 cm⁻¹), and bidentate carbonate (1402 cm⁻¹) are observed. The peaks of bicarbonate decrease gradually as the temperature increases and can be removed completely below 200 °C. With the further increase of temperature, the peaks ascribed to monodentate carbonate and bidentate carbonate vanish in succession below 300 °C, accompanied with the growth of some new peaks attributed to monodentate formate (1562 cm⁻¹, 1348 cm⁻¹) and bidentate formate (1518 cm⁻¹, 1379 cm⁻¹). It has been reported that monodentate formate and bidentate formate can be derived from the hydrogenation of monodentate carbonate and bidentate carbonate.[226] In addition to the carbonate and formate species, the peaks for linear CO (1992 cm⁻¹) and bridged CO (1909 cm⁻¹) species can be clearly seen since 200 °C and 275 °C, separately. CH₄ signal (3015, 1306 cm⁻¹) appears from 225 °C and increases with temperature. Resembling Ni/CeO₂-CN-OP, carbonate and formate species are observed on Ni/CeO₂-IM and their evolution has no obvious difference compared with Ni/CeO₂-CN-OP. However, linear CO on Ni/CeO₂-IM appear at higher temperature (250 °C) than that on Ni/CeO₂-CN-OP (200 °C).

Moreover, in-situ DRIFTS experiments were also carried out by switching off the reaction gas 13.3% CO₂/53.2% H₂/He after 30 min exposure at 300 °C and subsequently introducing the gas of 61.5% H₂/He (Fig. 7.10c and 7.10d). For both Ni/CeO₂-CN-OP and Ni/CeO₂-IM catalysts, the CO peaks disappear immediately (3 min) once upon switching off CO₂. After the depletion of the adsorbed CO, monodentate formate species continuously decrease. Meanwhile, the intensity of CH₄ peak decreases gradually. Consequently, it can be concluded that CO and monodentate formate species over the Ni/CeO₂ catalysts are both the active species in this methanation reaction, with the former as more active and dominant contributors to the low temperature methanation performance. It has been reported that oxygen vacancy is crucial for the CO₂ dissociation. To confirm the roles of oxygen vacancy in CO₂ methanation, the relationship between the oxygen vacancy and the CO₂ conversion is described. As shown in Fig. S17, an acceptable correlation between these two parameters is observed at 200 and 225 °C (higher testing temperature is excluded since the corresponding CO₂ conversion reaches the equilibrium). It should be noted that the determination coefficient (R^2) is 0.98 at 200 °C, but it decreases upon increasing the temperature to 225 °C (0.95), which is because the proportion of CH₄ formed from RWGS+CO hydrogenation pathway decreases at higher temperature. Thus, it indicates that oxygen vacancy indeed plays a vital role in the methanation reaction, especially at low temperatures.



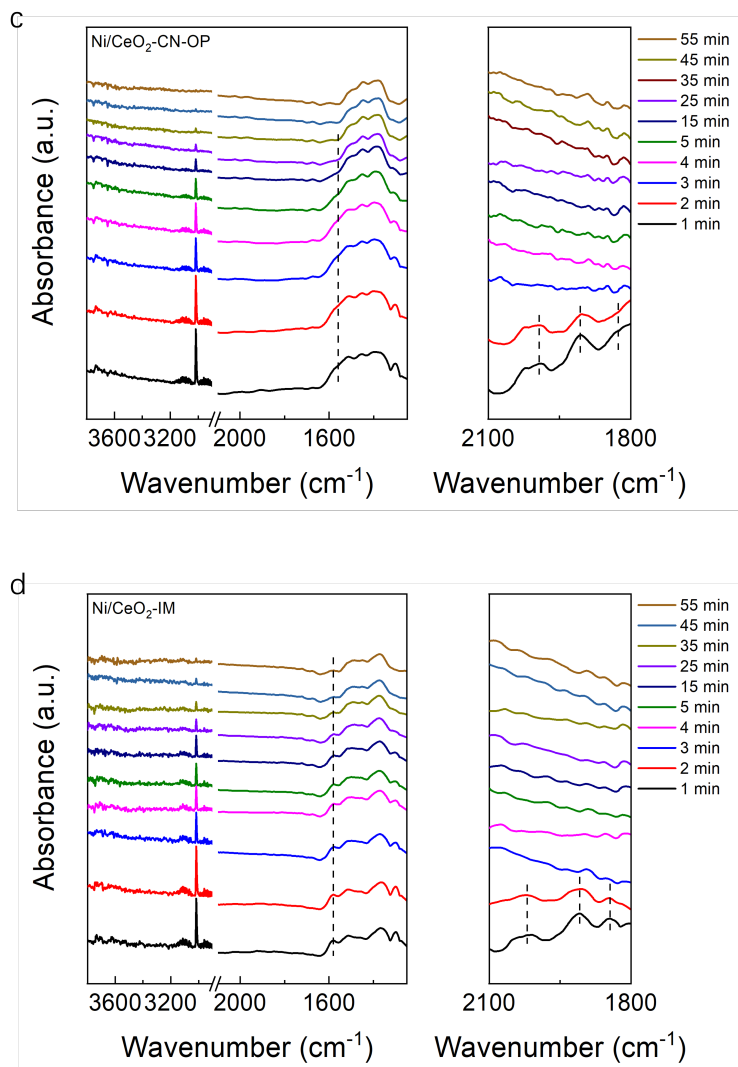


Fig. 7.10. In-situ DRIFTS results of CO₂ hydrogenation on (a) Ni/CeO₂-CN-OP and (b) Ni/CeO₂-IM catalyst; In-situ DRIFTS results of (c) Ni/CeO₂-CN-OP and (d) Ni/CeO₂-IM catalyst at 300 °C under continuous flow of gas 61.5% H₂/He after maintaining at 300 °C for 30 min under reaction gas (13.3% CO₂/53.2% H₂/He). Symbol definition: bicarbonate (♠), monodentate carbonate (♣), bidentate carbonate (♦), monodentate formate (*), bidentate formate (+), carbonyl (♥).

Furthermore, the evolution of monodentate formate on Ni/CeO₂-IM is slower than that on Ni/CeO₂-CN-OP observed from Fig. 10c and 10d, which is due to the H₂ dissociation on Ni/CeO₂-IM may not be efficient enough for hydrogenation of the formed monodentate formate species. The amount of chemisorbed H₂ is also calculated for Ni/CeO₂-CN-OP and Ni/CeO₂-IM. Ni/CeO₂-CN-OP shows higher amount of chemisorbed H₂ of 146 $\mu\text{mol/g}_{\text{cat}}$ than that of Ni/CeO₂-IM (94 $\mu\text{mol/g}_{\text{cat}}$), thus generating more dissociated hydrogen and further improving hydrogenation activity.

Based on these, the RWGS+CO hydrogenation pathway and the formate pathway occurring in parallel over the Ni/CeO₂ catalysts can be identified. CO₂ is adsorbed by the medium basic site over catalyst surface with the formation of monodentate carbonate, which can be hydrogenated to monodentate formate and then reacts with H atom until CH₄ is formed. In parallel, direct dissociation of CO₂ can be facilitated by surface oxygen vacancy and the generated CO is further hydrogenated to CH₄. Ni/CeO₂-CN-OP possesses a large amount of oxygen vacancy and medium basic site, which results in its higher catalytic performance.

7.4. Conclusion

In this work, a highly active Ni/CeO₂-CN-OP was prepared by one-pot method assisted with the C₃N₄. It was found that the Ni/CeO₂-CN-OP catalyst exhibited a high CO₂ conversion (82.6%) and CH₄ selectivity (99.4%) corresponding to a promising CH₄ generation rate of 178 mmol g_{cat}⁻¹ h⁻¹ at 250 °C. Compared to the reported works, this methane formation rate reached the highest level ever reported at the reaction temperatures at 250 °C. Besides, such catalytic activity could be nearly maintained during a 72 h-on-stream test. Both the RWGS+CO hydrogenation pathway and the formate pathway on Ni/CeO₂ were identified, with the former as the dominant one at lower temperature. The one-pot preparation method and the addition of C₃N₄ could increase the concentration of oxygen vacancy and the amount of surface medium

basic site, and correspondingly promote the activation of CO₂ and the formation of monodentate carbonate species. Consequently, the RWGS+CO hydrogenation pathway and formate pathway were enhanced.

Chapter 8 General conclusion and perspective

8.1 General conclusion

This thesis is developed to prepare Ni-based catalysts with high catalytic activity for CO₂ methanation and provide mechanism study on this process. There is great meaning to recycle the CO₂ originating from carbon-intensive energy sectors due to the great environmental and industrial advantage, provided H₂ can be produced via renewable pathways. Thus, development of catalysts for CO₂ hydrogenation to CH₄ has been extensively studied on different metal-based catalytic systems in search for high selectivity and low temperature operation. Among various transition metal catalysts, extensive studies have been performed on Ni-based catalysts in the CO₂ methanation reaction owing to the low cost and relatively high activity of Ni. However, because of the high activation energy required, high CO₂ conversion was difficult to achieve at low temperatures on Ni catalysts. High temperature methanation goes hand in hand with lower methane selectivity and often results in undesirable effects on the stability (coking problem) and lifetime of the catalysts as well as increased energy consumption. Therefore, this thesis deals with necessary components to prepare Ni-based catalysts with improved performance and provide an insight to mechanism of CO₂ methanation.

Increasing the Ni loading is a direct and effective way to boost the specific activity of catalyst. However, the optimal Ni loading generally does not exceed 20%, as the aggregation of Ni nanoparticles is observed with the further addition of Ni. Here, we prepared a kind of high loading (38 wt%) Ni/SiO₂ catalyst via sol-gel method. High specific area (455 m²/g) and high dispersion (11%) of small (4.6 nm) Ni nanoparticles were identified from the characterization. Consistently, these mesoporous Ni/SiO₂ catalysts displayed record specific activity (10.2 μmol g⁻¹ s⁻¹ at 250 °C), clearly outperforming other SiO₂ supported Ni-based catalysts. With these catalysts in hands, and using a combination of experimental and computational data, we also addressed a long-standing debate on the reaction mechanism. Over Ni catalysts, three different CH₄ formation pathways can be confirmed. Carbonyl from the

dissociation of CO_2 is hydrogenated to CH_4 in the RWGS+CO hydrogenation pathway, which is dominant at low temperature ($< 250\text{ }^\circ\text{C}$) due to its lowest energy barrier compared to the other two pathways. The formate pathway, correlated with the monodentate carbonate surface species, could proceed in parallel. C from the further dissociation of CO on the catalyst surface is hydrogenated to CH_4 in the C-O bond cleavage pathway.

To further improve the catalytic activity, the effect of various promoters was investigated. Herein, a series of bimetallic Ni-M/ SiO_2 catalysts (Mn, Co, and Cu) were successfully synthesized by sol-gel method and used for the CO_2 methanation reaction. Ni-Mn/ SiO_2 and Ni-Co/ SiO_2 shows higher activity, while Ni-Cu/ SiO_2 shows lower activity. The effect of doping on dispersion, reducibility and basicity do not seem to explain the activity trends. Instead, doping appears to affect the methanation mechanism, and this is shown to play the most critical role to determining the catalytic performance. RWGS+CO hydrogenation pathway and formate pathway are identified, with the former being dominant at lower temperature (below $250\text{ }^\circ\text{C}$). Cu addition inhibits those two pathways and results in a lower catalytic activity of Ni-Cu/ SiO_2 compared with Ni/ SiO_2 . RWGS+CO hydrogenation pathway could be promoted to the greatest extent by the Mn addition, and formate pathway could be enhanced to the greatest extent by the Co addition. Correspondingly, Ni-Mn/ SiO_2 and Ni-Co/ SiO_2 shows the highest performance at lower and higher temperature, respectively.

The formate pathway involves the stepwise hydrogenation of adsorbed CO_2 species into CH_4 with the monodentate formate from the hydrogenation of monodentate carbonate as an important intermediate. Monodentate carbonate originates from the adsorption of CO_2 on medium basic sites, and medium basicity is widely accepted as optimal for CO_2 methanation. RWGS+CO hydrogenation pathway involves the dissociation of CO_2 to CO, followed by the hydrogenation of CO to CH_4 . Thus, based on this fundamental understanding, herein, a highly active Ni on ceria catalyst was prepared by one-pot method assisted with the C_3N_4 . Our best catalyst (denoted “Ni/ CeO_2 -CN-OP”, where

CN stands for the addition of C_3N_4 during the preparation and OP stand for “one-pot”) catalyst exhibited a high CO_2 conversion (82.6%) and CH_4 selectivity (99.4%) corresponding to a promising CH_4 generation rate of $178 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ at 250°C . Compared to the reported works, this methane formation rate reached the highest level ever reported at the reaction temperatures at 250°C . Besides, such catalytic activity could be nearly maintained during a 72 h-on-stream test. The one-pot preparation method and the addition of C_3N_4 were shown to increase the concentration of oxygen vacancy and the amount of surface medium basic site, and correspondingly promote the activation of CO_2 and the formation of monodentate carbonate species. Consequently, the RWGS+CO hydrogenation pathway and formate pathway were enhanced.

8.2 Perspective

The available catalyst technology can reach near equilibrium CO_2 conversions over 300°C and $> 99\%$ of selectivity towards methane formation. However, there is a need for Ni-based catalysts to achieve high conversion at lower reaction temperature ($< 200^\circ\text{C}$) to obtain near 100% CO_2 conversion in further development. To achieve this goal, activation of CO_2 molecule at milder condition is crucial, which requires to develop new materials with high oxygen mobility and basic properties. Typically, partially reducible metal-oxide supports (ceria in this thesis) possess higher concentration of oxygen vacancy than inert supports (silica in this thesis). To further increase the reaction rate and selectivity towards CH_4 , the extent of the exposed Ni site (related to Ni loading, particle size, and dispersion) should also be highlighted.

This thesis work may provide future research prospects in several directions. First, the sol-gel method provides a way to prepare the high loading Ni-based catalyst and CeO_2 with oxygen vacancy facilitates the RWGS+CO hydrogenation pathway. Combining those two aspects, that is, adding CeO_2 as promoter to Ni/SiO_2 to prepare the $Ni-Ce/SiO_2$ catalyst, might create "one plus one greater than two" effect (synergy).

Second, the framework of the high loading bimetallic Ni-M/SiO₂ might exist after removing the SiO₂ matrix, and a better pore structure and more exposed site would be obtained. Third, Ni/CeO₂(CN)-IM already possesses a high activity at 250 °C. From the characterization, Ni particle over Ni/CeO₂(CN)-IM is big and Ni dispersion is low. Decreasing the Ni loading might ameliorate those two aspects and thus increase the performance.

Apart from the development of high active catalyst, another challenge has to be settled is the supply of “green H₂”. Only using the “green H₂” obtained via electrolysis using renewable electricity to split water into hydrogen and oxygen, the large-scale application of CO₂ methanation is meaningful. However, the fact is that, in Europe 2022, 96% of hydrogen was produced with natural gas, resulting in significant amounts of CO₂ emissions, which is totally the reverse reaction of CO₂ methanation.

Furthermore, greater focus would be placed on the catalyst development for industrial applications under harsh conditions. For instance, sulfur compounds, generally H₂S and carbonyl sulfide, are present in the feedstocks. Therefore, it is important to develop sulfur-resistant catalysts. Another example is the co-presence of CO and CO₂ in H₂-rich reformat gases; thus, the development of highly active and selective catalysts for methanation of CO and CO₂ are also of great importance.

Supporting information

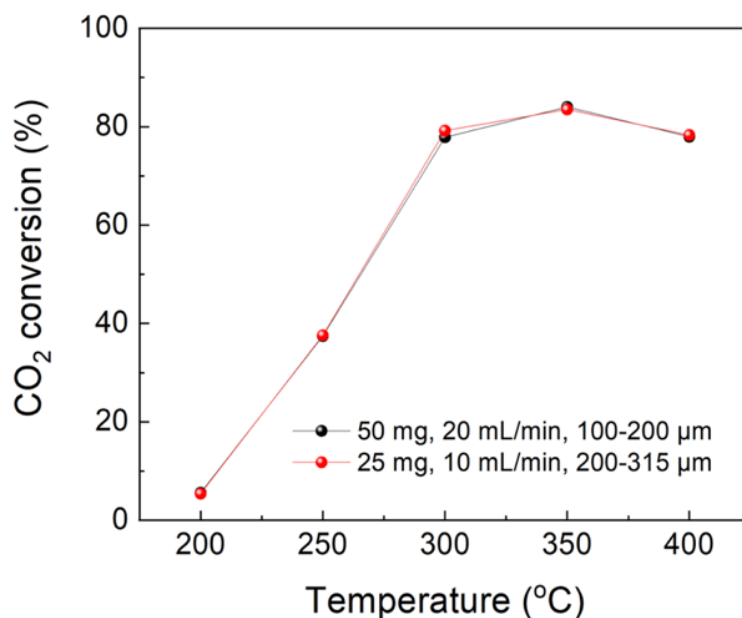


Fig. S1. CO₂ conversion over the 50 Ni/SiO₂ at different condition.

An extra performance test was performed for 50 Ni/SiO₂. To decrease the contacting time and keep the GHSV at 24000 mL g⁻¹ h⁻¹, the weight of sample and the total flow rate (CO₂:H₂:He is still 1:4:5) decreased to 25 mg and 10 mL/min, separately. The catalyst pellets increase to 200-315 μm. We can find that there is no obvious change of the CO₂ conversion at each testing temperature, confirming no mass transfer limitation existing in the tested condition.

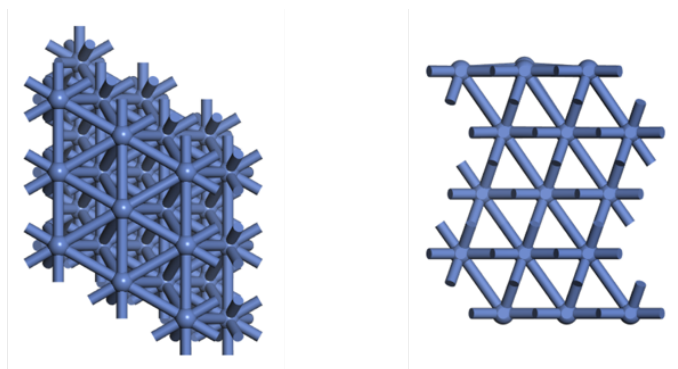


Fig. S2 The optimized configurations of Ni(1 1 1) 3×3 in top and side views.

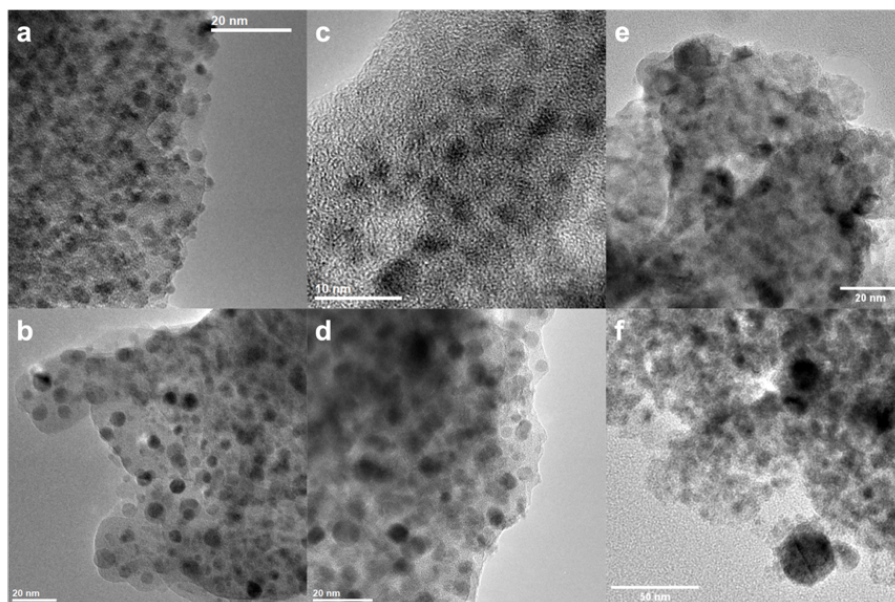


Fig. S3. TEM images of (a) calcined 30 NiO/SiO₂ and (b) reduced 30 Ni/SiO₂, (c) calcined 40 NiO/SiO₂ and (d) reduced 40 Ni/SiO₂, (e) calcined 60 NiO/SiO₂ and (f) reduced 60 Ni/SiO₂.

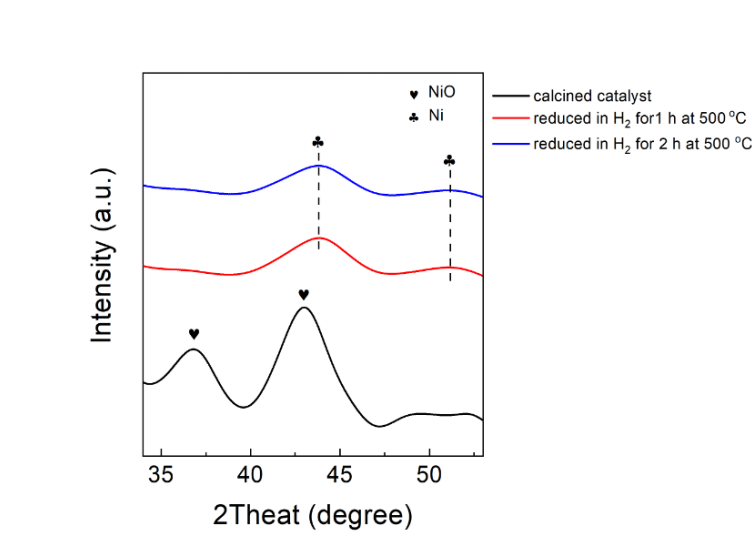


Fig. S4. In-situ XRD of 50 NiO/SiO₂ under H₂ at 500 °C.

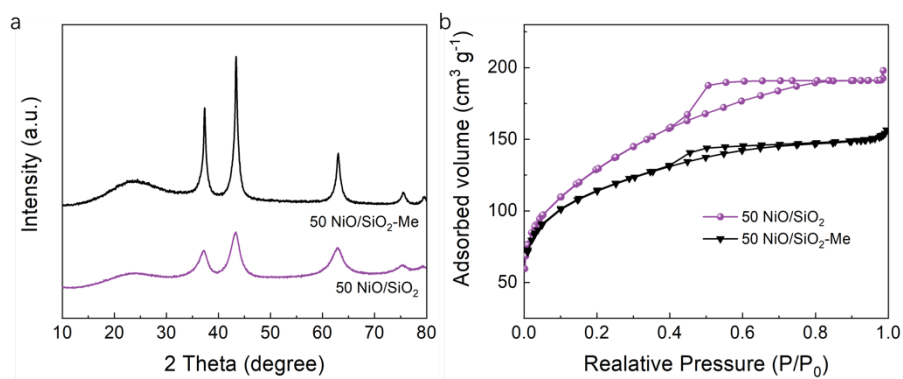


Fig. S5. (a) XRD patterns and (b) N₂ adsorption-desorption isotherms of calcined samples.

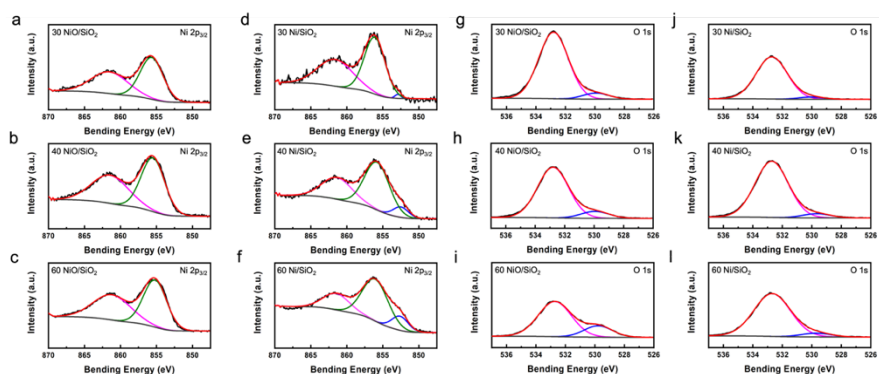


Fig. S6. XPS spectra of (a-f) Ni 2p_{3/2} and (g-l) O 1s for calcined NiO/SiO₂ and reduced Ni/SiO₂.

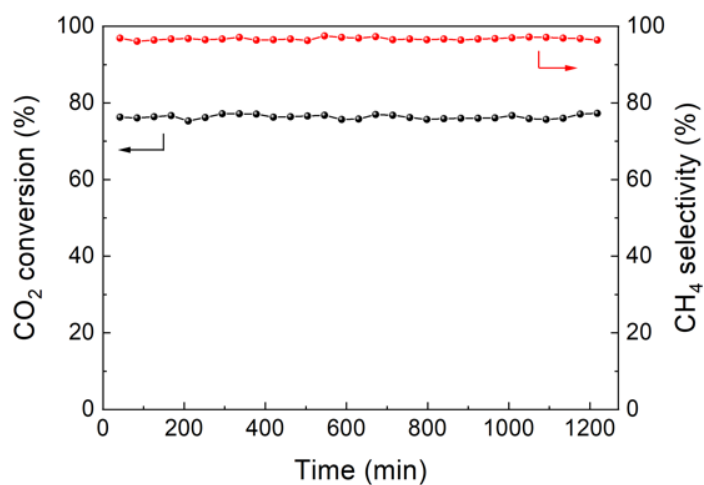
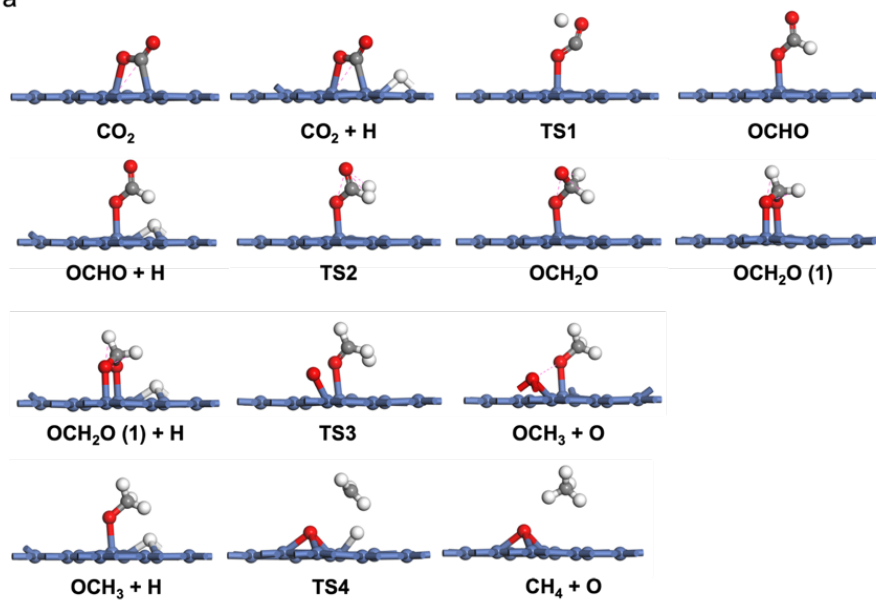
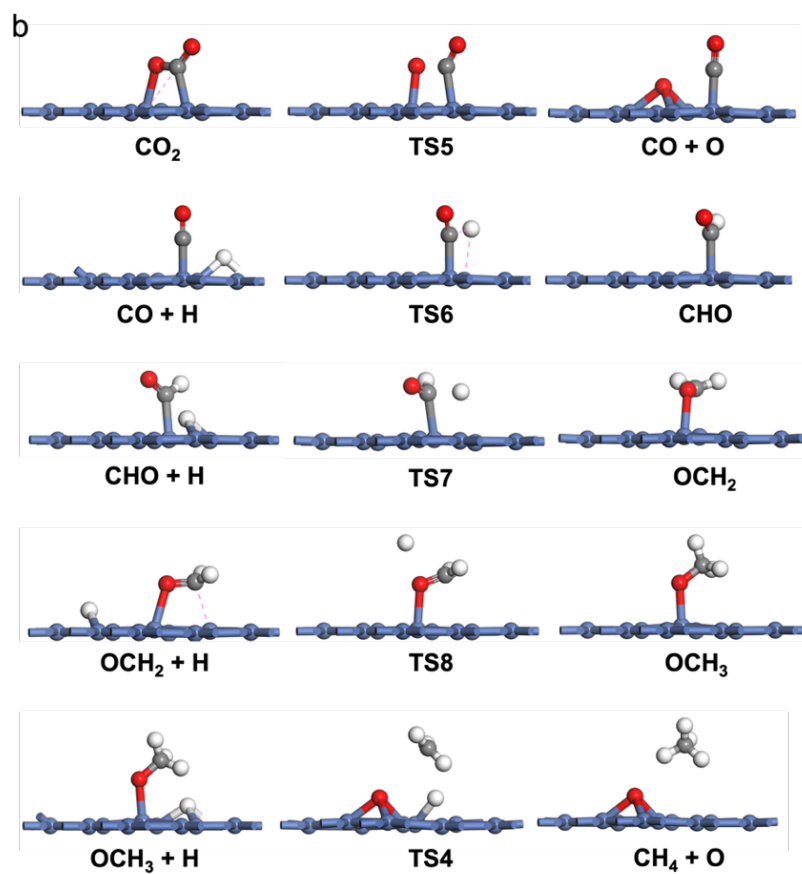


Fig. S7. Stability test for 50 Ni/SiO₂ catalysts (GHSV of 36000 mL g⁻¹ h⁻¹ at 300 °C for 50 h).

a





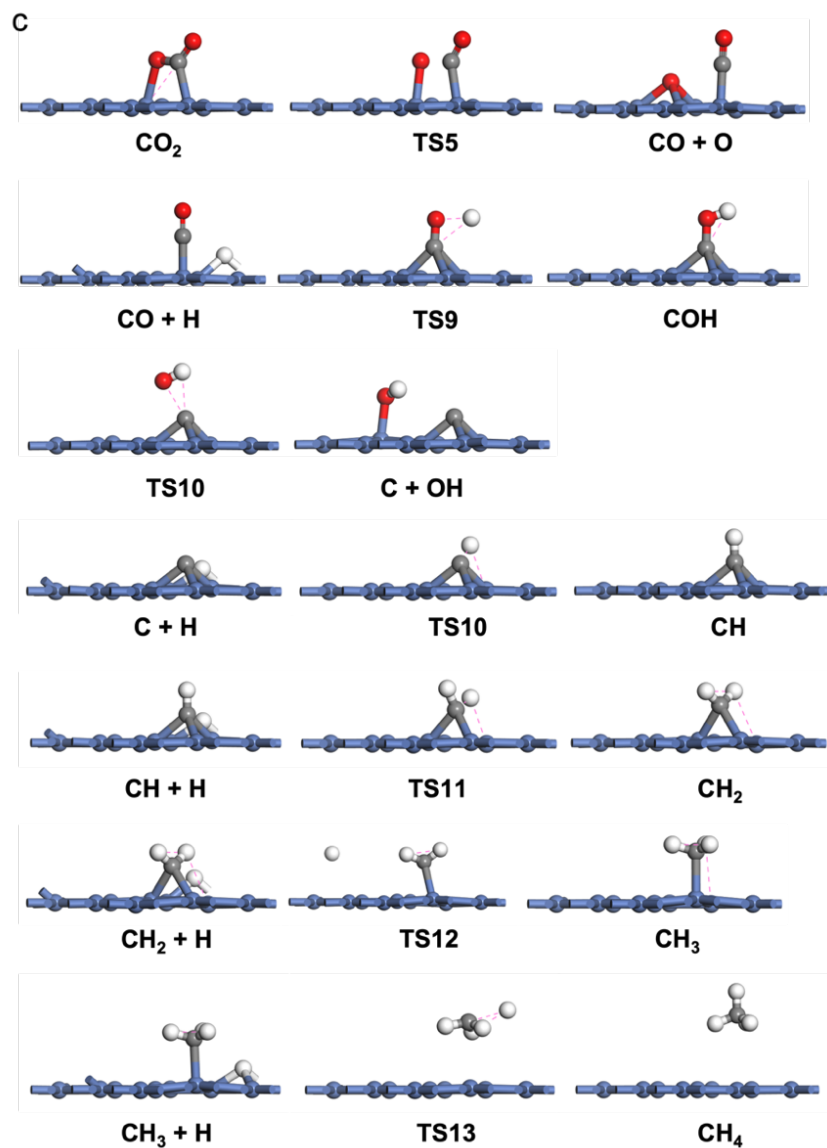
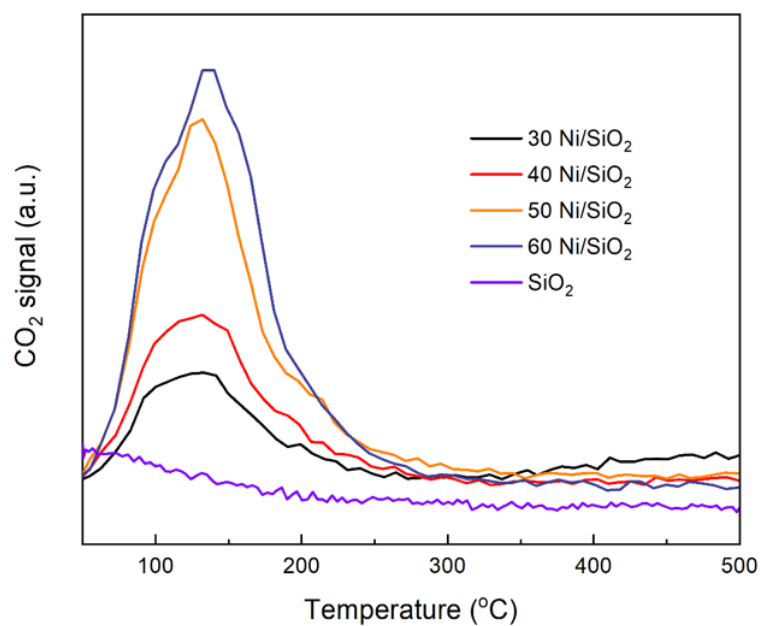
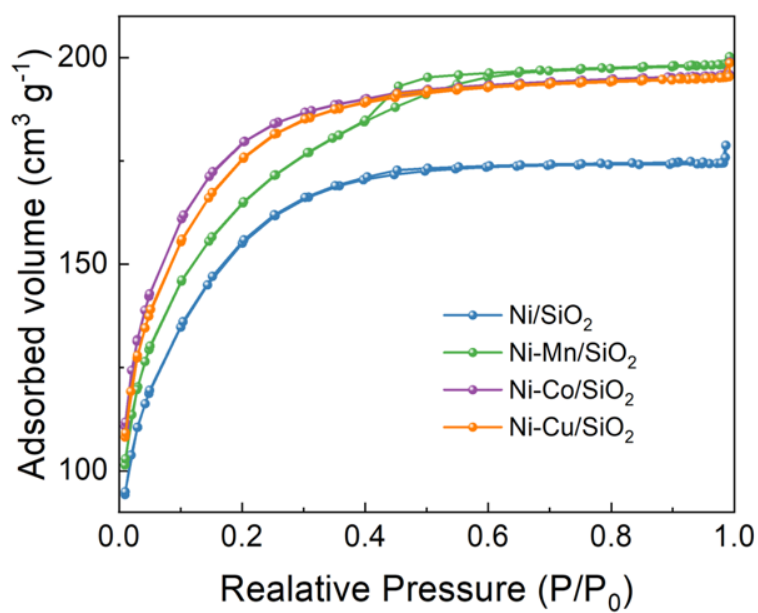


Fig. S8. The optimized configurations of the involved intermediates, initial states (IS), transition states (TS) and final states (FS) in (a) formate pathway, (b) RWGS+CO-hydrogenation pathway and (c) C-O bond cleavage pathway.

Fig. S9. CO₂-TPD of the reduced Ni/SiO₂ and SiO₂.Fig. S10. N₂ adsorption-desorption isotherms.

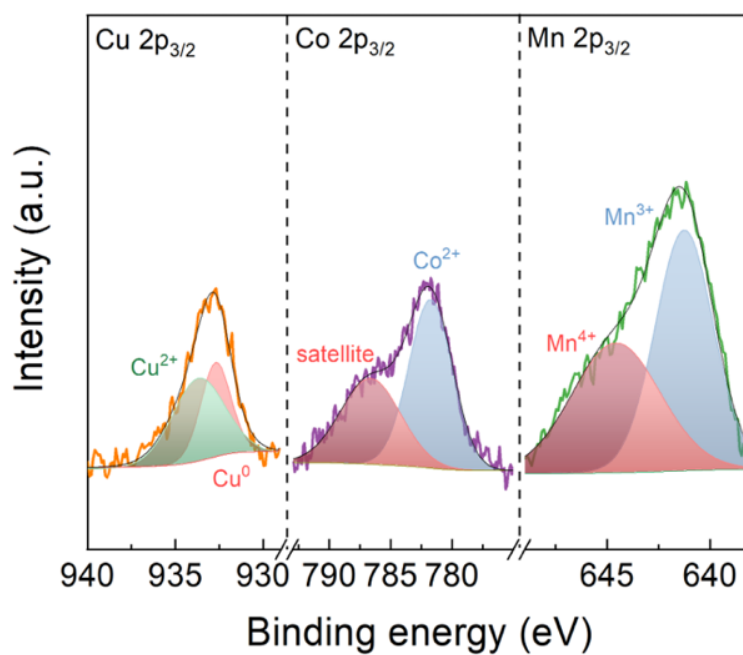


Fig. S11. XPS spectra of Mn 2p_{3/2}, Co 2p_{3/2}, and Cu 2p_{3/2} over the calcined catalysts.

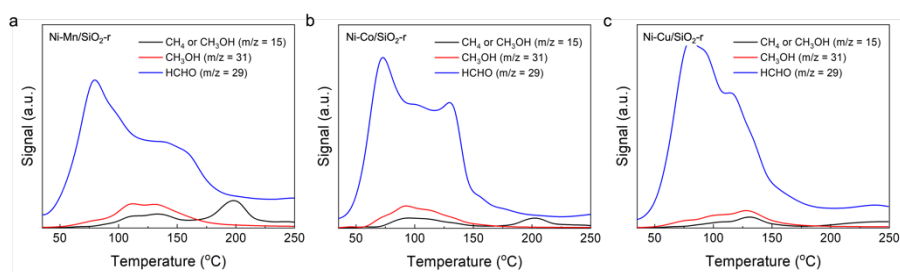


Fig. S12. HCHO-TPSR over Ni-M/SiO₂.

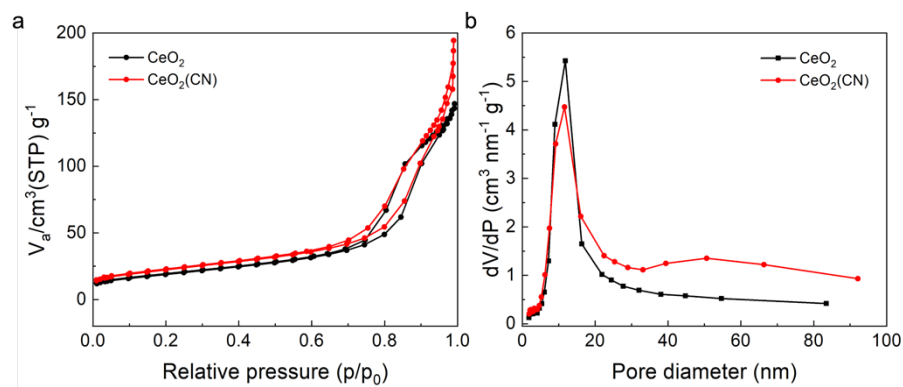


Fig. S13. (a) N_2 adsorption-desorption isotherms and (b) pore size distributions of the CeO_2 supports.

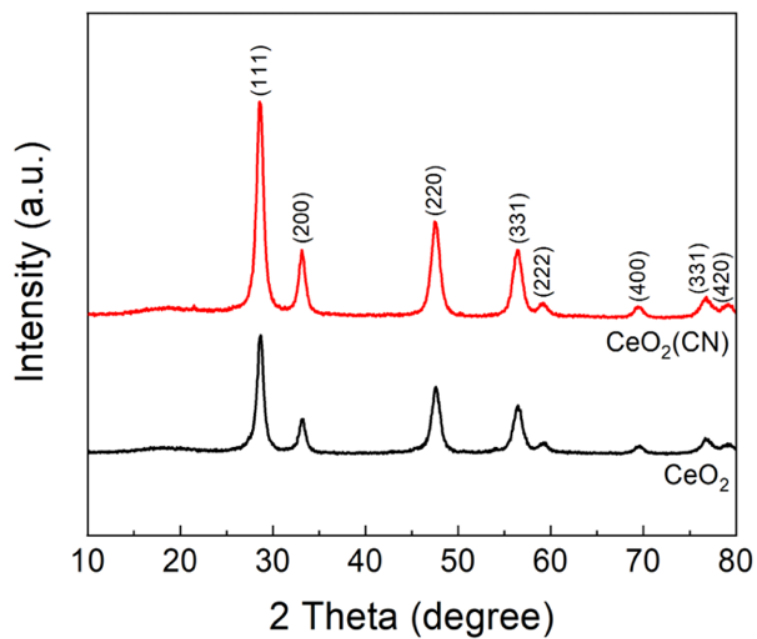
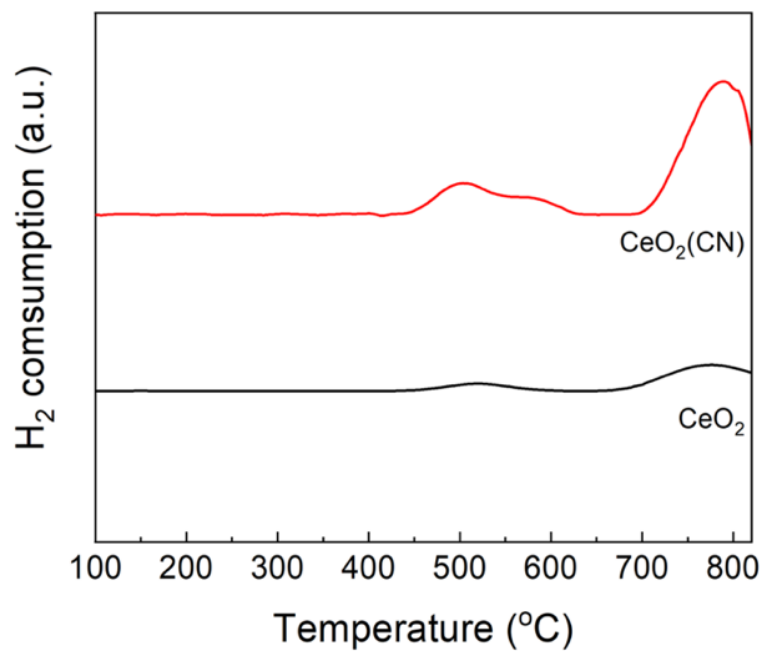
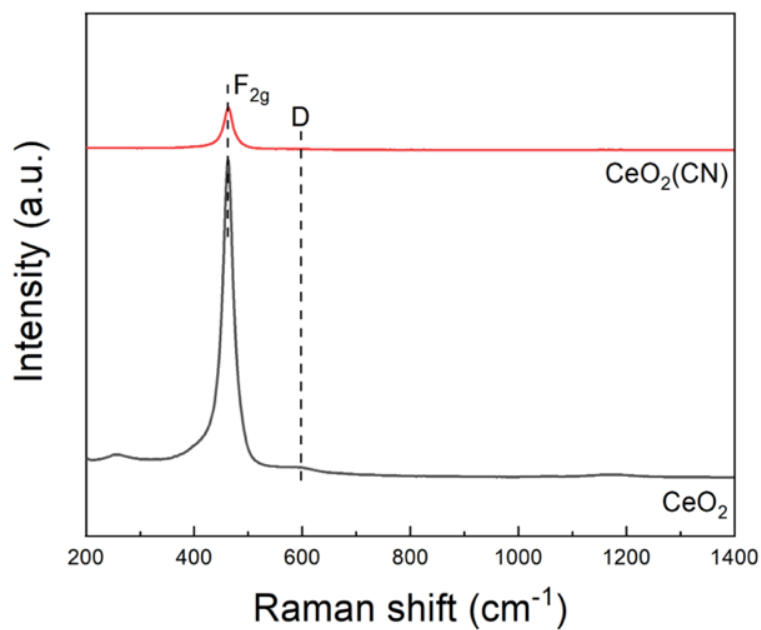


Fig. S14. XRD patterns of the CeO_2 supports.

Fig. S15. H₂-TPR of the CeO₂ supports.Fig. S16. Raman spectra of the CeO₂ supports.

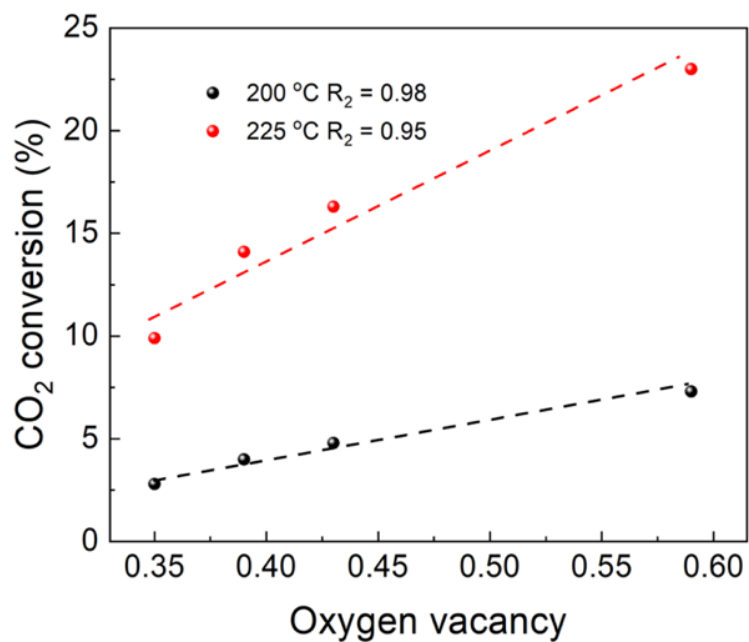


Fig. S17. Relationship between the oxygen vacancy (obtained from Raman) and CO₂ conversion at different reaction temperatures.

Table S1. XPS deconvolution results of Ni, O.

	Ni ⁰ BE (eV)	Ni ²⁺ BE (eV)	O _{Ni} BE (eV)	O _{other} BE (eV)	Ni/O _{Ni}
30 NiO/SiO ₂		861.5, 855.7	529.9	532.8	1.2
40 NiO/SiO ₂		861.5, 855.5	530	532.8	1.26
50 NiO/SiO ₂		861.5, 855.3	529.9	532.8	1.11
60 NiO/SiO ₂		861.2, 855.2	529.8	532.7	1.12
30 Ni/SiO ₂	852.6	861.7, 856.1	530.1	532.7	1.34
40 Ni/SiO ₂	852.5	861.3, 855.8	529.7	532.7	1.52
50 Ni/SiO ₂	852.8	861.1, 855.9	529.8	532.7	1.88
60 Ni/SiO ₂	852.6	861.5, 856.0	529.7	532.7	2.7

Table S2. The comparison of TOF values towards CO₂ conversion of the reported Ni catalysts for CO₂ methanation.

Catalyst	Preparation method	T (°C)	TOF (s ⁻¹)	Ref.
50 Ni/SiO ₂	Sol-gel	250	0.016	This work
50 Ni/SiO ₂ -IM	Impregnation	250	0.006	This work
25%Ni/SiO ₂	Ammonia evaporation	250	0.006	[256]
10%Ni/SBA-15-WI	Impregnation	250	0.012	[58]
10%Ni/SBA-15-AE	Ammonia evaporation	250	0.016	[58]
10%Ni/ZSM-5	Wet impregnation	250	0.008	[257]
31.6%Ni-MCF-P-30	Hydrothermal method	220	0.002	[258]
30%Ni-MCF-P-32-5L	Hydrothermal method	220	0.003	[259]
6%Ni/ZrO ₂	Citrate-complexing method	225	0.038	[260]
12%Ni/Al ₂ O ₃	Incipient wet impregnation	250	0.018	[261]
35%Ni/Y ₂ O ₃	Solution combustion synthesis	250	0.011	[61]
10%Ni/mpCeO ₂	Strong electrostatic adsorption	225	0.183	[75]

Table S3. Peak position and corresponding amount and percentage for CO₂-TPSR of the 50 Ni/SiO₂.

Purge	CO pathway			Formate pathway			CO-C pathway		
Temperature	position	amount	percentage	position	amount	percentage	position	amount	percentage
140 °C	210	1.45	17.4	260	2.71	32.5	375	4.17	50.1
200 °C	209	1.5	22.3	270	1.31	25.5	375	3.06	52.2
500 °C	213	0.94	18.9	268	1.26	25.5	369	2.75	55.6

Table S4. The comparison of the CO₂ methanation activity at 250 °C on a series of Ni-CeO₂ catalysts in literature.

	Reaction gases	GHSV (mL/g h)	Conversion (%)	Selectivity (%)	Specific activity (mmol/g h)	Reference
Ni/CeO ₂ -CN-OP			82.6	99.8	178	
Ni/CeO ₂ -OP	13.3%CO ₂ /53.2%H ₂ /33.5%Ar	36000	58.2	99.5	125	This work
Ni/CeO ₂ -IM			34.1	98.6	73	
Ni/CeO ₂ (CN)-IM			74.6	99.3	161	
Ni/CeO ₂ -R	20%CO ₂ /80%H ₂	20000	90.4	99.6	160	[191]
Ni/CeO ₂ -NR	20%CO ₂ /80%H ₂	30000	65.0	99.7	174	[35]
Ni/CeO ₂ -P	16%CO ₂ /64% H ₂ /20%He	56000	30.0	99.4	119	[241]
Ni/mpCeO ₂	8%CO ₂ /32% H ₂ /60%He	60000	70.2	99.5	149	[75]
NiNPs@CeO ₂ NF	20%CO ₂ /80%H ₂	36000	50.6	85.0	138	[170]
Ni/CeO ₂ -SGM	20%CO ₂ /80%H ₂	10000	80.5	95.8	69	[229]

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List of scientific communications

Publications:

1. CO₂ methanation with high-loading mesoporous Ni/SiO₂ catalysts: toward high specific activity and new mechanistic insights, J. Catal., 2023, <https://doi.org/10.1016/j.jcat.2023.07.021>. (First author)
2. CO₂ methanation: deciphering the role of dopant (Mn, Co, and Cu) in Ni/SiO₂ catalysts prepared by sol-gel chemistry. (Under review) (First author)
3. Enhanced low-temperature CO₂ methanation performance over Ni/CeO₂ catalysts prepared by facile one pot method with the addition of carbon nitride. (Under preparation) (First author)
4. CO₂ methanation with Ru@MIL-101 nanoparticles fixated on silica nanofibrous veils as stand-alone structured catalytic carrier, Appl. Catal. B, 2023 (320), <https://doi.org/10.1016/j.apcatb.2022.121972>. (Co-author)
5. CO₂ Methanation over cobalt nanoparticles embedded in ZIF-L-derived porous carbon, ChemCatChem, 2023 (15), <https://doi.org/10.1002/cctc.202201338>. (Co-author)
6. Solvent-free preparation of Ru/Al₂O₃ catalysts for CO₂ methanation: an example of frugal innovation, Chem. Mater., 2023 (35), <https://doi.org/10.1021/acs.chemmater.3c01746>. (Co-author)

Conferences:

- . International Sol-Gel Conference SOLGEL 2022, Lyon, France, CO₂ methanation with high-loading mesoporous Ni/SiO₂ catalysts: toward high specific activity and new mechanistic insights (Poster)
- . ICCDU 2023, Bari, Italy, CO₂ methanation with high-loading mesoporous Ni/SiO₂ catalysts prepared by solgel chemistry and the role of dopant (Mn, Co, and Cu) over Ni/SiO₂ catalysts (Oral presentation)

