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**CO₂ METHANATION: EFFECTIVE NI-BASED
CATALYSTS AND MECHANISMS OVER RU/AL₂O₃**

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**CO₂ methanation: effective Ni-based catalysts and
mechanisms over Ru/Al₂O₃**

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Abstract

The hydrogenation of CO₂ at atmospheric pressure casts a direction for researchers to recycle the atmospheric carbon and subsequently reduce the greenhouse gas effect. Several efforts have been devoted to the development of an effective and stable catalyst for this reaction.

Ni supported on Y₂O₃ catalysts were obtained from two different Y sources, Y₂O₃ that calcined from Y₄O(OH)₉(NO₃) and Y₄O(OH)₉(NO₃) directly. Compared to the ones from Y₂O₃ (denoted as Ni-Y₂O₃), the catalysts prepared from Y₄O(OH)₉(NO₃) (denoted as Ni/Y₂O₃) showed superior activity for CO₂ methanation, which was attributed to the enrichment of surface medium basic sites that of great importance for CO₂ activations. However, with high metal loadings such as 20%, strong basic sites appeared which resulted in a high sensitivity to coke formation. Moreover, the reaction mechanism for CO₂ methanation over Ni supported on Y₂O₃ has been proposed involving carbonates and formates species as key intermediates. The higher reactivity towards H₂ for formates over Ni/Y₂O₃ than that over Ni-Y₂O₃ was found, which probably was the rate-determining step for CH₄ formations. Temperature-programmed reduction by H₂ (H₂-TPR) further revealed that a stronger interaction between Ni species and the support for the reference Ni-Y₂O₃, if compared to that of Ni/Y₂O₃.

A W doped Ni-Mg mixed oxide catalyst (NiWMgO_x) was prepared by homogeneous precipitation and employed for the methanation of CO₂. The addition of W remarkably promoted the methanation activity if compared to the

undoped NiMgO_x catalyst with improved stability and anti-CO-poison ability. Characterization techniques including *in situ* diffuse reflectance infrared Fourier Transform spectroscopy (DRIFTS), temperature-programmed desorption of CO_2 (CO_2 -TPD) and H_2 -TPR were applied for both NiMgO_x and NiWMgO_x . The superior reactivity of monodentate formate towards H_2 than that of bidentate formate species was identified and doping with W favored the formation of the former during the methanation of CO_2 , which well agreed with the activity results. W addition also increased the formation and the stability of surface basicity sites, along with an enhancement of the Ni-Mg interaction in favor of anchoring the Ni sites, all of which were responsible for the enhanced CO_2 methanation activity and the improved stability.

Mechanistic studies of CO_2 methanation have been carried out on $\text{Ru}/\text{Al}_2\text{O}_3$. The structural configuration of Ru species over $\text{Ru}/\text{Al}_2\text{O}_3$ catalysts at different Ru loadings has been characterized by infrared reflection absorption spectroscopy (IRAS) for CO adsorption. Supported Ru monolayers, in which metal atoms directly interacted with the support, were plentiful over 1% $\text{Ru}/\text{Al}_2\text{O}_3$, exhibiting a high CO yield for the hydrogenation of CO_2 at ambient pressure. An increasing preference for methanation was observed on $\text{Ru}/\text{Al}_2\text{O}_3$ with higher Ru loadings, over which a tendency for the exclusive formation of three-dimensional (3D) nanoclusters of multilayers appeared. Density functional theory (DFT) calculations over $\text{Ru}_9/\text{Al}_2\text{O}_3$, as the representative model of supported Ru monolayers, and $\text{Ru}_{35}/\text{Al}_2\text{O}_3$, as the representative model of supported 3D nanoclusters,

demonstrated that the energy barrier of reversed water gas shift (RWGS) was lower than that of the methanation on Ru monolayers while CH₄ production was energetically favored on top sites of 3D Ru nanoclusters. Moreover, the incorporation of the peripheral O into the final products of CO₂ hydrogenation was predicted as a critical step during the RWGS at the metal-support interfaces, which was validated by isotope exchange mass spectrometry (MS) experiments.

Chapter 1 Background and Philosophy

1.1 Background on CO₂ hydrogenation

The atmospheric concentration of CO₂ has been drastically rising since the Industrial Revolution, due to the vast consumption of fossil fuels contemporarily. Human activities have resulted in an increase of 40% in the atmospheric CO₂ during the last few decades, from 280 parts per million by volume (ppm) to 399 ppm in 2015 [1], leading to an increasing concern on alleviating the global greenhouse effect. Specifically, attentions have been paid to impacts of the enhanced concentration of atmospheric CO₂ on the stability of the thermohaline circulation of North Atlantic Ocean [2-4], which is an essential composition of the global-scale ocean circulation that transports both energy and matters worldwide and has a significant impact on the climate of the Earth [5]. Modeling studies suggest that the thermohaline circulation will be permanently shut down if the atmospheric CO₂ concentration increases by 750 ppm in the next 100 years [6-8].

The governing of the atmospheric CO₂ concentration falls into not only the control of CO₂ emission [9, 10] but also the fixation of the current atmospheric CO₂ content [11-13]. National regulations have been issued worldwide to reduce the fossil fuel consumptions, such as restrictions of the plastic bags usage [14]. Moreover, international cooperation between countries is ongoing, making appreciable progress [15]. On the other hand, countless efforts have also been devoted to the fixation of CO₂ from the atmosphere by amine-based solvents,

metal-oxide-based adsorbents and organic adsorbents [9, 16-20].

Converting CO₂ into valuable products provides solutions for both the decrease of CO₂ concentration in emissions and the effective conversion of CO₂ after the fixation from the atmosphere. However, considering the reactant CO₂ is characterized by high thermodynamic stability, a selective catalytic reaction is needed to allow for an economic application. One industrial applied process of such chemical reactions is the synthesizing of urea from NH₃ and CO₂ [21]. The hydrogenation of CO₂ also shows great promise since the large-scale H₂ production is expected to be available at a low cost by photocatalytic water splitting [22-25]. Depending on the reaction conditions, the products of CO₂ hydrogenation falls into the following categories, ranging from methane [26-32], carbon monoxide [33-37], methanol [38-43], formic acid [44-47], dimethyl ether (DME) [48-50] and ethanol [51-54].

CO production by reversed water gas shift (RWGS) has attracted many attentions since the reaction produces synthetic gas, which, however, demands a higher temperature to achieve appreciable conversion with satisfying selectivity [55, 56]. Meanwhile, the methanol synthesis from hydrogenation of CO₂ is often associated with poor selectivity even at a high pressure [57-59]. Indeed, a lower temperature is preferred thermodynamically for methanol formation while a higher temperature is needed for CO₂ activation. As a result, obstacles for the application of methanol synthesizing from CO₂ hydrogenation lie in finding a highly selective catalyst operating at a mild reaction condition [60]. The hydrogenation of CO₂ into

formic acid often comes with a base additive in order to shift the reaction equilibrium forwards, accompanied by the formation of formate instead of formic acid [61-63]. Besides, formic acid formation is much more favored in a homogeneous system on organometallic complexes, such as the Ru complexes [64], leaving drawbacks in products separation and catalysts recycling [65]. For DME formation, CO₂ has to be converted into methanol first, followed by the dehydration of methanol [66, 67]. Thus, a two-catalyst system with a metallic catalyst for methanol synthesis and an acid catalyst for dehydration, or a bi-functioning catalyst with active sites of both types is needed [68, 69]. What is more, this process is characterized by low CO₂ conversion and poor selectivity to DME so far. Regarding to the ethanol produced from CO₂ hydrogenation, the emphasize has been placed on the modification of catalysts for methanol production to meet the needs [70]. However, still very few progress has been made due to the high activation energy for the chain growth [71]. As a comparison, the methanation of CO₂ operates at a relatively mild condition, with excellent activity and high selectivity [32, 72, 73]. Besides, the abundant CO₂ content on Mars provides a possible solution for the production of propellants indigenously for spacecraft via the Sabatier reaction. The simultaneously produced H₂O by methanation of Martian CO₂ can be further used for the life-support system of astronauts [74]. By carrying H₂ instead of directly CH₄ from the earth, the initial weight of a spacecraft can be reduced by 20-45% [75]. Thus, National Aeronautics and Space Administration (NASA) is greatly interested in exploring the

applications of methanation for the project of human colonization on Mars [76].

1.2 Aims and outlines

Generally, Ni-based catalysts have been selected for the industrial application of methanation of CO₂ due to the lower cost, if compared to the noble metal catalysts. Several methanation plants have been running worldwide, such as Audi e-gas plant in Werlte (Germany), Huaqing Energy Technology in Inner Mongolia (China). Consistent pursuits lie in the optimization of low-temperature activity, not only for the purpose of energy saving, but also for the reason that high temperature reaction is limited by the chemical equilibrium. Besides, the formation of mobile Ni carbonyls via the interaction between CO, as impurities in the feeding gas, and surface Ni species at low temperature leads to further deactivations. Although the reaction temperature can be fine controlled to stop this process, the unavoidable temperature fluctuation at the start-up and shutdown stage during regular maintenances exposes the system to high possibilities of deactivation. Thus, to improve the anti-CO-poisoning ability is another concern of the stability of Ni-based catalysts, besides from the regular issues of metal sintering and carbon deposition.

In chapter 4, we prepared a highly effective Ni supported on Y₂O₃ catalyst from Y₄O(OH)₉(NO₃) for CO₂ methanation, which exhibited CO₂ conversion of 88% and selectivity to CH₄ of 99% at 350 °C. The much-improved catalytic performance compared to the reference catalyst synthesized from Y₂O₃ has been interpreted based on the characterization results of X-ray diffraction (XRD), *in situ*

diffuse reflectance infrared Fourier Transform spectroscopy (DRIFTS), CO₂ temperature-programmed desorption (CO₂-TPD), H₂ temperature-programmed reduction (H₂-TPR).

The modification of Ni-Mg catalysts by dopant W has been studied in chapter 5. Robust Ni-W-Mg mixed oxides catalysts were obtained via homogeneous precipitation showing a yield of CH₄ of 84% at 300 °C, over which almost no activity loss was observed during exposure to CO-containing feeding gas for 100 h at 275 °C. The resulted catalysts are comprehensively characterized by transmission electron microscopy (TEM), XRD, *in situ* DRIFTS, CO₂-TPD, H₂-TPR, energy-dispersive X-ray spectroscopy (EDX) and thermo gravimetric analysis (TGA).

Although Ni-based catalysts are economically favored, noble metal catalysts, such as Ru, are much more excellent in terms of activity and stability [31, 77, 78]. Moreover, noble metal catalysts have been proved to act as all-around candidates for CO₂ involved reactions. The study of activation mechanism of CO₂ on noble metal catalysts has attracted countless attentions. For example, the activation of CO₂ by H₂ at atmospheric pressure over noble metal catalysts is beneficial for the coupling of this reaction into other systems, such as the removal of CO from CO₂-rich gas mixtures by selective methanation [79-81].

Thus, the mechanisms of CO₂ hydrogenation over Ru/ γ -Al₂O₃ were studied by experimental characterization and theoretical calculations. Kinetic measurements revealed a contrary dependence for CH₄ formation and CO

formation on the Ru loadings, which probably was associated with the different dominant surface sites when the Ru content varies. Density function theory (DFT) calculations suggested that CH₄ formation was more favored over the top Ru sites of a three-dimension (3D) nanocluster, which interacted with all surround sites by Ru-Ru bonds. As a comparison, CO was preferential produced over Ru sites that were bonded directly to the surface of the support, as in a monolayer. Details of the above mentioning work will be presented in chapter 6.

Chapter 2 Literature Review

Since the first report on methanation of CO₂ by Sabatier in 1902 [82], decades of efforts have been dedicated to the developments of highly efficient catalysts systems and the clarification of the reaction mechanisms. Noble metal-based catalysts, mostly Ru [29, 31, 77, 78, 83-86], Rh [87-90] and Pd [90-93], demonstrate both remarkable activity for CO₂ even at relatively low temperature with impeccable stability. As a comparison, non-noble metal catalysts, mostly Ni based [72, 73, 94-99], are intensively studied due to their lower cost and comparable catalytic performance.

2.1 The effect of structural compositions

CO₂ methanation is structure sensitive, with great dependence on the support, metal loadings, the presence of a dopant and metal support interactions.

2.1.1 *Studies of the supports*

Rh supported on various oxides have been attempted for CO₂ methanation by Lizuka et al. [100, 101], among which Rh/ZrO₂ demonstrated remarkably superior activity, due to the higher capability for CO₂ adsorption and the excellent ability for CO₂ activation. Similar works of screening for the best support for oxide-supported Pd catalysts were done by Erdohelyi et al. [93], who discovered that the dispersion of Pd differed significantly with varying supports, leading to a difference in the selectivity to CH₄ for CO₂ hydrogenation. Among the four

catalysts tested, Pd supported on Al_2O_3 , TiO_2 , SiO_2 and MgO , Pd/ TiO_2 was proved to be the most effective catalyst for CO_2 methanation. Over unsupported Pt nanoparticles, CO was primarily formed with only negligible formation of CH_4 for CO_2 hydrogenation [102]. Applying TiO_2 or SiO_2 as the support for Pt nanoparticles only increased the CO_2 conversion without any modifications on the selectivity.

For supported Ru catalysts, TiO_2 and $\gamma\text{-Al}_2\text{O}_3$ was shown to be relatively effective in optimizing CO_2 adsorption [84] and metal dispersions [103-105], which ultimately contributed to the superior activity [106]. The comparison between Ru/ TiO_2 and Ru/ $\gamma\text{-Al}_2\text{O}_3$ indicated that the effective metal-support interaction favoring the formation of active sites was more prevailing over Ru/ TiO_2 [103]. Zeolites have also been attempted as supports in Ru-based catalyst for CO_2 methanation. Compared to Ru/ SiO_2 , higher positive polarization of Ru was observed over Ru/ZSM-5, resulting in an accelerated transformation of the surface intermediates into CH_4 and ultimately higher methanation selectivity [104].

If compared to the noble metal catalysts system, Ni-based catalysts are more favorable in terms of cost efficiency. Generally, supported Ni catalysts are more effective for methanation of CO_2 than pure Ni [94, 107, 108]. Studies have been carried out to find a suitable support for Ni based catalysts to achieve the effective activation of CO_2 . A comparison between Ni catalysts with different oxide supports prepared by wet impregnation, including Ni/ MgO , Ni/ TiO_2 , Ni/ Al_2O_3 and Ni/ CeO_2 has been made by Tada et al. [98], the results of which clearly pointed out

that Ni/CeO₂ with the largest capability for CO₂ adsorption demonstrated the highest activity that close to the equilibrium data. More support candidates of oxides such as, Y₂O₃, Sm₂O₃, ZrO₂, and La₂O₃, were adopted and the activity of the resulted catalysts have been compared to Ni/CeO₂ and Ni/Al₂O₃ [109], in which Y₂O₃ was suggested as the most effective one. Mesostructured silica nanoparticles (MSN) were obtained via sol-gel method and applied as a support for Ni catalysts for CO₂ methanation [110, 111]. Compared to the Ni supported on MCM-41 (mobile crystalline material), HY (protonated Y zeolite), SiO₂ or γ -Al₂O₃, Ni/MSN showed superior activity, due to the enrichment of surface basic sites with increased surface porosity. Besides from the single oxide supports, Ni supported on mixed oxides such as Ce_xZr_{1-x}O exhibited both excellent activity and good stability for CO₂ methanation [99, 112, 113]. Recently, Al-Mg mixed metal oxides supported Ni catalysts were synthesized by Liu et al., which showed a great improvement in the low temperature performance for CO₂ methanation [114]. Moreover, zeolites, including USY [115], MCM-41 [116] and HY [110], and non-oxide supports, such as SiC [73] and metal–organic frameworks (MOFs) [72] have also been attempted as supports for Ni in CO₂ methanation.

2.1.2 Studies of the metal loadings

The primary impact of varying metal loadings on heterogeneous catalysts lies in changing the particle size. When Ru loadings were changed from 2.2% to 5.6%, the mean particles size was varied from 0.9 nm to 1.9 nm, which was associated with an increased capability for CO₂ dissociation [80]. Similarly, the particle size

increased from 3.6 nm to 15 nm when the Rh loading content increased from 1% to 5% over γ -Al₂O₃ [117], which resulted in an obvious catalytic difference. However, further characterization revealed an independence of CO₂ methanation reaction rate on the loadings at temperature from 185 °C and 200 °C, while larger particles favored higher CH₄ yields at lower temperatures. Similarly, detailed studies on Rh/TiO₂ with different loadings from 0.5% to 5% by Karelovic et al. showed that the methanation rate increased with increasing metal clusters size up to 7 nm at low temperatures [89], while further increase in the size of metal clusters to larger than 7 nm has no appreciable impact on the performance. An optimal dispersion of Ru on Al₂O₃ that was defined by the minimum apparent activation energy for CO₂ methanation was obtained by Kusmierz et al. [118]. Also a change in the activation energy for CH₄ formation has been observed with an interesting dependence on cluster size, with higher activation energy on a lower cluster size.

Besides from the above mentioning effects on particle sizes, varying metal loadings also causes a change in the structures of surface active sites. Over Ru/Al₂O₃ with relatively lower metal loadings, *ca.* 0.1%, where most surface Ru atoms were atomically dispersed, CO was preferentially produced with high selectivity for RWGS [119]. Conversely, higher Ru content resulted in the agglomeration of Ru atoms into big metal particles, which gave rise to the enhanced selectivity to CH₄. The same selectivity change was also observed over Pd/Al₂O₃ [120]. Although the turnover frequency of both CH₄ and CO were lower

over Pd/Al₂O₃ with smaller metal particles, the selectivity to CH₄ formation was obviously higher over catalysts with metal particles of larger sizes [121]. However, a contrary effect of Pd dispersion on the selectivity for CO₂ hydrogenation at atmospheric pressure has been reported, with the methane formation being more favored on highly dispersed Pd over TiO₂ [93]. Further size-function relationship was built on the quantification of surface atomically dispersed Rh atoms and Rh particles via CO adsorption DRIFTS experiments by Matrubu et al. [122]. Strong correlations were established between the amount of surface Rh atoms and the reaction rate of CO formations as well as the amount of surface Rh particles and the reaction rate of CH₄ formations. The mechanism for the selectivity of highly dispersed Rh atoms to CO formation over TiO₂ was further studied by DFT calculations [123].

Ru nanocrystals with different morphologies, including nanosphere (NS), irregular plates (IP), triangle plates (TP), and capped columns (CC) can be synthesized via a facile hydrothermal process [124]. The as-prepared nanocrystals were loaded onto commercial TiO₂ support, which were then tested for the selective methanation of CO in CO₂-containing gas mixtures. As a matter of fact, CO₂ methanation activity decided the CO methanation selectivity in this reaction. Although the catalyst of supported Ru NS showed the highest activity for sole CO conversion, the higher activity for CO₂ methanation compared to the rest catalysts resulted in prominently inferior selectivity for CO selective methanation over Ru(NS)/TiO₂.

The loadings of supported catalysts can affect the dispersion, the metal-support interaction and particle structures, which greatly shaped the catalytic behaviors of the prepared catalysts [125]. Two kinds of Ni species, active surface Ni crystallites and inactive highly dispersed Ni atoms, can be recognized over Ni/Al₂O₃ [96]. Obviously, the former was preferentially formed over higher Ni loadings, which was held responsible for the superior methanation activity. Similarly, over Ni/TiO₂, the methanation activity increased when Ni loadings increased from 5% to 10% and 15%. However, a further increase in Ni content caused almost no changes on the catalytic performance [126]. On the other hand, the selectivity of CO₂ methanation varied significantly by the metal loadings for Ni/SiO₂ [127]. High selectivity towards CO formation was observed over catalysts over catalysts of low Ni loadings of 0.5% while CH₄ formation was favored over 10% Ni/SiO₂.

2.1.3 Studies of the addition of dopants

To improve the performance of catalysts for CO₂ methanation, the introduction of an extra component as a dopant has been suggested. Adding CeO₂ into Ru/ γ -Al₂O₃ catalysts promoted the partial reduction of the system and facilitated the conversion of surface intermediates, improving the overall catalytic performance [77, 128]. Besides, the incorporation of an alkali precursor during the preparation of Ru/Al₂O₃, especially CsNO₃, can improve the dispersion of Ru on the resulted catalysts [129]. A small amount doping of W⁶⁺, as low as 1%, induced a 24 times increase in the specific activity of CO₂ methanation over Rh/TiO₂, along

with a reduction of 25-34 kJ/mol in the apparent activation energy and an ultimate improvement in the stability [130]. Improvements in the catalytic performance were also obtained by introducing promoters, such as MgO, which played the role as an effective active site for CO₂ binding over Pd/SiO₂[91, 92].

However, a contrary effect was observed after the addition of Ni in Ru/TiO₂, which resulted in an obvious decrease in the conversion rate of CO₂ methanation, if compared to the undoped Ru/TiO₂ [131]. Moreover, K addition utterly changed the hydrogenation behaviors of Rh/Al₂O₃, from highly selective methanation reaction to almost exclusive yields of CO [132, 133]. Nonetheless, an improvement in the stability was observed when Li was introduced into zeolite Y supported Rh for CO₂ hydrogenation at atmospheric pressure by Bando et al [134]. EXAFS revealed a disintegration of Rh particles in the atmosphere of CO₂ and H₂, which was suppressed by Li doping.

Furthermore, noble metals have also been applied as dopants in non-noble metal catalysts for CO₂ methanation, mainly to promote the dissociation of H₂. The improvement of Ru or Rh doping onto Ni/CeZrO_x for CO₂ methanation was ascribed to the better dispersion of Ni species that was induced by the confinement effect of the dispersed Ru or Rh atoms [112]. Nevertheless, the formation of ultra-thin bimetallic films at the surface region of Co₃O₄ nanorods was obtained by the introduction of Ru, which greatly enhanced the selectivity and activity over the resulted catalysts [135]. Conversely, while bimetallic Co-Pt nanoparticles (NPs) were almost inactive for CO₂ methanation, separated Co NPs and Pt NPs in close

proximity supported on silica showed high methanation activity [136]. Detailed investigations by *in situ* EXAFS spectroscopy revealed a long distance spillover of dissociated H from Pt NPs to Co NPs.

Several groups have reported improvements in the catalytic performance of the single-oxide supported Ni catalysts after the introduction of a dopant. An optimal doping amount of 1.5% for CeO₂ in Ni/Al₂O₃ was obtained, which was substantially attributed to a favorable interaction between the dopants and the active sites during the reaction [137]. Similarly, after a moderate addition of Co into Ni/SiO₂, a remarkable enhancement in the activity of CO₂ methanation at the temperature region of 250 °C to 350 °C can be obtained [138]. ZrO addition in Ni/Al₂O₃ played the role of an inhibitor for the formation of aluminates species, improving the dispersion of Ni [139]. Guo et al. studied the activity of alkaline-earth metal oxides, MgO, CaO, SrO and BaO, doped Ni/SiO₂ prepared via sequential impregnation for CO₂ methanation [140, 141]. Different roles of the dopant was revealed, in which SrO doping improved both the reactivity and stability, in contrast to that MgO addition generally inhibited the methanation reaction. As demonstrated by XPS, La₂O₃ addition in Ni/SiC catalysts by impregnation can alter the electron environment of Ni particles, which facilitated the activation of CO₂ and ultimately contributed to the enhanced activity for CO₂ methanation [73].

Interestingly, the catalysts of supported nanoparticles of alloys revealed a unique catalytic property. TiO₂, CeO₂ and ZrO₂ were used as the support for PtCo

catalysts [142]. While the CO₂ conversion by H₂ was comparable over all the three catalysts, PtCo/TiO₂ was active for the CO₂ methanation in comparison to that CO was selectively formed over PtCo/CeO₂ and PtCo/ZrO₂. Over the physical mixture of Rh/Al₂O₃ and Pd/Al₂O₃, where the formation of bimetallic particles on the surface was suppressed, Karelovic et al. observed greatly promoted activity for CO₂ methanation if compared to Rh/Al₂O₃ or Pd/Al₂O₃ along, which was obviously not presented over the supported bimetallic particles [90]. *In situ* DRIFTS results suggested that the CO₂ activation took place over both Rh and Pd particles, while the H₂ dissociation can only proceed on the surface of Rh particles. The facile spillover of dissociated H from Rh to Pd gave rise to the prominently improved performance.

2.1.4 Studies of the preparation methods

Studies have also been carried out to explore the effects of different preparation method on CO₂ methanation performance [143, 144]. The narrow particle size distribution of Ru over Ru/TiO₂ prepared by "dry" modification method using a barrel-sputtering instrument generated a superior catalyst for CO₂ methanation, with a reaction rate of 0.04 μmol·min⁻¹ g⁻¹ at room temperature [85]. Compared to the conventional impregnated Ru/CeO₂, Ru doped ceria oxides that was prepared via a combustion method exhibited improved activity and satisfactory selectivity for CO₂ methanation [29, 86]. A moderate amount of Ru doping by combustions not only resulted in enhanced reactivity of surface oxygen species but also promoted the reducibility of the oxide. Ru/Al₂O₃ catalysts were

prepared by three different methods and attempted for CO₂ hydrogenation, including spray reaction (SPR), traditional impregnation (IMP), and a combination method of these two [145, 146]. The kinetic results showed that the TOF of CO₂ on the catalysts prepared from SPR was one magnitude larger than the one prepared from IMP, which was assigned to the enrichment of active sites at the perimeters of the metal particles. Two types of SiO₂ supported Pd and Mg were prepared, one of Pd-Mg/SiO₂ by a reverse microemulsion and the other one of Mg/Pd/SiO₂ by impregnating Mg onto Pd/SiO₂ [91]. Significantly improved activity and strong stability for CO₂ methanation were observed over Pd-Mg/SiO₂, a possible benefit of the formation of stable Mg-Si structures. By photohole-oxidation-assisted method, ultra-fine Ru clusters of ~1.5 nm were anchored onto TiO₂ support at a density of $\sim 10^{17} \text{ m}^{-2}$, favoring the exposure of low-coordinated Ru sites [147]. As a result, high CO₂ conversion of nearly 100% was achieved at a temperature as low as 250 °C, in contrast to conversion of around 50% at the same temperature over the one prepared by impregnation. Moreover, in light of the strong metal support interaction via covalent binding, the excellent stability was further consolidated as no activity loss occurred for 240 h on stream and no sintering was observed on tested catalysts by TEM.

Ni/MgO catalysts were prepared via impregnation at different conditions and adopted for the methanation of CO₂ [97]. The precursors of Ni, the solvent for impregnation and the calcination temperature can significantly affect the dispersion of Ni on the calcined catalysts, which ultimately determined the activity

and the selectivity for CO₂ methanation. Ni-Mg nanoparticles that were encapsulated by porous silica shell structures were synthesized by Li and co-workers [148]. Isolated dispersed Ni particles were formed by the reduction of Ni-Mg solid solution that enclosed by silica shells, which demonstrated excellent catalytic performance of *ca.* 87% CH₄ yields at 300 °C. Furthermore, Ni_{1-x}/Ce_xZr_{1-x}O prepared via three different methods, impregnation (IMP), deposition–precipitation (DP) and urea combustion (UC) methods, were attempted for CO₂ methanation [99]. Among all the catalysts, impregnated catalysts showed not only higher Ni metal surface area, but also more oxygen vacancies and basic sites. Modifications on the traditional impregnations, i.e., impregnation-precipitation, co-precipitation and impregnation method were tried for preparing the ZrO-Al₂O₃ support for Ni catalysts [139]. Results revealed that the one prepared from impregnation-precipitation was more effective for CO₂ methanation. On the other hand, the catalyst prepared from the co-impregnation of Ni and Mg onto SiO₂ demonstrated better performance for CO₂ methanation than that prepared by the sequential impregnation [141]. Similar studies have been carried out on Al₂O₃ supported Ru and Ni nanoparticles [149]. With the improvement of surface segregations of Ru clusters by co-impregnation, highly dispersed metallic particles were obtained via a facile reduction process, which increased the amount of surface active sites for methanation.

Other preparation methods were also tried for Ni-based catalysts. Ni/TiO₂ prepared via first an optimized deposition-precipitation method followed by a

calcination-reduction process revealed a much improved low temperature activity for CO₂ methanation if compared to the one obtained via the traditional impregnation [126], which was resulted from the enhanced dispersion of Ni. By mixing the metal precursors with citric acid, a highly active Ni/MgO catalyst was prepared with enlarged metal surface area, benefits of the formation of solid solution of Ni-Mg [150]. Using carboxylic acid instead of citric acid, a mesoporous structure of Ni/MgO can be further obtained [151].

The advances in the nanotechnology bring in novel approaches to optimize the catalytic performance in heterogeneous catalysis. A catalyst consist of surface defected Ni nanocrystals embedded in the hierarchical Al₂O₃ matrix was obtained by a facile reduction process of NiAl-LDH precursors [152]. The successful doping of Ni into the Al₂O₃ matrix and the presence of abundant surface vacancy were confirmed by HRTEM, HAADF-STEM and EXAFS, both of which contributed to the largely enhanced low temperature activity and the stability of the resulted catalysts, if compared to the one prepared by traditional methods.

Furthermore, the catalysts used in methanation reaction often undergo an activation process in reduction atmosphere [107, 153, 154]. A catalyst with the metal surface that too oxidized or too reduced deteriorated the catalytic activity in CO₂ methanation [86]. The pretreatment conditions of the resulted catalysts have a significant impact on the catalytic performance [155, 156]. The room temperature methanation of CO₂ was achieved by the fine control of the surface composition of metallic Ru and RuO_x supported on TiO₂ by reduction at 220 °C in a H₂/Ar flow

for 1h [32]. As a comparison, the activity of the totally reduced catalysts at 500 °C as well as the unreduced RuO₂/TiO₂ was much inferior. The reduction temperature and duration of pretreatment over Ni²⁺ incorporated MCM-41 was varied to study the impact of the pretreatment condition on the catalytic performance by Du et al. [116]. The catalysts that pretreated in H₂ for 0.5h at 700 °C exhibited the best activity, because of that a catalyst of fully reduced Ni species in high dispersion could be obtained at this condition. Besides, by the photo-assisted excitation of catalysts, the reaction rate of CH₄ formation sharply increased.

2.2 The reaction mechanisms

Although enormous efforts have been devoted to understand the reaction mechanism for CH₄ formation from CO₂ hydrogenation, some disputes remain, such as whether it involves CO as key intermediates.

2.2.1 Studies of reaction mechanisms on noble metal based catalysts

The interaction between CO₂ and Ru/TiO₂ resulted in the formation of three different types of adsorbed CO, depending on the oxidation state of Ru at the time of the exposure [157]. Importantly, the adsorption mode of CO by CO₂ dissociation decided their reactivity towards dissociated or gaseous H₂. Long exposure to CO₂ and CO₂ + H₂ caused an oxidation of Ru particles, which changed the configuration of the adsorbed CO. It is worth of mentioning that the co-adsorption of dissociated H or O atoms with CO on the same Ru sites largely enhanced the reactivity of CO species. By DRIFTS transient experiments, the

formation of CH_4 was observed accompanied by a direct decrease of the linear adsorbed CO, which was obvious different from the CO methanation mechanism that involved the formation of methylene groups as key intermediates.

DRIFTS studies on the low temperature methanation of CO_2 over Ru/TiO_2 and $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ were carried out by Prairie et al., who unveiled that CO_2 methanation involved CO species that formed by a rapid reversed water gas shift via HCOOH as a key intermediate [103]. However, CH_4 production was almost independent on the coverage of adsorbed CO, suggesting that the formation of CO from CO_2 was not the rate-determining step, in accordance with the insensitivity of methanation reaction rate to the CO_2 concentration in the feeding gas. On the other hand, the reaction exhibited a *ca.* one half-order dependence on the concentration of H_2 , indicating a necessity of the dissociated H in the conversion of CO, which served as the rate-determining step.

CO_2 hydrogenation over Rh/TiO_2 resulted in the formation of linear adsorbed CO, bridged CO, active carbon species (including CH_x), and inactive carbon species on Rh particles, along with formate and carbonates species on the support [130, 158]. Although introduction of W doping deteriorated the formation of active carbon and facilitated the formation of inactive carbon, the supply of dissociated H atoms has been promoted, causing a net result of an overall improvement in the catalytic performance on Rh/TiO_2 . Also, it was worth mentioning that the Rh-CO bonds have been weakened after W doping, a probable consequence of the modification on the electron state of Rh particles. The weakened Rh-CO bonding

favored the co-adsorption of H₂, leaving more possible active sites for H₂ activation and H atoms assisted CO dissociation.

CO₂ methanation was performed over Rh/Al₂O₃ at low temperatures between 50 °C and 150 °C [87, 117]. *In situ* DRIFTS confirmed the formations of gem-dicarbonyl species and linear CO species on Rh particles as a result of the dissociative adsorption of CO₂, which was affected by the oxidation states of the Rh particles. Interestingly, the dissociative adsorption of CO₂ caused an oxidation of the Rh particles, which then altered the adsorption configuration of CO. Transient experiment suggested that gem-dicarbonyl species was more reactive towards the formation of CH₄. Besides, a lower activation energy for CO₂ methanation than that for CO methanation was observed, which suggested that CO was more likely a byproduct other than an intermediate in CO₂ methanation.

Several studies have shown that the reaction rate of CO₂ hydrogenation was higher than that of CO hydrogenation at almost identical reaction conditions. To study the difference, *in situ* DRIFTS studies were carried out [159], which revealed that the coverage of adsorbed CO species played a key role in the catalytic reaction. Although adsorbed CO was important intermediates for CH₄ formation, a maximum value in the CH₄ formation rate can be obtained when the CO coverage varied from 0 to saturation. Thus, the results of the kinetic measurements can be interpreted as the suppression of CH₄ formation by overly covered Rh sites by CO adsorption, which hindered the dissociation of H₂. Obviously, the CO coverage derived from the adsorption of CO in CO and H₂ was

much higher than that from the dissociative adsorption of CO_2 in CO_2 and H_2 . A similar retardation on CO_2 methanation by weakly adsorbed CO due to the suppression of the conversion of surface carbon species, which was a key intermediate in both CO methanation and CO_2 methanation, was observed by Fujita et al. [160]. Besides, EXAFS characterization of zeolite Y supported Rh in the feeding gas of CO_2 methanation revealed a CO-assisted dissociation of Rh atoms from the particles [134], which probably prevented the Rh particles from being fully covered by CO and subsequently left adequate sites for the dissociation of H_2 . As a result, the methanation of CO_2 continued without significant formation of gaseous CO. Another effective way to avoid the blockage of H_2 activation sites was to provide other surface sites that were not involved in the adsorption of CO_2 . By mechanical mixing the active carbon supported Ni (Ni/AC) with Rh/ Al_2O_3 , the *in situ* supply of dissociated H species to Rh/ Al_2O_3 was achieved by H_2 activation on Ni/AC, which led to higher methanation activity than the theoretical prediction [88].

The mechanistic studies on Pd/ Al_2O_3 and Ru/ Al_2O_3 were carried out by Wang and co-workers, via the combination of kinetic measurements and DRIFTS coupled mass spectrometry (MS) experiments [78, 121]. The tremendously different activation energy for the formation of CO and CH_4 at different metal loadings indicated that these two reactions did not share the same rate-determining steps, and/or not activate over the same surface structures. Moreover, similar reaction orders of CH_4 formation and CO formation on H_2 and CO_2 pressures over

Pd/Al₂O₃ of different loadings suggested that the reaction pathway was not affected by the size of metal particles. As a comparison, an appreciable difference was observed for the CH₄ formation orders under varied H₂ and CO₂ pressures over 0.5% Ru/Al₂O₃ and 5% Ru/Al₂O₃, especially the CO₂ pressure, revealing a possibility of differences in the activation mechanisms for the reactants over Ru particles of different sizes. The direct dissociation of CO₂ into adsorbed CO and adsorbed O without the presence H₂ was negligible over both catalysts. A possible reaction mechanism was proposed based on the results of DRIFTS-MS, with CO₂ being firstly activated by surface hydroxyls on the support to form bicarbonates. The following step involved the conversion of bicarbonates species by migrated H species to form formates, which were further hydrogenated by adsorbed H to yield CO. The reactivity of the formed CO varied significantly by the adsorbing sites. Low coordination metal sites resulted in the formation of inert geminal dicarbonyls. Specifically, over Pd/Al₂O₃, the stability of CO differed, which was held responsible for the activity difference. At a low metal loading, the surface Pd sites with inferior ability to retain CO prevailed, resulting in high selectivity to CO.

In CO₂ methanation atmosphere, distinct peaks in the DRIFTS spectra that assigned to adsorbed CO, carbonates and formate species were clearly distinguishable over Ru/Al₂O₃ and CeO₂ doped Ru/Al₂O₃ [77]. The reactivity of these surface species towards H₂ were studied by switching the feeding gas from the CO₂ methanation feeding gas to H₂/Ar, which clearly suggested that formate species acted as the key intermediates for CO₂ methanation. Noticeably, the

consumption of formate was faster over CeO_2 doped catalysts. This improvement in the reactivity of surface formate led to much-improved CO_2 methanation activity over $\text{Ru/CeO}_2/\text{Al}_2\text{O}_3$.

Traa et al. carried out kinetic measurements of CO_2 methanation over Ru/TiO_2 , the results of which showed no evidence to support that the CO_2 methanation pathway involves species as intermediates [106]. Thus, a Hougen-Watson-type rate expression was applied to explain the kinetic data under the assumption that the conversion of surface carbon species into CH_4 was the sole rate-determining step. Moreover, an accumulation of formate species on $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ during the exposure to CO_2 and H_2 was observed, which indicated that formate species was either a spectator or an insignificant precursor [84]. The most active reaction pathway for CH_4 formation was the dissociation of CO_2 into CO , which was further hydrogenated into surface carbon species and then CH_4 . Marwood et al. found the presence of two types of formate species over Ru/TiO_2 , one adsorbed at the metal support interface and the other one adsorbed on the support, along with adsorbed CO in a gas mixture of CO_2 and H_2 [161]. Although these two types of formate species were readily transformed from one to another at the surface of the catalysts, it was suggested that only the one at the interface could react with dissociated H supplied from the metal particles to produce CO and finally participate in the formation of CH_4 . Similarly, a formate species was observed when exposing $\text{Ru/Al}_2\text{O}_3$ catalysts to H_2 and CO_2 at a temperature higher than 100°C , besides from the prominent formation of adsorbed CO [84]. The

evolution of the spectra suggested that formate was firstly formed at Ru sites and then migrated to the support.

Recently, Wang and co-workers proposed an active site depended activation mechanism via CO or formate over Ru/CeO₂ [31]. The surface properties of Ru/CeO₂ were studied by operando XANES, IR, and Raman to reveal the presence and evolution of oxygen vacancy. The steady-state isotope transient kinetic analysis (SSITKA)-type *in situ* DRIFT spectroscopy suggested that CH₄ formation via formate required the participation of hydroxyl groups, Ce(III) species and oxygen vacancy over Ru/CeO₂. The adsorbed CO₂ was firstly hydrogenated into formates, which was then dissociated into methanol. The next step, which was also the rate-determining step, was the hydrogenation of methanol to CH₄. A Ru/ α -Al₂O₃ without the surface oxygen vacancy was used as a reference, over which only the CO reaction pathway was activated over the surface of the metal particles. It should be mentioned that the observed activation temperature for the formate route was much lower than that for the CO route.

DFT calculations were applied to understand the reaction mechanisms of CO₂ methanation over noble-metal based catalysts. Akamaru and co-worker carried out the DFT calculation of CO₂ methanation over Ru slabs and model Ru/TiO₂ catalysts [162]. The adsorption energy of CO₂ was much higher over Ru/TiO₂ if compared to that over the Ru particles. For the methanation of CO₂ on Ru clusters over Ru/TiO₂, CO₂ adsorption at two possible sites, the top sites and the side sites, proceeded via two different reaction routes to form CO and ultimately contributed

to the formation of CH_4 . Thus, these two types of surface sites were both the active sites for CO_2 methanation over Ru/TiO_2 .

Moreover, the CO_2 hydrogenation mechanism over Ru (0001) was investigated via DFT calculations by Avanesian and co-workers [163]. Results showed that CH_4 was formed by CO_2 dissociation into adsorbed CO and adsorbed O , which was hydrogenated into CHO^* and H_2O . The following step involved the dissociation of CHO^* into CH^* and O^* , which was the rate determining step for CO_2 methanation. Over supported PtCo catalysts [142], DFT calculations were carried out to verify the reaction pathway for CO_2 methanation that was postulated from the AP-XPS and FTIR results. Two reaction pathways were proposed associated with $\text{HCOO}^*/\text{HOCO}^*$ and CH_3O^* (Figure 1.1), respectively. Over PtCo/TiO_2 , CO was favored through the $\text{HCOO}^*/\text{HOCO}^*$ reaction pathway as reversed water gas shift. In comparison, applying ZrO_2 as the support provided increasing active sites for the CH_3O^* reaction pathway while the $\text{HCOO}^*/\text{HOCO}^*$ reaction pathway was still active.

Figure 1.1 Potential energy diagrams for the synthesis of CO and CH₄ through the RWGS and CO hydrogenation pathway involving HCOO*/HOCO* (a) and CH₃O* (b). [68]

2.2.2 Studies of reaction mechanisms on Ni-based catalysts

Fujita et al. carried out *in situ* DRIFTS of both CO methanation and CO₂ methanation over Ni/Al₂O₃ and they observed several different adsorbed CO

species [164]. In gas mixture of CO₂ and H₂, two types of bridged adsorbed CO species with different adsorption strength were observed along with formate species and linear CO. Interestingly, the amount of linear CO species, which covered the reaction sites and suppressed the production of CH₄ during CO methanation, was negligible during CO₂ methanation, which was held responsible for the observed difference in the methanation activity.

Over Ni/SiO₂, Falconer et al. found that the CO₂ adsorption volume was increasing with the elevated temperature from room temperature to 200 °C while higher temperature caused an obvious decrease in the CO₂ adsorption capacity [95]. Importantly, CO₂ desorption at elevated temperature resulted in the formation of adsorbed CO and adsorbed O, suggesting the CO₂ was dissociative adsorbed on Ni/SiO₂. Kinetic measurements over Ni/SiO₂ revealed a moderate dependence of CH₄ formation on the concentration of H₂ and CO₂ only at low partial pressure [165]. Moreover, the activation energy obtained was temperature sensitive, in agreement with that a complex Langmuir-Hinshelwood mechanism was needed for describing the reaction pathway for CO₂ methanation, which probably involved the dissociative adsorption of CO₂ into CO. Similarly, the temperature-programmed reaction of adsorbed CO and of CO₂ uncovered a comparable reaction mechanism for CO methanation and CO₂ methanation [96].

As demonstrated by the results of DRIFTS experiments on NiUSY [115], CO₂ exhibited almost zero interactions with the catalysts without H₂, due to the abundant acidity on the zeolite support. With the help of H₂, formates and

carbonyls were formed by CO₂ adsorption. Both species were active towards the formation of CH₄ but activated at different reaction temperatures. At medium temperature, only the CO reaction pathway was activated and a CO-saturated metal surface induced a poison-like effect. Formate species was converted to CH₄ only at temperature higher than 350 °C, while CO species was consumed at a higher rate and more active sites were available for the conversion of formates.

Two different reaction pathways were also proposed over Ni/SiO₂ [127], with one involving the dissociation of formate intermediates into CO and the subsequent conversion of CO into CH₄ or the desorption into gaseous CO, named as the consecutively pathway. The other one, the parallel reaction pathway, was considered as competitive conversion of formates via the dissociation into CO or the hydrogenation into CH₄. Over 0.5% Ni/SiO₂, the consecutive reaction pathway was prevailing due to the scarcity of active sites for H₂ dissociation. To the contrary, the high concentration of dissociated surface H species over 10% Ni/SiO₂ enabled the direct hydrogenation of formates into CH₄.

Over Ni/Ce_{0.5}Zr_{0.5}O₂, three different carbonate species were observed, monodentate carbonates, bidentate carbonates and hydrogen carbonates species, which were correspondingly correlated to the adsorption sites of CO₂ [113]. While bidentate carbonates were too unstable to participate in the methanation reaction, monodentate carbonates and hydrogen carbonates were converted into formate specie, which served as key intermediates in CH₄ formation. However, the reactivity of monodentate carbonates was directly decided by the adsorbing sites.

Further studies revealed that two different kinds of formates can be obtained, monodentate formate from the hydrogenation of monodentate carbonates adsorbed on medium basic sites and bidentate formate from hydrogen carbonates [166]. Transient experiments suggested that monodentate formate was more reactive towards hydrogen to form CH₄.

Apart from experimental characterization, theoretical computations were also applied to examine the reaction mechanism over Ni-based catalysts for CO₂ methanation. DFT calculations of CO₂ activation over γ -Al₂O₃ supported Ni clusters of two different sizes, consist of 13 atoms and 55 atoms respectively, were carried out by Silaghi et al. [167]. The CO₂ adsorption strength and reactivity was much higher over smaller clusters, Ni₁₃, than that over the bigger clusters, Ni₅₅, due to the presence of higher ratio of edges sites, which were the most active sites on the particles. Admittedly, compared to the bare Ni, Al₂O₃ supported Ni nanoparticles exhibited a much higher binding energy for CO₂, regardless of the metal particle size, which was attributed to the extra electron transfer from the support to adsorbed CO₂. The interface between metal particles and the support demonstrated unique properties for CO₂ activation in the aspect of stabilizing dissociated O by the Al sites from the support. Each Ni cluster was selectively loaded onto two different facets of γ -Al₂O₃, (100) facet and (110) facet, to allow for a comprehensive comparison. Two reaction pathways were clearly identified on each system, which took place at the particle and particle-support interface, respectively. The most reactive one was the direct CO₂ cleavage at the interface

between Ni₅₅ and γ -Al₂O₃(110). Moreover, by carrying out DFT calculations on both Ni₄ supported on dry γ -Al₂O₃ (110) and hydroxylated γ -Al₂O₃ (110), the alteration of reaction pathways of CO₂ hydrogenation by the hydroxyl groups on the support has been revealed [168], particularly the formation of two key intermediates, formate and CO. On the dehydroxylated surface, the reaction energy for formate formations was obviously higher than that for CO formation while the activation barrier was lower, which suggested that formate formation was kinetically favored while CO formation was preferred thermodynamically. A contrary results was identified for the hydroxylated surface. A similar calculation was carried out on Pd/Al₂O₃ [169], which revealed that CO formation was both kinetically and thermodynamically favored over dehydroxylated surface while formate formation was more preferred kinetically over hydroxylated surface.

Ni(110) was chosen as a model surface for the study of Ni-based catalysts for CO₂ methanation. By the application of the atomic hydrogen beam in ultra-high vacuum experiments including temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and high-resolution electron energy loss spectroscopy (HREELS), a hydrogen assisted dissociation of CO₂ into CO was observed over Ni(110) by Eley-Rideal (ER) reaction pathway at low temperature via a carboxyl intermediate, other from the conversion of formates [170]. Further DFT calculation revealed that the formate species was not an active intermediate in any possible reaction path. Combined the experimental data with theoretical calculations, the adsorption configuration of CO₂ on Ni(110) was identified as a 'V'

type with C atoms directly bonding to the surface, accompanied by negative charges that were transferred from Ni atoms [170]. However, at the approach of an H atom to the C, the two O atoms in the adsorbed CO_2 became sensitive to coordination with Ni sites. As a consequence, CO_2 flipped over with two O atoms bond to the surface as a 'Y', thus formate species was formed. Another experimental investigation of the reduction of CO and CO_2 by H_2 on the Ni(110) single crystal surface has been carried out by Roiaz and co-workers [30]. Near ambient pressure XPS (NAP-XPS) spectra showed that adsorbed O formed from the CO_2 dissociative adsorption facilitated the formation of stable carbonates when interacted with an extra CO_2 . Besides, activated CO_2^- species was detected, which can undergo a dissociation process into CO and O or act as a reactive species towards hydrogenation into CH_4 . The proposed mechanism based on the obtained experimental data was presented in Figure 1.2.

Figure 1.2 Qualitative scheme of the reaction network involving RWGS, CO methanation, and CO_2 methanation processes. [97]

2.3 The effect of the presence of impurities

An inhibition effect of H₂O content on the methanation of CO₂ has been observed, which was attributed to the consumption of the active formate species adsorbed at the interface by H₂O to form hydrogen carbonates. Moreover, a H₂O-induced disintegration of Ru particles in methanation reaction gas mixtures was reported by Abdel-Mageed and co-workers [81, 171, 172], which they attributed to the accelerated formation of Ru–dicarbonyl species that favored the rupture of Ru-Ru bonds. With the decrease in the mean Ru particles size, the CO₂ methanation was suppressed and the selective methanation of CO was increased.

The formation of Ni(CO)₄ species at low temperature in CO-rich feeding gases was reported, which facilitated the aggregation of Ni particles, leading to the deactivation for Ni based catalysts [173]. A mechanism of CO-hindered CO₂ methanation has also been proposed over Rh/SiO₂, the exposure of which to CO and CO₂ resulted in very similar DRIFTS spectra, with primary features of linear CO and bridge CO [159]. The CO covered surface limited the access of the reactant to the active sites.

Besides, the effect of oxygen content on the catalytic performance was discussed [87]. With a small amount of O₂ addition in the feedings, an improvement in the activity was observed, however the presence of a high concentration of O₂ resulted in an obvious decrease in the CO₂ conversion.

The chloride remaining was observed over noble metal catalysts, especially Ru and Rh, which was proposed to impact significantly on the catalytic

performance [174, 175]. During the selective CO methanation for the removal of CO from fuel processors, the chloride content in Ru/Al₂O₃ catalysts promoted the activity for CO methanation, while kept the CO₂ methanation activity at an acceptably low level. The same effect has been observed regardless of the origin of chloride in the system, from the metal precursors or intentional addition after the preparation.

Chapter 3 Techniques of Characterization, Synthesis, and Catalytic Reactions

Owing to the advances in the material science, especially the nanotechnology, aspirations in designing an appropriate catalyst for a specific catalytic reaction have been rising. However, the design of a high efficient catalyst system for heterogeneous catalysis relies on the establishment of structure-performance relations. To study the structure of the catalysts in an atomic or molecular level, sophisticated characterization on the prepared catalysts is needed. Besides, a better understanding of the reaction mechanisms can be obtained with the help of *in situ* characterization, which plays a significant role in the fine control of the catalytic reactions. Thus, in this chapter, a variety of characterization methodologies will be briefly introduced, along with the preparation process for the catalysts used in this thesis.

3.1 Techniques of Characterization

3.1.1 Characterization of structures

X-ray diffraction refers to a technique used to discriminate the crystalline structures by analyzing angles and intensities of X-ray beams diffracted by the crystallized atoms [176]. Besides, the obtained diffraction pattern provides insight into atomic structures, such as the mean position of the atoms in the crystals, the chemical bonds and so on. In this thesis, powder XRD patterns were recorded on a Bruker Advance 8 X-ray diffractometer using a Ni filtered Cu K α

radiation ($\lambda = 0.154$ nm), operated at 40 kV and 40 mA. XRD data were collected between 10 and 90 $^{\circ}(2\theta)$ with a resolution of 0.02 $^{\circ}(2\theta)$.

The surface area of a solid catalyst plays a decisive role in the actual contact opportunity between the reactants and the active sites. Usually, a high surface area can improve the dispersion of the supported metals and contribute to superior catalytic performance [72]. Brunauer–Emmett–Teller (BET) theory is often used for the analysis of the specific surface area, based on the physical adsorption pattern of probe gas molecules, N₂ in most cases [177]. In this thesis, the N₂ adsorption-desorption isotherms were measured using a Quantachrome Autosorb-1C instrument at liquid N₂ temperature (-196 $^{\circ}\text{C}$). Prior to the N₂ physisorption, all the catalysts were outgassed at 300 $^{\circ}\text{C}$ for 5 h in vacuum. The specific surface areas were calculated by BET equation at P/P_0 in the partial pressure range of 0.05 - 0.35.

The interaction between an electron beam and ultra-thin samples allows for a visualization of the morphology of catalysts in atomic scale after the processing of the electronic signals. By transmission electron microscopy (TEM), the morphology, structures and sizes of the specimen are obtained as a straightforward image. With the help of high-voltage electron beam, the differentiation of atom arrangements and atomic-scale defects can be achieved by high-resolution transmission electron microscopy (HRTEM). Moreover, coupling HRTEM with energy-dispersive X-ray spectroscopy (EDX) enables the elemental analysis of the

targeted area of the testing sample. In this thesis, TEM images were obtained on a JEOL JEM-2100F, which was operated at 200 kV. HRTEM-EDX was performed on JEOL 2010 of Ultra High Resolution (UHR) pole piece equipped with EDAX EDX Detector which was operated at 200 kV. Prior to characterization, samples were dispersed in ethanol by ultrasonic vibration, which was then dropped and dried on carbon-coated copper grids.

3.1.2 Characterization of active sites

Inductively Coupled Plasma (ICP) technique is used to determine the element content in a solution. In this thesis, this was performed after the digestion of the solid by an acid solution. The concentration of elements in the obtained solution was then analyzed by Dualview Optima 5300 DV ICP-OES (Optical Emission Spectrometry) system.

The chemisorption of probe molecular on metal particles gives a quantitative correlation between the adsorption volume and the amount of exposed surface metal sites, which is directly corresponded to the active sites on supported catalysts. Moreover, the amount of exposed metal atoms can be further used to determine the metallic surface area, metal dispersions and even the particle size by assuming a hemisphere shape for metal particles. The most commonly used probe molecular are CO and H₂ [178]. In this thesis, the H₂ chemisorption was carried out on a Quantachrome Automated chemisorption analyzer. Approximately 200 mg of catalyst was reduced in H₂ stream at 500 °C for 60 min, followed by Ar purge at 500

°C for 60 min. Then, the catalysts were cooled down to 30 °C for the H₂ chemisorption measurements. A stoichiometry correlation of 2:1 was assumed between H₂ and surface metal atoms.

However, the fast spillover of H on noble metal particles results in an overestimation for the metal dispersions during normal H₂ chemisorption. The stepwise H₂ titration of the O pre-covered metal surface at a proper temperature offers more accurate information on the exposed metal surface for most metals, such as Ru [179]. Thus, H₂-O₂ titration is carried out in this thesis, on a Micromeritics Autochem II 2920 instrument equipped with a TCD detector to estimate the amount of surface metal sites. Typically, 100 mg of catalysts were loaded into a U-tube reactor for analysis. All samples were pretreated in H₂ flow for 60 min at 500 °C and then purged with Ar for 30 min before cooling to 30 °C in the same atmosphere. A gas flow of 10% O₂/Ar was passed over the samples for 30 min to allow for the formation of O fully covered metal surfaces. After switching the feeding gas to pure Ar, samples were heated up to 250 °C and held there. After the signal is stable, pulses of 10% H₂/Ar were dosed at 5 min intervals until all the surface oxygen were consumed. The exposed Ru surface sites was calculated with the assumed stoichiometry of H₂/Ru = 5/2.

Moreover, the configuration of the adsorbent on a catalyst reflects the surface structure of the adsorbing sites, which can be differentiated by infrared spectroscopy. Thus, the adsorption of carbon monoxide (CO) accompanied by infrared reflection

absorption spectroscopy (IRAS) at 25 °C were performed in this thesis, on an FTIR spectrometer (Nicolet is-50) equipped with a smart collector and an MCT/A detector cooled by liquid nitrogen. Prior to each experiment, the sample was also pretreated at 500 °C for 60 min in 10% H₂/He and then cooled down in He flow to 25 °C. The background spectra were collected after 60 min in He purge, followed by the introduction of 10% CO/He to start the chemisorption. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹.

Temperature-programmed desorption (TPD) refers to a technique that observes the interaction between the probe molecular and the specimen. The TPD profiles of an acid/basic probe are characterization of the surface basicity/acidity on the samples, which play crucial roles in heterogeneous catalysis. In this thesis, CO₂-TPD experiments were performed using a Micromeritics Autochem II 2920 instrument equipped with a TCD detector. Prior to TPD experiments, samples of 100 mg were pretreated at 500 °C in H₂ for 60 min and cooled down to room temperature. Then the sample was exposed to 20% CO₂/Ar for 60 min, followed by Ar purge for another 60 min. The temperature was raised to 500 °C at a ramp of 10 °C /min and the the signals of CO₂ ($m/z = 44$) were recorded by a quadrupole mass spectrometer (MKS Cirrus).

Temperature-programmed reduction (TPR) is often used to study the reducibility of supported catalysts. H₂-TPR measurements for the catalyst samples were conducted on Micromeritics Autochem II 2920 instrument equipped with a

TCD detector in this thesis. After being pretreated under an air flow in a quartz U-tube reactor at 500 °C for 60 min, the samples were cooled down to room temperature in Ar flow. Then 10% H₂/Ar was introduced to pass through the catalyst bed until a stable TCD signal was observed. Subsequently, a temperature ramping program from room temperature to 1000 °C at rate of 10 °C /min was performed, and the H₂ consumption was monitored by TCD after the removal of H₂O.

Coke depositions were determined on a PerkinElmer Diamond TG/DTA equipment. The spent catalysts was heated under N₂ stream up to 800 °C with a ramp of 10 °C/min. The coke formation was quantified by the weight loss of aged sample during the stability test after the deduction of reference data offered by fresh catalysts.

X-ray absorption spectroscopy (XAS), including both extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) provides information of the coordination environment of local atoms and the average oxidation state, which are difficult to assess by other techniques [180]. The EXAFS of Ru–K edges in this thesis were measured in florescence mode and transmission mode, respectively, at room temperature on the BL14W1 beam line, Shanghai Synchrotron Radiation Facility (SSRF). The storage ring was operated at 3.5 GeV with 200 mA as an average storage current. The synchrotron radiation was monochromatized with a Si (3 1 1) double crystal monochromator.

3.1.3 Techniques for the study of reaction mechanisms

In situ techniques offers a chance for the study of reaction mechanisms at a 'real' reaction condition. With the fast developments in vacuum technology, many characterization can now be carried out *in situ*, such as Raman spectroscopy [181], X-ray photoelectron spectra (XPS) [182] and so on. *In situ* diffuse reflectance infrared Fourier Transform spectroscopy (DRIFTS) is one of the most powerful techniques to study the reaction mechanisms, especially from the perspective of the surface intermediates. In this thesis, *in situ* DRIFTS experiments were performed on an FTIR spectrometer (Nicolet is-50) equipped with a smart collector and an MCT/A detector cooled by liquid nitrogen. The temperature was controlled precisely by an Omega programmable temperature controller. Prior to each experiment, the sample was pretreated at 500 °C for 60 min in H₂ and then cooled down to the desired temperature. The background spectra were collected in flowing Ar and automatically subtracted from the sample spectrum. The gas mixture was controlled by mass flow controllers. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹.

Isotope-exchange mass spectrometry (MS) experiments provide a traceable evidence for the evolvement of reactants, an essential part of reaction mechanisms. For the MS experiments in this thesis, 100 mg of as-calcined catalysts was loaded into a fixed bed quartz reactor and followed by reduction at 500 °C for 60 min under 10% H₂ /He (flow rate =50 mL/min). Pure He or different mixtures (1%

$C^{18}O_2$ (95% ^{18}O , Linde North America Inc.) or $C^{16}O_2$, and/or 4% H_2 diluted in He) were switched and introduced into the reactor. The gases at the outlet of the reactor were analyzed by a mass spectrometer (GAM 300, InProcess Instruments) by following the evolution of the $m/z = 48$ ($C^{18}O_2$), 15 (CH_4), 20 ($H_2^{18}O$), 18 & 17 ($H_2^{16}O$), 30 ($C^{18}O$), 28 ($C^{16}O$) with the response time of the mass spectrometer following a change in gas concentration being less than 2 s.

In heterogeneous catalysis, theoretical calculations broaden the exploration horizons for mechanistic studies, among which density functional theory (DFT) calculation is one of the most popular after the refining of the approximations in 1990s [183]. DFT calculations were carried out to investigate the catalytic reaction mechanism of CO_2 hydrogenation on Al_2O_3 supported Ru clusters in this thesis. The Al_2O_3 supported Ru35 cluster and single layer Ru9 cluster were constructed by binding the Ru35 and single layer Ru9 cluster onto a γ - Al_2O_3 (100) surface. The unit cell of the amorphous Al_2O_3 surface for periodic DFT calculation has a dimension of $10 \times 13 \times 18 \text{ \AA}$, with a vacuum space of $15 \text{ \AA}$. All the calculations were carried out using the GGA functional with a projector-augmented wave basis set implemented in the Vienna Ab initio Simulation Package [184-186]. The energy cutoff of 350 eV was used. In the Al_2O_3 supported systems, atoms in the top two layers of the Al_2O_3 slab and adsorbed species were allowed to relax while the bottom layers of the Al_2O_3 slab were kept frozen.

3.2 Synthesis methodologies

3.2.1 Materials

yttrium(III) nitrate hexahydrate $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich, >99.9%), ammonium paratungstate $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$ (Alfa Aesar, >99.9%), ammonium molybdate tetrahydrate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich, >99.9%), iron(III) nitrate nonahydrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, >99.9%), cobalt(II) nitrate hexahydrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, >99.9%), manganese(II) nitrate tetrahydrate $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Aldrich, >99.9%), copper(II) nitrate trihydrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sigma-Aldrich, >99.0%), nickel(II) nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, >98.5%), magnesium nitrate hexahydrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, >99.9%), oxalic acid $\text{HO}_2\text{CCO}_2\text{H}$ (Sigma-Aldrich, >99.0%), Urea NH_2CONH_2 (Sigma-Aldrich, $\geq 99.5\%$), Ruthenium (III) Acetylacetonate (Sigma-Aldrich, >97%), aluminum oxide Al_2O_3 (Sigma-Aldrich, $\geq 99.9\%$), chloric acid HCl (Sigma-Aldrich, 36-38 wt.%), ethanol (Sigma-Aldrich, >99.8%)

3.2.2 Preparation of Ni supported on Y_2O_3

Two support precursor were adopted for the preparation of Ni supported on Y_2O_3 . The first one was obtained by the hydrothermal treatment of $\text{Y}(\text{NO}_3)_3$ solutions with the addition of urea at 100 °C for 12 h. The precipitate after filtration was then calcined in air for 4 h at 500 °C and used as the second one.

Traditional impregnation method was adopted, during which the support was immersed into a solution containing desired amounts of $\text{Ni}(\text{NO}_3)_2$ under a constant stirring for 0.5 h. Then the excess water was removed in a rotary evaporator at 80 °C. The dried product was calcined in air at 500 °C for 4 h. The final products were denoted according to the precursors of the supports as $\text{Ni}/\text{Y}_2\text{O}_3$, the precipitates, and $\text{Ni}-\text{Y}_2\text{O}_3$, the calcined products, respectively.

3.2.3 Preparation of Ni-Mg mixed oxides catalysts

The homogenous precipitation preparation is a method commonly used for preparing mixed oxides catalysts, which is excellent in improving the mixing conditions and the interactions between components [187]. The Ni-Mg and doped Ni-Mg catalysts used in chapter 5 were obtained via homogenous precipitation preparation. During a typical procedure, desired amounts of $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was firstly dissolved in water ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was applied for dissolving $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), followed by mixing with an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Subsequently, excessive urea aqueous solution was added into the mixed solution. The solution was heated to 90 °C and held for 12 h under constant stirring. After filtering and washing with deionized water, the resulting precipitant was dried at 100 °C overnight and calcined at 500 °C for 4 h in air. For comparison, Ni_aMgO_x ($a=0.5, 0.8, 1.0, 1.2$) catalyst was also prepared following the same procedure.

3.2.4 Preparation of Ru supported on γ -Al₂O₃

Ru/Al₂O₃ catalysts with metal loadings of 1, 2 and 3 wt.% were prepared on a commercial γ -Al₂O₃ powder by the incipient wetness method. Typically, the required amount of solid ruthenium (III) acetylacetonate was dissolved in a volume of ethanol, based on the pore volume of the support. The obtained solution was then added dropwise onto the support under intensive mixing. The resulting solid was dried for 12 h at 80 °C and the catalysts were then obtained via calcination at 500 for 2 h under 20% O₂/He (flow rate = 100 mL/min).

3.3 Catalytic reactions

Prior to the activity tests, 100 mg of catalyst was *in situ* reduced in a H₂ gas flow of 30 mL/min at 500 °C for 60 min in a fix-bed quartz tube micro-reactor. The catalytic activity measurements were carried out at atmospheric pressure by passing a gaseous mixture of CO₂ (5 %) and H₂ (20 %) in He balance at a total flow rate of 100 mL/min (GHSV ~ 40,000 h⁻¹). The inlet and outlet flows were analyzed by an on-line gas chromatograph (Agilent 6890) equipped with both a FID and a TCD detector. The sampling data were collected when reaction reached a steady state (60 - 120 min after reaching the desired reaction temperature). The kinetic measurement was performed the same way, keeping the CO₂ conversion below 15% by varying the amount of catalysts used. The conversion of CO₂ and the selectivity/yield to CH₄ and CO were calculated by the following equations,

$$\text{CO}_2 \text{ conversion (\%)} = \frac{[\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}}{[\text{CO}_2]_{\text{in}}} \times 100$$

$$\text{CH}_4 \text{ selectivity (\%)} = \frac{[\text{CH}_4]_{\text{out}}}{[\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}} \times 100$$

$$\text{CO selectivity (\%)} = \frac{[\text{CO}]_{\text{out}}}{[\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}} \times 100$$

$$\text{CH}_4 \text{ yield (\%)} = \frac{[\text{CH}_4]_{\text{out}}}{[\text{CO}_2]_{\text{in}}} \times 100$$

$$\text{CO yield (\%)} = \frac{[\text{CO}]_{\text{out}}}{[\text{CO}_2]_{\text{in}}} \times 100$$

Chapter 4 Ni/Y₂O₃ catalysts for CO₂ methanation

Recently, Y₂O₃ has been introduced as a promoter in several catalysts systems to enhance the catalytic performance [188]. The dispersion of Cu over Cu/ZnO/Al₂O₃ catalysts was significantly improved by the introduction of a moderate amount of Y₂O₃ [189]. Similarly, Y₂O₃ was introduced into Cu–SAPO-34 catalysts to promote the activity for selective reduction of NO_x by NH₃ via an enrichment of the isolated Cu species and surface acidic sites [190]. Over Ni/Al₂O₃, Y₂O₃ addition not only increased the catalytic activity of autothermal reforming of methane with CO₂ into syngas but also improved the anti-sintering ability and minimized the carbon deposition [191].

Y₂O₃ has also been directly applied as a support for Ni based catalysts. The surface oxygen mobility over Ni/Y₂O₃ was held responsible for a distinct contribution to the oxidative reforming reaction of ethanol [192, 193] and oxy-CO₂ reforming of methane [194]. By calcination of the products synthesized via co-precipitation and hydrothermal treatment at different temperatures, the catalytic performance of Ni/Y₂O₃ for the hydrogenolysis of furanic compounds confirmed that the metal support interface was active and selective in the C-O bond hydrogenolysis [195].

In this chapter, Y₄O(OH)₉(NO₃) was synthesized by a facile hydrothermal treatment, the calcination of which resulted in the formation of Y₂O₃. The calcined Ni/Y₂O₃ samples after loading Ni onto Y₄O(OH)₉(NO₃) were attempted for CO₂

methanation. Catalytic test results suggested that Ni/Y₂O₃ with the optimal Ni loadings of 10%, demonstrated superior catalytic performance than the reference one prepared from Y₂O₃, denoted as Ni-Y₂O₃. Characterization by CO₂-TPD and H₂-TPR revealed that using Y₄O(OH)₉(NO₃) as the precursor favored the necessary interaction between Ni and supports, resulted in the formation of abundant medium basic sites that was essential for the effective CO₂ activations. Moreover, the reaction mechanisms studied by *in situ* DRIFTS suggested that the carbonates species formed by CO₂ adsorption was converted to formates in a fast way over both catalysts. However, the further conversion of formates into CH₄ was clearly more favored over Ni/Y₂O₃.

4.1 Activity test results

4.1.1 Catalytic performance

Activity test results of the Ni/Y₂O₃ of different loadings along with the reference 10Ni-Y₂O₃ were presented in Figure 4.1. For all the tested catalysts, the catalytic behaviors have been limited by the thermodynamic equilibrium in the high temperature region. Over 2% Ni/Y₂O₃, the CO₂ conversion increased monotonically with ramping temperature, exhibiting value of 78% at 425 °C, which was close to the equilibrium data. With increasing loadings, the reaction pattern for CO₂ conversion shifted to lower temperature. The maximum CO₂ conversion over 5% Ni/Y₂O₃ and 10% Ni/Y₂O₃ was 84% and 88% at 350 °C.

Figure 4.1 (A) CO₂ conversion and (B) CH₄ & CO yields over catalysts with different Ni loadings and different support precursors. Dashed line - thermodynamic equilibrium conversion values.

It was worth mentioning that the CO₂ conversion reached the equilibrium conversion at a temperature as low as 350 °C over 10% Ni/Y₂O₃ and 20% Ni/Y₂O₃. Surprisingly, increasing Ni loadings from 10% to 20% only resulted in an unappreciable increase of about 4% in the CO₂ conversion at 325 °C, considering that the Ni loadings have doubled. Furthermore, the reference 10Ni-Y₂O₃ catalyst that using the calcined results of Y₂O₃ as the impregnation support demonstrated a much inferior catalytic activity with the highest CO₂ conversion of only 46% at 300 °C, if compared to 78% over 10% Ni/Y₂O₃ at the same temperature. On the other hand, the maximum yield of CO was below 4% for all the catalysts tested (Figure 4.1B), suggesting that Y₂O₃ served as an effective and selective support for the methanation of CO₂ over Ni-based catalyst.

4.1.2 Stability of catalysts

The stability test was carried out over 10% Ni/Y₂O₃, 20% Ni/Y₂O₃ and 10% Ni-/Y₂O₃ at 325 °C under the same reaction atmosphere as the activity test (Figure 4.2). For the 10% Ni/Y₂O₃ and 10% Ni-/Y₂O₃, no activity loss was observed during 60 h on stream. As a comparison, the activity of 20% Ni/Y₂O₃ began to decrease after *ca.* 15 h, which has not stopped even after 60 h. The continuous activity loss reached about approximately 10%, from *ca.* 88% to *ca.* 78%.

Figure 4.2 Stability test results of 10% Ni/Y₂O₃, 20% Ni/Y₂O₃ and 10% Ni-/Y₂O₃ at 325 °C

Since a relatively low temperature was adopted for the stability test, the possibility of particle sintering was responsible for the activity loss can be ruled out. The used catalysts were tested by TGA analysis to demonstrate any trace of carbon depositions by monitoring the weight changes during the temperature ramp (Figure 4.3). A substantial amount of 4.9% weight loss was observed for 20% Ni/Y₂O₃, in contrast to that no appreciable weight change can be recognized for the rest two catalysts, which clearly pointed out that coke formation over 20% Ni/Y₂O₃ was held responsible for the activity loss.

Figure 4.3 TG profiles of the spent catalysts after the stability test.

4.2 Characterization of the catalysts

4.2.1 Structural characterization

XRD patterns of the as-prepared Y₂O₃ supported Ni catalysts were presented in Figure 4.4. Reflections of Y₄O(OH)₉(NO₃) were clearly identified on the samples that directly obtained after the hydrothermal precipitation. Distinct diffraction peaks assigned to Y₂O₃ were observed over all the other samples. Peaks at 37.2 ° and 62.8 ° ascribed to NiO were distinguished only when the Ni loadings was as high as 20%, reflecting that the Ni was either highly dispersed on Y₂O₃ or existed in amorphous form over the as-prepared catalysts except 20% Ni/Y₂O₃.

Figure 4.4 XRD patterns for Ni/Y_2O_3 with different loadings and reference $Ni-Y_2O_3$ catalysts, along with the precursor of the support as directly used after hydrothermal precipitation.

Table 4.1 showed the specific surface area estimated from the N_2 physisorption at $-196\text{ }^\circ\text{C}$. The highest surface area of $90.52\text{ m}^2/\text{g}$ was observed on 10% $Ni-Y_2O_3$ by directly applying Y_2O_3 as the precursor of the support. Noticeably, the series of Ni/Y_2O_3 catalysts exhibited a decrease in surface area from $82.31\text{ m}^2/\text{g}$ to $73.19\text{ m}^2/\text{g}$ when Ni content was changed from 2% to 20%, suggesting probable structural interaction between Ni ions and the support

precursor during the impregnation process. Besides, the Ni contents obtained by ICP-EOS analysis were highly comparable to the nominated value, indicating that the difference in the activity for 10% Ni-Y₂O₃ and 10% Ni/Y₂O₃ was not resulted from any Ni loss during preparations.

Table 4.1. BET surface area, Ru content and CO₂ adsorption volume estimated from the CO₂-TPD profiles.

Sample	BET surface area (m ² /g)	Ni content ^a (%)	CO ₂ adsorption volume ^b (μmol/g)
2% Ni/Y ₂ O ₃	82.31	1.96	40.4
5% Ni/Y ₂ O ₃	81.32	5.04	67.6
10% Ni/Y ₂ O ₃	77.14	10.11	126.2
20% Ni/Y ₂ O ₃	73.19	21.01	188.6
10% Ni-Y ₂ O ₃	90.52	10.05	82.1

^a Obtained from ICP-EOS analysis.

^b Estimated from CO₂-TPD results.

4.2.2 Characterization by temperature-programmed reaction

To examine the surface basicity of the as-prepared catalysts, CO₂ temperature programmed desorption was carried out, with the results being shown in Figure 4.5. Over 2% Ni/Y₂O₃, only one peak at around 85 °C was observed, which was attributed to desorption of CO₂ adsorbed on weak basic sites. With increasing Ni loadings to 5 %, a new peak at *ca.* 190 °C resulted from desorption of CO₂ on medium basic sites appeared, besides from the one of weak basicity. Further increase in the Ni content to 10% led to an enlargement in the CO₂ desorption pattern without significant changes. However, an extra peak at a higher temperature of *ca.* 318 °C was presented when the Ni content was changed to 20%, indicating the presence of an appreciable amount of strong basic sites. On the other hand, the CO₂ desorption behaviors of 10% Ni-Y₂O₃ exhibited a similar two-peak pattern to that of 10% Ni/Y₂O₃, but different in the integrated peak area under the curves. Obviously, 10% Ni/Y₂O₃ demonstrated more available basic sites than 10% Ni-Y₂O₃, which probably was induced by the proper interaction between the metal ions and the support precursors during the impregnation.

Figure 4.5 CO₂-TPD profiles of Ni/Y₂O₃ with different loadings and reference Ni-Y₂O₃ catalysts.

According to the literatures, CO₂ adsorbed on the surface hydroxyls on the support of weak basicity can be effectively converted to form active carbonate species, which further reacted with the dissociated H atoms to form CH₄ [196]. Similarly, combined CO₂ TPD results with DRIFTS studies, Pan et al. suggested that the surface oxygen sites of medium basicity promoted the formation and transformation of active monodentate carbonates, while CO₂ adsorbed on strong basic sites cannot participate in the methanation reaction.

Figure 4.6 H₂-TPR profiles of Ni/Y₂O₃ with different loadings and reference Ni-Y₂O₃ catalysts.

H₂-TPR profiles of Ni/Y₂O₃ of different loadings along with 10% Ni/Y₂O₃ were presented in Figure 4.6. The 2% Ni/Y₂O₃ and 5% Ni/Y₂O₃ showed two H₂ consumption peaks at 297 °C and 324 °C, which were assigned to the ‘unsupported’ free Ni species and the Ni species weakly interacting with the Y₂O₃ support [109, 197], respectively. Nonetheless, only one peak at 324 °C appeared over 10% Ni/Y₂O₃ and 20% Ni/Y₂O₃, suggesting that an adequate Ni content was crucial to achieve an appropriate interaction between Ni and Y₂O₃. The free unsupported Ni nano-particles was shown to be significantly less active for the methanation of CO₂

than the supported ones [167] (also can refer to the results in chapter 5), which was the main reason for the inferior activity of catalysts with low Ni loadings. As a comparison, the 10% Ni-Y₂O₃ demonstrated an apparently different H₂-TPR profile from the rest with a distinct peak at higher temperature, 454 °C, besides from the one at 324 °C, which was attributed to the reduction of Ni species deep in the support. The appearance of this peak of high temperature reflected that using different impregnation precursor for the support changed the interaction pattern between the metal particles and the support [198, 199].

4.3 Mechanistic studies

Figure 4.7 Dynamic changes of *in situ* DRIFTS spectra over 10% Ni/Y₂O₃ recorded as a function of time in a flow of H₂ at 300 °C after being exposed CO₂ for 30 min.

To study the reactivity of surface species formed by CO₂ adsorption towards H₂, DRIFTS spectra was taken after the adsorption of CO₂ for 30 min at 300 °C over 10% Ni/Y₂O₃ with He purges for 60 min to remove the physisorbed CO₂ and any gaseous residues, and then the inlet gas was switched to H₂ while the surface species were closely monitored (Figure 4.7). The adsorption of CO₂ resulted in the formation of two big bulges centered at 1512 cm⁻¹ and 1378 cm⁻¹, along with a distinct peak at 1296 cm⁻¹, all of which were substantially attributed to different carbonates species by previous studies [79, 168, 200]. Moreover, shoulder peaks at 1655 cm⁻¹, 1592 cm⁻¹, 1443 cm⁻¹ and 1211 cm⁻¹ were clearly distinguishable. While the one at 1592 cm⁻¹ was also ascribed to surface carbonates species, the rest three peaks were assigned to hydrogen carbonates [107, 109, 164, 201]. After He purge, the introduction of H₂ resulted in the immediate formation of peaks at 1621 cm⁻¹, 1601 cm⁻¹, 1362 cm⁻¹ and 1341 cm⁻¹, accompanied by an obvious attenuation of the peaks of carbonates at 1592 cm⁻¹, 1512 cm⁻¹ and 1378 cm⁻¹, especially the one at 1296 cm⁻¹. The four new peaks were divided into two groups, one of 1621 cm⁻¹ and 1341 cm⁻¹, and one of 1601 cm⁻¹ and 1362 cm⁻¹, which were assigned to monodentate formate species and bidentate formate species respectively on the basis of frequency difference between the two peaks [115, 127, 166]. Most importantly, the peaks at 3010 cm⁻¹ and 1301 cm⁻¹ assigned to methane appeared after the introduction of H₂. The bands of formate species reached a peak in 5 min with the continuous consumption of carbonates, suggesting a transformation of

carbonates into formate species with the steady supply of H_2 , which agreed well with the literatures [77, 161]. After that, the peaks of formate species gradually attenuated, which has almost decreased by a half after 30 min, along with the continuous formation of surface methane species. The evolvement of the DRIFTS spectra suggested that carbonates formed by the adsorption of CO_2 was firstly hydrogenated into formate and then the final products, methane.

To give a better understanding of the activity difference between Y_2O_3 supported Ni catalysts prepared from different Y sources, the same DRIFTS experiments were carried out over 10% Ni- Y_2O_3 and the results were presented in Figure 4.8. Similar spectra was obtained after CO_2 adsorption, with the presence of peaks of carbonates at 1592 cm^{-1} , 1512 cm^{-1} , 1378 cm^{-1} and 1296 cm^{-1} , along with hydrogen carbonates at 1655 cm^{-1} , 1443 cm^{-1} and 1211 cm^{-1} . Moreover, the monodentate formate peaks at 1621 cm^{-1} and 1341 cm^{-1} were recognizable before the introduction of H_2 , which probably was resulted from the CO_2 adsorbed on the surface hydroxyl groups. After the introduction of H_2 , hydrogen carbonates and carbonates species generally were consumed with an appreciable formation of formate species. However, unlike to that on 10% Ni/ Y_2O_3 , the peaks ascribed to formate species was continuing rising even after the exposure to H_2 for 60 min. Noticeably, the peak at 3010 cm^{-1} of surface methane species diminished quickly and disappeared after 5 min, suggesting that the conversion of formate species into methane has been degraded, which was probably resulted from the scarcity of

active sites of medium basicity. Similar reaction pathway to that of 10% Ni/Y₂O₃ was proposed, with the adsorbed CO₂ being firstly converted into formate specie and then methane. However, as deduced from the evolvement of DRIFTS spectra, the conversion of formate has been largely hindered over 10% Ni-Y₂O₃, which probably resulted from the lack of the active sites for this reaction step.

Figure 4.8 Dynamic changes of *in situ* DRIFTS spectra over 10% Ni-Y₂O₃ recorded as a function of time in a flow of H₂ at 300 °C after being exposed CO₂ for 30 min.

4.4 Summary

Two Y-containing precursors were adopted for the preparation of Ni on Y₂O₃ catalysts by the traditional impregnation method, with one obtained directly from hydrothermal precipitation, Y₄O(OH)₉(NO₃), and the other from the calcination of

the precipitates, Y_2O_3 . With the same Ni loadings of 10%, the catalysts prepared from $\text{Y}_4\text{O}(\text{OH})_9(\text{NO}_3)$ displayed superior catalytic activity for CO_2 methanation, over which a higher amount of surface basic sites of medium strength was observed in CO_2 -TPD profiles. H_2 -TPR profiles further demonstrated a stronger interaction between the support and Ni over the samples obtained from the calcined precursors, which led to the lessened presence of active reduced Ni particles. DRIFTS spectra showed that the CO_2 adsorption resulted in the formation of carbonates, which was then converted into formate after the introduction of H_2 . The subsequent conversion of formate species into CH_4 was faster over the catalysts prepared from $\text{Y}_4\text{O}(\text{OH})_9(\text{NO}_3)$, which was held responsible for the superior activity.

Chapter 5 W-doped Ni-Mg mixed oxide catalysts for CO₂ methanation

Although Ni/Y₂O₃ was effective for CO₂ methanation, the raising demand for rare earth elements in several other fields has led to a concern in the cost. The conventional metal oxides remains as the most promising support to optimize Ni-based catalysts for CO₂ methanation because of their high thermal stability and low cost [165]. Among those, MgO showed the potential because the strong interaction between Ni species and MgO favored the formation of highly dispersed small Ni particles, which contributed to the great enhancement of CO₂ methanation activity [97, 141, 150, 202]. Further modifications of the surface properties can be achieved by controlling the formation of ‘ideal’ Ni-Mg solid solution [203, 204]. Ni-MgO nanoparticles encapsulated by porous silica shell, Ni_{0.8}Mg_{0.2}O@SiO₂, revealed a remarkable improvement in CO₂ conversion with high stability if compared to the encapsulated NiO without MgO [148]. To the contrary, the presence of MgO was considered to lower the methanation activity due to the poor reducibility of Ni-Mg solid solution [24]. These two apparently contradictory results indicate that the fine-tuning of the interaction between Ni species and MgO support plays an essential role in optimizing the performance of Ni-Mg catalysts for CO₂ methanation.

On the other hand, improvement of the long-term stability of Ni-based catalysts in CO₂ methanation at high temperature requires more efforts. The deactivation of catalyst by coke formation and sintering of metal particles is

accelerated when a large amount of heat is released as the exothermal reaction further proceeds [110, 141, 149]. Besides, the poison effect of CO via the formation and the migration of mobile $\text{Ni}(\text{CO})_4$ species on catalyst surface during the methanation reaction cannot be ruled out [173, 205]. Nevertheless, several researchers substantiated that the formation of Ni-Mg solid solution was beneficial for the resistance against deactivation over MgO supported Ni catalysts [150]. For instance, there were two types of NiO species in MgO doped Ni/ Al_2O_3 catalyst: the ‘free’ NiO and highly dispersed NiO species. However, only the latter one can prevent the agglomeration of Ni crystallites and improve the catalytic activity and stability due to the strong interaction between NiO species and MgO additives [206]. Similar results were reported by Wang et al. [207], who synthesized a durable Ni/MgO catalysts for the CO_2 reforming of methane with remarkable resistance to sintering and coking. The stability enhancement over their catalysts was attributed to the ‘anchoring’ of metallic Ni by surface defects on the support, which were formed at the vicinity of the reduction sites of Ni species located in the Ni-Mg solid solution. Furthermore, the incorporation of a third component, such as Ru [148], Sr [140], Co [208] has been investigated to improve the stability of Ni-based catalysts for CO_2 methanation. Recently, a synergistic effect between Ni and W in mixed Ni-W-Ce oxide catalysts has been reported, which displayed significant effectiveness in minimizing the coke formation and stabilizing the metal particles for ethanol steam reforming [209].

In this chapter, a series of W-doped Ni-Mg mixed oxide powder catalysts were prepared by a homogeneous precipitation method and attempted in CO₂ methanation. NiWMgO_x with Ni:W:Mg molar ratio being 1:1:1 exhibited both excellent methanation activity and CH₄ selectivity. The stability test at 400 °C for 100 h revealed only a negligible activity loss for NiWMgO_x. The promotional effect of adding W into the Ni-Mg mixed oxide catalyst was further investigated by *in situ* DRIFTS, CO₂-TPD and H₂-TPR.

5.1 Activity test results

5.1.1 CO₂ methanation activity of catalysts with different Ni/Mg molar ratio

CO₂ conversion over NiO, MgO and Ni_aMgO_x (a=0.5, 0.8, 1.0, 1.2) catalysts along with reference Ni/MgO(imp) (synthesized with the same metal composition as Ni_{1.0}MgO_x) prepared by impregnation method were presented in Figure 5.1. Ni_{0.5}MgO_x exhibited relatively poor activity at temperature lower than 300 °C. Both Ni_{0.8}MgO_x and Ni_{1.0}MgO_x with higher Ni loadings showed enhanced activities towards CO₂ methanation, especially at the low temperature. At 300 °C, the CO₂ conversion reached 70 % over Ni_{1.0}MgO_x with 99 % selectivity to CH₄.

Figure 5.1 (A) CO₂ conversion and (B) CH₄ selectivity over catalysts with different Ni : Mg molar ratio. Dashed line - thermodynamic equilibrium conversion values. Conditions: CO₂ 5 %, H₂ 20 %, He as balance, GHSV ~ 40,000 h⁻¹.

As a reference, Ni/MgO(imp) showed the poorest CO₂ conversion of less than 20 % at the same temperature, implying that the homogeneous precipitation preparation method improved the dispersion of active Ni species on Ni-Mg mixed oxide catalysts for CO₂ methanation. However, further increasing Ni loading to Ni/Mg=1.2 led to a noticeable decrease in CO₂ conversion, possibly due to the aggregation of surface Ni particles [72, 127]. Pure NiO and MgO presented significantly inferior activity towards CO₂ methanation together with low selectivity to CH₄, indicating the essential role of the synergetic interaction between Ni and Mg for CO₂ methanation. Based on the activity measurements, the Ni_{1.0}MgO_x was chosen as the catalyst for further optimization.

5.1.2 CO₂ methanation activity over different transition metal doped catalysts

The NiMgO_x catalysts doped by different transition metals at the molar ratio of 1:1:1 including W, Mo, Fe, Co, Mn and Cu were synthesized by the same homogeneous precipitation method and tested for CO₂ methanation. As shown in Figure 5.2, NiCuMgO_x showed an obviously different reaction pattern from other catalysts, with higher reactivity for RWGS than methanation of CO₂. The addition of Mo into Ni-Mg mixed oxide resulted in a slight decrease of the low temperature activity. Mn- and Fe-doped catalysts showed the remarkably decreased CO₂ conversion than NiMgO_x and a significant decrease of selectivity to CH₄ was observed over NiFeMgO_x.

Figure 5.2 (A) CO₂ conversion and (B) CH₄ selectivity over NiMgO_x catalysts doped by different transition metals. Dashed line - thermodynamic equilibrium conversion values. Conditions: CO₂ 5 %, H₂ 20 %, He as balance, GHSV ~ 40,000 h⁻¹.

In contrast, Co and W doping resulted in an enhancement of both CO₂ conversion and CH₄ selectivity. The corresponding CO₂ conversion at 300 °C over NiWMgO_x and NiCoMgO_x were 86 % and 74 % respectively. Compared to the conversion of 70 % over undoped NiMgO_x catalysts, a significant improvement of catalytic activity was observed on NiWMgO_x, which was worth further discussing.

5.1.3 Influence of W dopant molar ratio

Figure 5.3 CO₂ conversion over NiW_bMgO_x (b = 0.50, 0.75, 1.00, 1.25) catalysts.

Dashed line - thermodynamic equilibrium conversion values. Conditions: CO₂ 5 %, H₂ 20 %, He as balance, GHSV ~ 40,000 h⁻¹.

At the W: Ni molar ratio of 0.50, a slight increase of CO₂ conversion was observed compared to the undoped NiMgO_x (Figure 5.3). Further increasing the W molar ratio in Ni-W-Mg to 0.75 and 1.00 improved the catalytic performance for CO₂ conversion. However, an apparent decline of CO₂ methanation activity was observed when the relative W addition ratio was increased to 1.25. Noticeably, the reference NiWO_x catalyst possessed remarkably inferior activity for CO₂ methanation to NiWMgO_x, indicating that W cannot completely replace the role of Mg as the support for Ni catalysts. The maximum CO₂ conversion was attained when W : Ni molar ratio reached 1 : 1 in Ni-W-Mg oxide catalysts.

5.1.4 Influence of CO

CO was observed as an impurity for CO₂ in certain sources such as the waste gas emission from power plants [115, 210], the presence of which was reported to inhibit the methanation of CO₂ by strong interaction with the surface of Ni particles [131]. Figure 5.4 showed the catalytic activity of NiMgO_x and NiWMgO_x in the presence of 1 % CO in the feeding gas for CO₂ methanation. A small downshift of CO₂ conversion at temperature lower than 350 °C was found for both catalysts while the high temperature activity remained almost intact, suggesting that the mixed oxide catalysts suffered from confined inhibition effects by the interactions between CO and Ni surface.

Figure 5.4 CO₂ conversion over NiMgO_x and NiWMgO_x in the presence of CO and stability test result (insert). Stability test is run at 275 °C. Dashed line - thermodynamic equilibrium conversion values. Conditions: CO₂ 5 %, H₂ 23 %, CO 1 %, He as balance, GHSV ~ 40,000 h⁻¹.

Apart from the influence mentioned above, the formation of mobile Ni carbonyl species and subsequently growth of Ni particles at low temperature by the facilitation of CO was also the main cause for the deactivation of Ni-based catalysts [173]. Thus, the long-term performance of both samples in the presence of 1 % CO were studied at 275 °C for 100 h. CO addition resulted in an immediate decrease of approximately 6 % in CO₂ conversion over both NiMgO_x and NiWMgO_x, 45 % to 38 % and 67 % to 61 % respectively, a consequence of the

competitive adsorption of CO. Nonetheless, after exposing to CO-containing reaction gas for 80 h, the CO₂ conversion over NiMgO_x drastically decreased from 38 % to 22 %, while NiWMgO_x showed almost no deactivation with CO₂ conversion, remaining above 60 % for up to 100 h. The fact that NiWMgO_x demonstrated excellent activity and anti-CO-poisoning ability indicated NiWMgO_x was also of great promise for applications in methanation of CO₂ from realistic CO-containing sources.

5.1.5 Stability of catalysts

Figure 5.5 Stability test result of NiMgO_x and NiWMgO_x catalysts, with activity comparison between spent catalysts after 100 h on stream and fresh catalysts (insert). Dashed line - thermodynamic equilibrium conversion values. Conditions: 400 °C, CO₂ 5 %, H₂ 20 %, He as balance, GHSV ~ 40,000 h⁻¹.

The primary obstacle to the application of Ni-based catalysts for methanation is the deactivation at high temperature as a result of sintering of active species. Thus, both NiMgO_x and NiWMgO_x were tested at 400 °C in the same reaction gas used above for 100 h. Prior to the stability test, the catalyst was also *in situ* reduced at 500 °C under H₂ stream for 60 min. As shown in Figure 5.5, no activity loss occurred for NiWMgO_x during the long-term test at 400 °C and the selectivity remained at around 98 %. In contrast, the decrease in CO₂ conversion from 78 % to 68 % was observed over NiMgO_x. After the stability test, the CO₂ methanation activities of the spent catalysts, denoted as NiMgO_x-s and NiWMgO_x-s, were subsequently tested repeatedly (as displayed in Figure 5.5). No obvious change of CO₂ conversion over NiWMgO_x-s was inspected at each temperature point compared to the freshly prepared catalyst, while NiMgO_x-s demonstrated a significant activity loss in contrast to the fresh NiMgO_x. These results indicated that doping W greatly enhanced the stability of Ni-Mg mixed oxide catalyst, the reasons of which will be further discussed below.

5.2 Mechanistic studies

5.2.1 Surface intermediates formed in the gas mixture of CO₂ and H₂

The surface intermediates during CO₂ methanation over NiMgO_x and NiWMgO_x were studied by *in situ* DRIFTS at 300 °C. As presented in Figure 5.6, the most predominant bands formed were the sharp peak at 1603 cm⁻¹ and the

broad one centered at 1511 cm^{-1} after passing H_2 and CO_2 for 60 min over NiMgO_x . It also should be noted that two shoulder peaks at 1368 and 1343 cm^{-1} were observed on top of the large hump centered at 1380 cm^{-1} . The appearance of characteristic bands of methane at 1301 and 3010 cm^{-1} (results not shown) were in good accordance with the excellent activity. Passing CO_2 and H_2 over NiWMgO_x for 60 min resulted in the appearance of another new shoulder peak at 1624 cm^{-1} in addition to those peaks mentioned above, which was probably too weak to be observed over NiMgO_x as it was covered by the strong peak at 1603 cm^{-1} . In addition, evidently stronger bands at 1603 and 1368 cm^{-1} were observed over NiWMgO_x than those on undoped NiMgO_x .

Figure 5.6 *In situ* DRIFTS of CO_2 methanation ($\text{CO}_2 + \text{H}_2$) at 300°C .

Several formate and carbonate species were observed over Ni-based catalysts in the DRIFTS spectra between 1700 and 1200 cm^{-1} during the methanation of CO_2 [113, 115, 166]. For formate species over Ni-based catalysts, the adsorption configuration is distinguished by the frequency difference ($\Delta\nu$) between $\nu_s(\text{OCO})$ and $\nu_{\text{as}}(\text{OCO})$. A $\Delta\nu$ larger than 250 cm^{-1} often indicated the formation of monodentate configuration, while a $\Delta\nu$ less than or close to 250 cm^{-1} was ascribed to the bidentate formate species [103, 127, 166]. Thus, in this study, the bands at 1624 and 1343 cm^{-1} were assigned to the $\nu_s(\text{OCO})$ and $\nu_{\text{as}}(\text{OCO})$ of monodentate formate species and the bands at 1603 and 1368 cm^{-1} were ascribed to the bidentate formate species, correspondingly. For the assignment of the bands at 1511, 1445 and 1380 cm^{-1} , different kinds of carbonates have been proposed, including monodentate carbonate [211], bidentate carbonate [113, 166] and tridentate carbonate [212]. In the presence of H_2 , carbonates can be hydrogenated into formate species and further participated in the methane production [11, 34]. Also the direct decomposition of carbonates has been proposed in this process, resulting in the possible formation of CO besides from CO_2 , which then followed the reaction pathway of the methanation of CO to yield methane [41]. However, no observance of CO(ads) in our study suggested that the CO_2 methanation reaction pathway over NiWMgO_x involved the hydrogenation of carbonates species into formate species other than the direct decomposition of carbonates [42, 43]. Similar reaction pathway has also been reported for Pd-Mg/ SiO_2 [11], NiUSY zeolites [34]

and Ni/Ce_{0.5}Zr_{0.5}O₂ [36]. Thus, the carbonates species can serve as the precursors for the formate species during methanation of CO₂. As key intermediates for CO₂ methanation, the reactivity of different formate species was studied by several groups. Pan et al. [113, 166] recently found that the monodentate formate species reacted more rapidly with H₂ than the bidentate formate species and further contributed to the enhanced CO₂ methanation activity. Inspired by this, in this study, we will focus on the role of formate species, which is derived from the hydrogenation of active carbonates in the methanation of CO₂. Thus these three peaks at 1511, 1445 and 1380 cm⁻¹ were generally ascribed to the carbonates family.

5.2.2 The reactivity of surface intermediates towards H₂

To obtain the reactivity of these surface species towards H₂ over NiWMgO_x, the reaction gas was switched to 20 % H₂/Ar after exposure to CO₂+H₂ for 60 min, and the resulted spectra were presented in Figure 5.7A. The pair peaks at 1624 and 1343 cm⁻¹ nearly vanished in 5 min simultaneously after switching the reaction gas to H₂/Ar, which confirmed the assignment of these two peaks to the same species of monodentate formate. A similar trend of synchronized decrease in intensity was observed for the two bands of bidentate formate at 1603 and 1368 cm⁻¹. Besides, a relatively slower decrease of the peaks due to the carbonates family was observed with no appearance of new peaks, suggesting that carbonates species reacted with H₂ to form formate species [11, 77, 161, 166].

Figure 5.7 (A) Dynamic changes of *in situ* DRIFTS spectra over NiWMgO_x as a function of time in a flow of H₂ at 300 °C after being exposed to a flow of CO₂ + H₂ for 60 min at 300 °C. (B) Time dependence of the relative peak area ratio to the initial peak area of monodentate formate and bidentate formate species.

In order to quantitatively compare the change of these two surface formate species mentioned above, the spectra in the range of 1250 to 1900 cm^{-1} were converted into Kubelka-Munk function and fitted on the basis of the assignments above. The peak areas in the Kubelka-Munk function after the desired time of reaction with H_2/Ar were further defined as A , and the initial areas as A_0 . Figure 5.7B showed the peak area ratio A/A_0 of 1624 and 1603 cm^{-1} as a function of time-on-stream after exposure to 20 % H_2/Ar . Switching the feed gas to H_2 resulted in a significant decrease of approximately 90 % monodentate formate species in the first 5 min whereas the peak area of surface bidentate formate species only decreased 50 % on the same time scale. After reacting with H_2 for 30 min, the bands of monodentate formate species were decreased by 95 % compared to only 60 % for the peak at 1603 cm^{-1} of bidentate formate species. These results confirmed that the monodentate formate was more active toward H_2 than the bidentate formate species over NiWMgO_x . The W addition in Ni-Mg mixed oxide catalysts unambiguously facilitated the formation of monodentate formate species, which should be a key factor in the enhanced CO_2 methanation activity.

5.3 Characterization of the catalysts

5.3.1 Structural characterization

The XRD patterns of the as-calcined and reduced NiMgO_x and NiWMgO_x samples along with NiO and MgO as references were shown in Figure 5.8A. The

characteristic reflections at 37.3 °, 43.4 °, 62.9 °, 75.5 ° and 79.4 ° for NiO and the reflections at 37.2 °, 43.2 °, 62.4 °, 74.8 ° and 78.9 ° for MgO were observed, corresponding to (111), (200), (220), (311) and (222) of the face-centered cubic (fcc) NiO and MgO phase, respectively. Distinct peaks at 37.2 °, 43.2 °, 62.7 °, 75.2 ° and 79.2 ° were observed on calcined NiMgO_x and NiWMgO_x and all peaks showed close to or in between the same kind of diffraction peaks of NiO and MgO. For instance, as shown in Figure 5.8B, the (220) peak of NiO (62.9 °) and MgO (62.4 °) shifted towards each other to merge into a single peak at 62.7 °, implying the formation of solid solution phase in NiMgO_x and NiWMgO_x [148]. After reduction in a flow of H₂ for 60 min at 500 °C, sharp peaks ascribed to metallic Ni at 44.4 ° (111), 51.8 ° (200) and 76.4 ° (220) appeared and the peaks assigned to Ni-Mg solid solution were still discerned for both catalysts (denoted as NiMgO_x-r and NiWMgO_x-r, respectively). No peaks assigned to W species were observed in the XRD patterns of NiWMgO_x, neither on the calcined sample nor on the reduced one, suggesting that W species were highly dispersed in NiMgO_x matrix in stabilized state.

Figure 5.8 (A) XRD patterns and (B) enlargement of patterns in the range of 61 $^{\circ}$ - 64 $^{\circ}$ for NiMgO_x and NiWMgO_x catalysts. (NiMgO_x-s and NiWMgO_x-s: The spent catalysts after the stability test were re-calcined in air for 60 min at 500 $^{\circ}$ C)

Figure 5.9 TEM images of (A) NiMgO_x and (B) NiWMgO_x catalysts.

NiMgO_x and NiWMgO_x have been characterized by TEM to show the morphologies. It can be seen that the TEM image of NiMgO_x in Figure 5.9A consisted of nanosheets with varying particle sizes, from 15 nm to 35 nm. No appearance of metal particles suggested that a homogeneous Ni-Mg solid solution was formed after the calcination. W addition resulted in a decrease of the size of the nanosheets (~10 nm) with no discernable agglomeration of Ni or W particles, indicating that W has entered the solid solution matrix, as shown in Figure 5.9B. Energy-dispersive X-ray (EDX) elemental mapping (Figure 5.10) clearly showed that the distribution of Ni and Mg elements was relatively homogeneous in NiMgO_x. Similar trends were observed for Ni, W and Mg elements in NiWMgO_x (Figure 5.11). These results suggested that the catalysts consisted of metallic Ni particles, dispersed W species and Ni-Mg solid solution support under high-temperature reduction atmosphere after being reduced in H₂ at 500 °C. The spent catalysts after the stability test were calcined in air for 60 min at 500 °C and characterized by XRD. It should be noted that the reflection of (220) peak of NiMgO_x-s (62.8 °) has slightly shifted closer towards the same diffraction peak of NiO (62.9 °), suggesting a possible structural change of the solid solution. As a comparison, the diffraction peaks of NiWMgO_x-s remained almost unchanged if compared to the fresh catalysts.

Figure 5.10 (A) The HRTEM image of NiMgO_x and corresponding EDX elemental mapping: (B) Ni and (C) Mg.

Figure 5.11 (A) The HRTEM image of NiWMgO_x and corresponding EDX elemental mapping: (B) Ni, (C) Mg and (D) W.

5.3.2 Characterization of structural changes after stability tests

Table 5.1. BET surface area and CO₂ adsorption volume estimated from the CO₂-TPD profiles.

Sample	BET surface area	CO ₂ adsorption volume
	(m ² /g)	(μmol/g)
NiMgO _x	48.94	10.23
NiMgO _x -s	45.37	10.01
NiWMgO _x	52.83	5.09
NiWMgO _x -s	52.41	4.25

Figure 5.12 TG profiles of the spent NiMgO_x and NiWMgO_x catalysts after the stability test. The reduced fresh catalysts were used as references.

As shown in Table 5.1, similar BET surface areas (about $50 \text{ m}^2/\text{g}$) were obtained over as-calcined NiMgO_x and NiWMgO_x , whereas a slight decrease (48.94 to $45.37 \text{ m}^2/\text{g}$) in the surface area was observed on $\text{NiMgO}_x\text{-s}$ catalyst after the stability test. The metallic surface area of both fresh and spent catalysts was determined by H_2 chemisorption after reduction at 500°C for 60 min, as listed in Table 5.1. The metallic surface area of $\text{NiMgO}_x\text{-s}$ decreased from $7.01 \text{ m}^2/\text{g}$ to $3.94 \text{ m}^2/\text{g}$ after the stability test, compared to the negligible variations for $\text{NiWMgO}_x\text{-s}$, $7.62 \text{ m}^2/\text{g}$ to $7.55 \text{ m}^2/\text{g}$. Inspired by Aziz et al. [25], TGA analysis was carried out

under a N_2 flow to estimate the coke content formed during the stability test. The reduced fresh catalysts were studied under the same condition and used as references (Figure 5.12). The results showed that 3.8 % coke content was formed on $NiMgO_x$ -s while the coke formation on $NiWMgO_x$ -s was below the detectable level.

To further reveal the change of surface properties during the stability test, CO_2 -TPD was carried out for the fresh and spent catalysts over both $NiMgO_x$ and $NiWMgO_x$ to determine the basic strength and CO_2 adsorption capacity (Figure 5.13). For all the catalysts tested, two strong CO_2 desorption peaks, a sharp peak at 113 °C and a broad one centered at 198 °C, were identified. The former peak was attributed to the desorption of CO_2 from weak basic sites, probably Mg sites and unreduced Ni sites on the solid solution support, while the latter one could be assigned to desorption of CO_2 that adsorbed near or on the Ni particles with medium basicity [202, 213]. The weak and medium basic sites are both beneficial for the activation of CO_2 while the CO_2 adsorbed on strong basic sites cannot participate in the methanation reaction [37]. *Operando* IR studies over NiUSY zeolites showed that both the CO_2 adsorbed on the weak basic sites of the support and the CO_2 adsorbed on the Ni particles can react with the atomic H to form formate species and further contribute to the production of methane [34]. Similar results were reported by Pan et al. over $Ni/Ce_{0.5}Zr_{0.5}O_2$ [36]. Thus, the total amount of CO_2 adsorption over each sample was estimated from the area under CO_2 -TPD

peaks and listed in Table 5.1. The volume of CO₂ desorbed from NiWMgO_x was almost twice of that from NiMgO_x, 102.3 μmol/g to 50.9 μmol/g, indicating that W addition prominently increased the amount of surface basic sites. After stability test, the NiWMgO_x-s showed almost the same CO₂ adsorption volume as the fresh one, while NiMgO_x-s had only 42.5 μmol/g CO₂ uptake compared to 50.9 μmol/g for the fresh NiMgO_x catalyst. Therefore, the W addition not only increased the amount of CO₂ adsorption sites but also remarkably promoted the stability of those sites according to the CO₂-TPD detection.

Figure 5.13 CO₂-TPD profiles of both fresh and spent NiMgO_x and NiWMgO_x catalysts.

Figure 5.14 H₂-TPR profiles of both fresh and spent NiMgO_x and NiWMgO_x catalysts.

Figure 5.14 displayed the H₂-TPR profiles of both NiMgO_x and NiWMgO_x along with the spent samples after the stability test. Prior to the reduction by H₂, samples were *in situ* pretreated in air at 500 °C for 60 min. A prominent H₂ consumption peak at 391 °C was clearly identified for fresh NiMgO_x, which was attributed to the reduction of Ni located at the outermost layer of the support [214, 215]. The small peak at around 757 °C could be assigned to the reduction of Ni²⁺ located deep in the lattice of the Ni-Mg solid solution [206]. After the stability test,

a small shoulder peak appeared at 290 °C over NiMgO_x, referring to the reduction of ‘unsupported’ free NiO, accompanied by the obvious decrease of the area under the peak at 391 °C. The change of H₂-TPR profile of NiMgO_x-s indicated that the Ni species in the outmost layer of the solid solution lost their interaction with the support during the stability test, resulting in the formation of free NiO and probably further sintering of Ni particle, which could be the main cause of the deactivation of NiMgO_x catalysts. The formation of free NiO agreed well with the XRD results of NiMgO_x-s. On the other hand, the H₂-TPR profile of fresh NiWMgO_x showed a H₂ consumption bulge between 300 - 900 °C along with a crest at 757 °C, which ascribed to the reduction of Ni species having different interaction strength with the support of Ni-Mg solid solution. The continuous H₂ consumption at the high temperature region pointed out that a diversity of Ni species were formed as a result of diffusion of NiO into the support after the W addition, from the outmost layer to subsurface layer and then to the deep lattice. It also has been reported that the NiWO₄ can be formed over Ni-W-Al mixed oxide by calcination at 1000 °C, which can be reduced by H₂ at approximately 800 °C [216]. However, the assignment of the peak at around 757 °C to Ni species located deep in the lattice of the solid solution was well supported by the lack of NiWO₄ peaks in the XRD patterns and the fact that a much lower calcination temperature was used in this study. No appearance of new peaks for the NiWMgO_x-s indicated that no change occurred in the interaction between Ni and the solid solution

support during the stability test for W doped Ni-Mg mixed oxide catalysts.

After being pretreated in H_2 at 500 °C for 60 min, the NiO species in the outmost layer, which less strongly interacted with the support, and NiO species of moderate interaction strength in subsurface layer and a part of NiO species located in deep lattice of Ni-Mg solid solution can be reduced to active metallic Ni [151, 214]. The reduction of those NiO species left different amounts of defects in accordance with their interaction strength with the support, which then became the anchoring sites for the Ni particles [207, 209]. Compared to the rest two kinds, NiO in the outmost layer with less anchoring sites was more fragile and more sensitive to structure change, as demonstrated by the transformation of this species into free Ni on $NiMgO_x$ after stability test, the sintering of which was responsible for the activity loss.

During the methanation over $NiWMgO_x$ catalysts, CO_2 can adsorb on Mg sites on the solid solution support [11], and probably also Ni sites [34], while H_2 was dissociated on metallic Ni particles [36]. The atomic H then reacted with the adsorbed CO_2 species to form formate species [37]. W doping promoted the formation of active monodentate formate species, leading to enhanced methanation activity. Furthermore, as shown in the H_2 -TPR profiles of $NiWMgO_x$, the addition of W gave rise to an enhancement of the diffusion of NiO into the Ni-Mg solid solution, which increased the anchoring sites for the reduced metallic Ni, resulted in strong resistance against sintering and promoted stability of $NiWMgO_x$.

5.4 Summary

The methanation of CO₂ was performed over a novel NiWMgO_x catalyst with W species highly dispersed in Ni-Mg solid solution matrix. Superior catalytic performance with CO₂ conversion of 83 % and CH₄ selectivity of 99 % was obtained at a low temperature (300 °C). NiWMgO_x catalyst also possessed a great anti-CO-poison ability and strong resistance against coke formation, demonstrating a long lifetime in the highly exothermic atmosphere of CO₂ methanation, over which indiscernible activity loss was observed during the stability test performed for 100 h either in the presence of 1 % CO gas at 275 °C or at a high temperature of 400 °C. *In situ* DRIFTS spectra revealed that the formation of monodentate formate species as active intermediates during CO₂ methanation process was facilitated by W-modified surface with comparison to Ni-Mg mixed oxide catalysts, which subsequently contributed to a significantly enhanced catalytic activity. Moreover, the W species played a critical role in promoting the formation of the surface CO₂ adsorption sites and enhancing their stability, according to CO₂-TPR results. Besides, H₂-TPR demonstrated that, with the aid of W addition, Ni-Mg interaction was strengthened via favoring the anchoring of the active Ni species and resistance to sintering, leading to largely enhanced stability of NiWMgO_x catalyst.

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Chapter 6 Combined experimental and theoretical studies of CO₂ hydrogenation over Ru/Al₂O₃ at ambient pressure: the role of interface O atom.

Although the methanation process has been thoroughly studied from the beginning of the 20th century, ambiguities remain for the activation mechanism, which is not only beneficiary for optimizing catalytic methanation systems, but also providing theoretical insights for other CO₂ utilization processes. A bi-functional mechanism was verified for oxides supported Pd catalysts, over which H₂ was dissociated over Pd particles and supplied to the CO₂ that adsorbed at a suitable metal oxide support to produce methane [91, 120, 121]. A similar reaction mechanism was also observed for Ni-based catalysts [113, 217]. Besides, the direct active dissociation of CO₂ over the metal particles has been proposed for Ru and Rh catalysts [87, 149, 154, 162, 218]. Another type of surface site with unique property that worth mentioning is the interface of supported catalyst, where dual sites of both a metal atom and a support atom are presented, which help to bind and activate the reactants more effectively [219, 220]. Besides, the direct contact with the oxide support changes the electron state of the interfacial metal atoms, leading to its distinctive catalytic properties. The incorporation of interface O atoms of oxide support in the reaction was observed as a result of the active participation of the interface in the reaction between CO and O₂ [221]. Recent

investigations have shown that the metal-oxide interface also played an essential role in CO₂ hydrogenation catalyzed by supported metal catalysts [122, 142, 167]. The catalytic behaviors of metal particles of different sizes have also been tentatively attributed to the acceleration of the dissociation of CO₂ at the metal-support interface [167, 222].

Herein, the hydrogenation of CO₂ over Ru/Al₂O₃ catalysts of three different loadings was examined, with the varying Ru structural configuration identified by the combination of EXAFS, H₂-O₂ titration and IRAS spectra for CO adsorption. Over 1% Ru/Al₂O₃, the catalyst with the lowest Ru loading, Ru monolayer, in which Ru atoms interact with the support directly, presented in a comparable density to that of three dimensional (3D) nanoclusters over 1% Ru/Al₂O₃, which exhibited high selectivity towards CO formation for the hydrogenation of CO₂ at ambient pressure. At higher Ru loadings, 3D Ru nanoclusters of multilayers were formed exclusively with an increase of active sites at the plateau of Ru nanoclusters. The catalytic activity test exhibited a contrary dependence for CH₄ and CO formation on the loadings, suggesting that two products were preferentially formed over different active sites. DFT calculations over two distinct Ru/Al₂O₃ models revealed that the RWGS pathway demonstrated a higher energy barrier than the methanation pathway on the top sites of 3D Ru nanoclusters while the CO formation was more favored on Ru sites with direct connection with the oxide surface. Besides, the stronger adsorption energy of CO₂ on Ru monolayers

led to a probable bias for the activation sites of CO_2 when both types of Ru sites were observed at a similar concentration. These results explained the variations in the activation energy for CO formation and CH_4 formation when changing the Ru loadings. The interchange between the O atom at the interface Ru-O-Al structure and the gaseous reaction was found as a result of the dissociation of CO_2 at the peripheral Ru sites, which was further proved experimentally by the isotope exchange.

6.1 Catalytic performance and characterization

6.1.1 Catalytic performance

Figure 6.1 CO_2 conversion (Left Axis) and CO yields (Right Axis) of Ru/Al₂O₃ catalysts with different metal loadings.

The temperature dependence of the CO₂ hydrogenation activity between 175 and 450 °C over the three different loading catalysts was presented in Figure 6.1. Since only two products, CH₄ and CO, were detected in the outlet gases, only the yield of CO was shown. Among the tested catalysts, 3% Ru/Al₂O₃ showed the highest CO₂ conversion activity in the entire tested temperature range with the onset temperature at around 200 °C and the maximum conversion of *ca.* 80% at 400 °C. A similar CO₂ conversion pattern but with a shift towards higher temperature was observed when decreasing the Ru loading to 2%. The CO₂ conversion started at 225 °C and increased monotonically over 1% Ru/Al₂O₃. On the other hand, the CO yield started at around 300 °C and increased with ramping temperatures for all three catalysts, but with a contrary dependence on the Ru loadings to that of the CO₂ conversion. The CO yield was the highest over 1% Ru/Al₂O₃ (*ca.* 17% at 450 °C), which was twice of that correspondingly produced over 3% Ru/Al₂O₃, suggesting that CO formation was suppressed while methane was favored with increasing Ru loadings.

Arrhenius plots of CH₄ and CO formation TOF (calculated on the basis of the Ru contents) of the as-prepared Ru/Al₂O₃ with different loadings were displayed in Figure 6.2, which showed excellent linearity in the temperature regime explored. The CH₄ TOF was the lowest over 1% Ru/Al₂O₃ and increased with increasing Ru loadings, while CO TOF demonstrated similar linearity but with contrary dependence on Ru loadings. Over 3% Ru/Al₂O₃, the apparent activation energy for

CH₄ formation was 64.2 kJ/mol while that for CO was 76.3 kJ/mol. The obviously higher formation energy of CO than that of CH₄ suggested these two reactions proceeded at different surface sites and/or follow different reaction pathways.

Figure 6.2 Arrhenius plots of CH₄ (Hollow Symbols) and CO (Solid Symbols) formation TOF over 1%, 2% and 3% Ru/Al₂O₃.

Moreover, a variation in CH₄ formation energy and CO formation energy was observed when changing the Ru loadings. When the Ru content was changed from 2% to 1%, the apparently activation energy for CH₄ formation estimated from the slopes increased from 66.5 to 73.6 kJ/mol, while that for CO formation decreased from 73.8 to 67.1 kJ/mol. Similarly, a change in activation energy of CH₄ and CO₂ formation on Pd/Al₂O₃ with different loadings has been attributed to the difference in active sites of the limiting steps for those two reactions, the metal and oxide

support surface, respectively [121]. A discrepancy in the apparent activation energy for CH_4 formation has also been observed for $\text{Rh}/\text{Al}_2\text{O}_3$ of different metal sizes [117].

6.1.2 Characterization on the structure of metal particles

Figure 6.3 (a, b, c) k^3 -weighted χ function and (d, e, f) corresponding Fourier transforms obtained on 1 % $\text{Ru}/\text{Al}_2\text{O}_3$ (top), 2 % $\text{Ru}/\text{Al}_2\text{O}_3$ (middle panels) and 3 % $\text{Ru}/\text{Al}_2\text{O}_3$ (bottom panels) catalysts (upper panels) or 15% water (lower panels).

Solid lines are EXAFS data, and dashed lines are fits.

Table 6.1 Structural parameters of the Ru/Al₂O₃ catalysts with different Ru loadings obtained from EXAFS spectra.

Sample	CN ^a	DWF ^b (10 ⁻³ Å)	r ^c (nm)	E ₀ ^d	d (nm)	Dispersion ^e (%)
1% Ru/Al ₂ O ₃	6.51 ± 0.4	3.51 ± 0.72	2.67 ± 0.01	2.62 ± 0.42	0.94	70.8
2% Ru/Al ₂ O ₃	7.29 ± 0.4	4.17 ± 0.21	2.67 ± 0.01	2.39 ± 0.50	1.27	52.4
3% Ru/Al ₂ O ₃	7.43 ± 0.4	4.27 ± 0.45	2.67 ± 0.01	2.49 ± 0.46	1.32	50.5

^a CN: Ru–Ru first shell coordination number.

^b DWF: Debye–Waller factor.

^c r: Ru–Ru first shell bond distance.

^d E₀: Energy shift.

^e Dispersion: Calculated on the basis of diameters estimated from CN

EXAFS data of the local environment of the coordinated atoms is highly responsive to changes in the particle dimensions. Recently, a correlation between the Ru-Ru first shell coordination number (CN) and the average diameter of metal particles was established by Karim [171, 223] by assuming an *hcp* hemispheric shape. Therefore, EXAFS experiments were performed over Ru/Al₂O₃ of the three different loadings and the resulted spectra were fitted carefully (Figure 6.3). To give a satisfactory fit, a bi-shell fitting including Ru–Ru and Ru–O was also tried, however only a single Ru–Ru scattering shell can fit the measured spectra, with the resulted structural parameters being presented in Table 6.1. An increase of CN from 6.51 to 7.29 was observed when Ru loading was changed from 1% to 2%, corresponding to an increase of the Ru particle size from 0.94 to 1.27 nm. Nonetheless, the further increase of Ru loading to 3% only resulted in a very small increase of the CN to 7.43, equaling to a particle diameter of 1.32 nm. Bearing in mind the assumption of hemispheric shapes for the metal particles, the dispersions of the three as-prepared catalysts were calculated and presented in Table 6.1

Table 6.2 Structural parameters obtained from H₂-O₂ titration and the fraction of different surface structures estimated from IRAS spectra for CO adsorption (Figure S1).

Sample	Total surface metal sites	Dispersion ^a	Ru sites at the periphery (2130 & 2070 cm ⁻¹)	Ru sites on monolayers (~ 2070 cm ⁻¹)	Ru top sites on multilayer clusters (2000 - 2050cm ⁻¹)
1% Ru/Al ₂ O ₃	$2.63 \times 10^{19}/\text{g}$	44.5%	10.0 %	45.4 %	44.6 %
2% Ru/Al ₂ O ₃	$4.14 \times 10^{19}/\text{g}$	35.1%	9.7 %	6.8 %	83.5 %
3% Ru/Al ₂ O ₃	$5.71 \times 10^{19}/\text{g}$	32.2%	8.4 %	1.1 %	90.5 %

^a Calculated from the H₂-O₂ titration results

However, with the TEM technology available, we cannot obtain a direct observation of the metal particles due to the unsuccessful differentiation of the Ru particles from the support. Thus, H₂-O₂ titration was carried out to further investigate the variation in the amount of exposed surface sites of the as-prepared catalysts, in which oxygen pre-covered Ru surface was readily titrated by 10% H₂/Ar at 250 °C with the results being presented in Table 6.2. The amount of surface metal sites estimated from the H₂ consumption was 2.63×10^{19} , 4.14×10^{19} and 5.71×10^{19} /g for 1% Ru/Al₂O₃, 2% Ru/Al₂O₃ and 3% Ru/Al₂O₃, respectively, corresponding to a metal dispersion of 44.5%, 35.1% and 32.2%, which was significantly lower than the values obtained from the above EXAFS estimations. The discrepancy in dispersion values suggested that the assumption of hemispheric shapes used in EXAFS data was not adequately accurate for the description for the catalysts in this study. Consequently, a model of multilayer particles has been proposed with the merit in modeling large Ru clusters with a low CN [223].

In combining with surface sensitive characterization, the chemisorption of probe molecular can offer helpful information on the structure of metal particles in light of the decisive role of surface sites on the adsorbing configurations [224]. For examples, the different chemisorption configurations of the gaseous probe molecules can be easily recognized by infrared spectroscopy and correlated to the interaction extent between surface sites and the support [122, 225]. Inspired by this,

the adsorption of carbon monoxide (CO) accompanied by infrared reflection absorption spectroscopy (IRAS) at 25 °C was performed over the *in-situ*-reduced Ru/Al₂O₃ catalysts, and the resulted spectra after the chemisorption for 30 min were presented in Figure 6.4. Two peaks of high frequency (HF) at approximately 2130 and 2072 cm⁻¹, along with one at a lower frequency (LF) between 2000 and 2050 cm⁻¹ were observed over all the catalysts. For a better comparison, the spectra were displayed in Kubelka–Munk (KM) units and normalized by the peak height at 2130 cm⁻¹. The peak at the LF region was assigned to the linear CO adsorbed on Ru⁰ top sites of metal particles that interacted with all surrounding sites by Ru-Ru bonds [226, 227]. The blue shift of this peak when increasing the coverage was resulted from the dipole-dipole coupling when adsorbed on bulk metal particles, which was well documented [228, 229].

Figure 6.4 IRAS spectra for CO adsorption at 25 °C of Ru/Al₂O₃ catalysts.

The other two peaks at a higher frequency, 2130 and 2072 cm^{-1} , were associated with the CO adsorbed on Ru that was perturbed by bonds from the support [229, 230]. The disproportional intensity of these two peaks suggested that at least two different surface species were accounted for the rise of the peaks at 2130 and 2072 cm^{-1} . Thereafter, the peak at 2130 cm^{-1} was ascribed to the symmetric stretches of bicarbonyl species, which adsorbed at the peripheral interfacial Ru sites of metal particles. Noticeably, the peak at 2072 cm^{-1} was contributed from both the asymmetric stretches of bicarbonyl species and the vibration of linear adsorbed CO on Ru sites of monolayers. The assignment of these two peaks has been substantiated in previous studies [26, 227, 229-231]. The IRAS spectra were deconvoluted based on the above assignments into Gaussian sub-bands (Figure 6.5), which then served as quantitative indications of different surface structures using the coefficient values acquired by Yokomizo et al. [230], 26×10^6 for linear adsorbed CO and 13×10^6 for bicarbonyls, and the results were listed in Table S1. The portion of bicarbonyl species varied insignificantly. The percentage of Ru top sites of large metal particles has almost doubled when Ru loadings increased from 1% to 2%, while further increasing Ru loading to 3% only resulted in a relatively small increase in this ratio. Thus, by the evolvement of the IRAS spectra for CO adsorption, it can be concluded that both Ru monolayers and 3D metal clusters of multiple layers were present in an appreciable concentration over 1% Ru/ Al_2O_3 in contrast to that 3D metal clusters were prevailing over

Ru/Al₂O₃ with metal loadings of 2% and 3%.

Figure 6.5 The deconvoluted spectra of the IRAS for CO adsorption.

6.2 First-principle calculations

6.2.1 Optimization of model Ru/Al₂O₃ structures

DFT calculations were performed over two representative Ru/Al₂O₃ model structures to gain a better understanding of the reaction mechanisms between CO₂ and hydrogen. The first calculation model adopted was a Ru₃₅ nanocluster resided on the fully dehydroxylated (100) terminations of γ -Al₂O₃ surface (Figure 6.6a). After relaxation, the Ru₃₅ cluster was stabilized on the Al₂O₃ (100) surface by bridging through Ru-Al and Ru-O bonds, with a bond length of 2.55-2.60 and

1.98-2.07 Å, respectively. The structure of the second model, single layer Ru₉ on Al₂O₃ was obtained after the adsorption and optimization of the Ru monolayer of 9 atoms on the Al₂O₃ (100) surface, which resulted in the formation of a no-plane single layer structure (Figure 6.6b). The calculated bond length of Ru-Al and Ru-O were 2.50-2.53 and 1.89-2.04 Å in Ru₉/Al₂O₃(100), respectively, slightly shorter than those in Ru₃₅/Al₂O₃ (100), suggesting that the interactions between Ru atom and Al₂O₃ surface in Ru₉/Al₂O₃ (100) were stronger than that in Ru₃₅/Al₂O₃.

Figure 6.6 The optimized structure of Ru₃₅ cluster on Al₂O₃ catalysts (a) and single layer Ru₉ on Al₂O₃ (b).

6.2.2 Calculation on the CH₄ formation pathway

The calculated reaction pathways for CO₂ reduction to CH₄ on both Ru₃₅/Al₂O₃ and single layer Ru₉/Al₂O₃ were shown in Figure 6.7 and Figure 6.8. In general, the calculated reaction mechanism of CH₄ formation on Ru₃₅/Al₂O₃ is similar to that on Ru₉/Al₂O₃, starting with the formation of the HCOO* species (“*” represents an adsorbed species) [11, 31], which is then hydrogenated to HCOOH* and further to H₂COOH* [59, 232, 233]. As a result of the cleavage of the C-OH

bond, the dissociation of H_2COOH^* leads to the formation of both H_2CO^* and OH^* , followed by further hydrogenation of H_2CO^* into H_3CO^* and OH^* into H_2O^* , respectively. The next step is proceeded via the cleavage of the C-O bond of H_3CO^* to produce H_3C^* and O^* , which is then hydrogenated into CH_4 and H_2O . The rate-limiting step of the CH_4 pathway on $\text{Ru}_{35}/\text{Al}_2\text{O}_3$ is found to be the second hydrogenation step of the HCOO^* species, with a predicted barrier of 0.69 eV (66.53 kJ/mol) from H_2COOH^* to H_2CO^* . The formation pathway of CH_4 on $\text{Ru}_9/\text{Al}_2\text{O}_3$ is similar to that on $\text{Ru}_9/\text{Al}_2\text{O}_3$ but with a relatively higher energy barrier of 0.80 eV (77.14 kJ/mol).

Figure 6.7 Potential energy profiles for CO₂ hydrogenation to CH₄ on Ru₃₅/Al₂O₃ and Ru₉/Al₂O₃.

Figure 6.8 The optimized structure of important station points on potential energy profiles for CO₂ hydrogenation to CH₄ on Ru₉/Al₂O₃.

6.2.3 Calculation on the CO formation pathway

The reaction pathway for the reversed water gas shift significantly differs over Ru₃₅/Al₂O₃ and Ru₉/Al₂O₃ (Figure 6.9). The CO₂ adsorbed on the top sites of the Ru₃₅ cluster directly dissociates into CO* and O*, which is the rate-determining step for the CO formation pathway, holding a reaction energy of -0.88 eV and an energy barrier of 0.84 eV (80.04 kJ/mol). The resulted O* that adsorbed at an adjacent Ru site is then reduced by the adsorbed hydrogen species via two steps to produce H₂O. Compared to the CH₄ pathway, the CO formation holds a higher energy barrier, implying that the CH₄ reaction is more favorable on the top site of Ru₃₅/Al₂O₃. On the other hand, the adsorption of CO₂ is remarkably stronger over Ru₉/Al₂O₃ than that over Ru₃₅/Al₂O₃. The activation energy for the CO production on the supported Ru single layers is 0.71 eV (68.47 kJ/mol), appreciably lower than that on Ru₃₅/Al₂O₃. Interestingly, DFT calculation demonstrates that, over Ru₉/Al₂O₃, the O* atom dissociated from CO₂ can easily bridge with the Lewis acid center of Al atoms to form a new Al-O-Ru Bond, which is an exothermic step with an energy reduction of 0.34 eV, resulting in the formation of the structure IN1. The next step is the hydrogenation of an interfacial O atom via two transition states, TS1 and TS2 with an energy barrier of 0.31 and 0.29 eV, respectively. As a consequence, a dynamic incorporation of the interfacial O into the final products of CO₂ hydrogenation is expected.

Figure 6.9 Potential energy profiles for CO₂ hydrogenation to CO on Ru₃₅/Al₂O₃ and Ru₉/Al₂O₃, along with the structure IN1.

Variations in particle structures have been reported to cause changes in the dissociative behaviors of H₂ on supported metal catalysts. Nevertheless, there is no consensus on this issue. By H₂-D₂ exchange reaction, H₂ dissociation was found to be independent on the particles sizes of Au on TiO₂ [234]. A synergetic effect between metal particles and the support at the perimeter interface of Au/TiO₂ was suggested to be responsible for activated H₂ dissociative adsorption, due to the fact that Au atoms at the peripheral alone were inactive towards for H₂ dissociation [235]. For Ru/Al₂O₃, energetically favorable sites for H₂ dissociation were prevailing over larger nanoparticles, resulting in a promoted dissociation of H₂ into H atoms with high diffusivity [236]. However, a contrary trend was observed on Ru/TiO₂, over which a promoted formation of dissociated H with a high mobility was associated with a high metal dispersion [237]. Nonetheless, the H₂ dissociation on Ru was considered to be fast enough to reach equilibrium and not a

rate determining step during CO₂ methanation [78]. Thus, the H₂ dissociation step is not discussed herein.

The energy barriers obtained above suggest that the production of CH₄ over top sites of Ru₃₅/Al₂O₃ is easier than that on Ru₉/Al₂O₃ while the production of CO on Ru₉/Al₂O₃ is more facile than on top sites of Ru₃₅/Al₂O₃. Considering the Ru clusters of these two models occupy similar cross section on the support after the relaxation, the difference in reaction pathway shall be interpreted as a result determined by the properties of the reaction sites other than merely the metal particle size effect. For CO₂ adsorbed on Ru sites in monolayers, more negative charges can be transferred to the adsorbed CO₂^{*} than that on top Ru sites of multilayer clusters, due to the direct electron contribution from the underneath oxide support [167], which relatively favors the dissociation of CO₂ [86]. Furthermore, the exchange between O atoms dissociated from CO₂ and O atoms in the interface Ru-O-Al structures of the periphery of metal particles is expected as a spontaneous process accompanying the RWGS at the vicinity of the metal-support interface. With increasing Ru metal loading, the ratio of Ru sites with similar local environments to that of the top sites of Ru₃₅/Al₂O₃ to that of the Ru sites directly linked to the support increases, resulting in an increase in the selectivity to CH₄ for CO₂ hydrogenation.

Over 1% Ru/Al₂O₃, the Ru monolayer with similar structure to that of Ru₉/Al₂O₃ was observed in a considerable amount besides from 3D nanocluster, as

demonstrated by IRAS spectra for CO adsorption (Figure 1). DFT calculations revealed that CO₂ adsorption was energetically favored on monolayers than on top sites of large clusters, which led to a preference for hydrogenation sites for CO₂ when both sites were presented in a comparable concentration, resulting in high selectivity to produce CO on 1% Ru/Al₂O₃. Increasing Ru loading led to the formation of large 3D nanoclusters, which resembled the Ru₃₅/Al₂O₃ model used in the calculations. As a consequence, the CH₄ formation rate increased and the CO formation was suppressed.

On the other hand, the apparently higher formation energy of CO than that of CH₄ observed over 3% Ru/Al₂O₃ has also been reported by Kwan et al. [119], which is in good agreement with our calculation results that those two reactions were carried out preferentially on different surface Ru structures over Ru/Al₂O₃, Ru sites that interact directly with the support and the top Ru sites, respectively. Thereafter, the variation in apparent activation energy when changing Ru loading can be attributed to the structural differences in the predominant metal structures. Over 1% Ru/Al₂O₃ catalyst, the activation energy of CH₄ and CO obtained from the kinetic measurement is 73.6 kJ/mol and 67.1 kJ/mol, respectively, which were highly comparable to our calculated value on Ru₉/Al₂O₃. This was validated by the fact that the representative Ru structure on 1% Ru/Al₂O₃ is similar to Ru₉/Al₂O₃. To the contrary, CH₄ formation held an activation energy that ~14 kJ/mol lower than CO formation over Ru₃₅/Al₂O₃. Admittedly, increasing Ru loading led to the

enrichment of Ru sites with similar local environment to that of the top sites of $\text{Ru}_{35}/\text{Al}_2\text{O}_3$, which not surprisingly, resulted in the increase of the activation energy of CH_4 and the decrease of that of CO [84]. Another calculation result that worth mentioning is that on the vicinity of the peripheral interface, the adsorbed CO_2 follows the RWGS to yield CO, resulting in the formation of new Ru-O-Al structures, probably leading to the exchange of O atoms between gaseous reaction and the interfacial O bonds, which will be further discussed below.

6.3 Mass Spectrometry Experiments

6.3.1 Methanation of C^{18}O_2 and H_2

Figure 6.10 MS signals as a function of time when H_2 was added into the feed gas of $\text{C}^{18}\text{O}_2/\text{He}$ over 3% $\text{Ru}/\text{Al}_2\text{O}_3$ at 350 °C.

Figure 6.11 MS signals as a function of time when H_2 was added into the feed gas of $\text{C}^{18}\text{O}_2/\text{He}$ over 3% $\text{Ru}/\text{Al}_2\text{O}_3$ at 350 °C for the second running, which is previously exposed to C^{18}O_2 and H_2 for 90 min at 350 °C.

Mass spectrometry (MS) experiments of CO_2 hydrogenation at ambient pressure with the substitution of C^{16}O_2 by its isotope products C^{18}O_2 were carried out to study the incorporation mechanism of peripheral O into the final products, while the mass signals of possible products were monitored in the effluent gas (Figure 6.10). After a stable mass signal was reached in the CO_2/He only feeding gas, H_2 was introduced into the gas mixture ($\text{H}_2 : \text{CO}_2 = 4\% : 1\%$). Interestingly, a prominent signal pattern was found for $m/z=18$, with a distinct peak at *ca.* 6 min, which was obviously different from the result of exposing the tested catalysts to the same reaction mixture for the second run after an interval of He purge for removing unreacted surface species (Figure 6.11).

Figure 6.12 Comparison of MS signals of $m/z=18$ and $m/z=17$ as a function of time when H_2 was added into the feed gas of $C^{18}O_2/He$ over 3% Ru/Al_2O_3 for two consecutive runs at 350 °C.

The difference in the signal pattern for $m/z=18$ in the two consecutive runs reflects that a consumable component in the solid catalysts have participated in the reaction. It is worth mentioning that the signal of $m/z=18$ also received contributions of the ^{18}O fragment from $C^{18}O$, $C^{18}O_2$ and $H_2^{18}O$, besides from the major contribution from $H_2^{16}O$. However, no similar peak-like feature over the dominant m/z signals of the three products ($m/z=30$, 48 and 20) suggested the observed pattern of $m/z=18$ can informatively represent the change of the $H_2^{16}O$ concentration, which, in the initial few minutes, has largely exceeded the amount that produced from the 5% $C^{16}O_2$ presented in the isotope-labeled $C^{18}O_2$ gas. This

conclusion was further supported by the resemblance of the signal pattern of $m/z=17$ to that of $m/z=18$, which was the second dominate fragment signals of H_2^{16}O and free from other interferences.

6.3.2 Methanation of C^{16}O_2 and H_2 over the isotope-labeled catalysts

Figure 6.13 DRIFT spectra collected when the 3% $\text{Ru}/\text{Al}_2\text{O}_3$ (initially in H_2 and CO_2 flow at $350\text{ }^\circ\text{C}$ for 90 min) was heated up to $450\text{ }^\circ\text{C}$ in He at a ramp of $20\text{ }^\circ\text{C}/\text{min}$, which was then exposed to 10% H_2/He and held there for 5 min, 30 min and 60 min (from bottom to top).

To show the dynamic interchange between the peripheral O and the products, another test with no isotope labeled reactant ($\text{C}^{16}\text{O}_2 + \text{H}_2$) was then performed with the used catalyst after the above isotope exchange test. Prior to the exposure to C^{16}O_2 and H_2 at 350 °C, the catalyst was treated at 450 °C under 10% H_2/He for another 60 min to remove any unreacted surface species (Figure 6.13).

Figure 6.14 MS signals as a function of time when H_2 was added into the feed gas of $\text{C}^{16}\text{O}_2/\text{He}$ over 3% $\text{Ru}/\text{Al}_2\text{O}_3$ at 350 °C, which is previously exposed to C^{18}O_2 and H_2 for 90 min at 350 °C.

The *in situ* DRIFTS was carried out to explore the effective removal of the surface species formed at 350 °C in the gas mixture of CO_2 and H_2 by 10% H_2/He treatment at 450 °C for 60 min. After exposure to CO_2 and H_2 for 90 min, distinct bands at 2000 cm^{-1} and 1595 cm^{-1} were observed. While the former one was ascribed to CO^* [81], the latter together with the small one at 1390 cm^{-1} , were

assigned to formate species [31], which served as the intermediates for RWGS and methanation, respectively. Furthermore, the observed peaks in the CH_x region at 3017 cm^{-1} and 2906 cm^{-1} were the vibration bands of CH_4^* and CH_3^* species [218]. Upon heating up to $450\text{ }^\circ\text{C}$ in He at $20\text{ }^\circ\text{C/min}$, the band of CO^* disappeared quickly while the rest peaks were still recognizable. However, after switching the reaction gas to 10 % H_2/He , the remaining surface species vanished in less than 30 min, which substantiated that the treating process at $450\text{ }^\circ\text{C}$ can effectively remove the surface species formed during the CO_2 hydrogenation at $350\text{ }^\circ\text{C}$.

Figure 6.15 MS signals as a function of time when H_2 was added into the feed gas of $\text{C}^{16}\text{O}_2/\text{He}$ over pristine 3% $\text{Ru}/\text{Al}_2\text{O}_3$ at $350\text{ }^\circ\text{C}$. The pristine catalysts refers to as-calcined catalysts which is only pretreated in 10% H_2/He for 60 min at $500\text{ }^\circ\text{C}$ before the test.

After H_2 addition in the reaction gas, the signal of $m/z=20$ (H_2^{18}O) immediately rose and peaked at around 6 min, indicating a substantial yield of H_2^{18}O , besides from the expected formation of C^{16}O and CH_4 (Figure 6.14). Nevertheless, the absence of C^{18}O and C^{18}O_2 has fully excluded the possibility that the ^{18}O elements of H_2^{18}O were originated from any gaseous or residual C^{18}O_2 . The pristine 3% $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst without the previous exposure to C^{18}O_2 and H_2 was tested following the same procedure, the results of which showed no detectable formation of H_2^{18}O (Figure 6.15). These results clearly proved that H_2^{18}O was originated from the incorporation of O^{18} implemented during the last exposure to isotope-labeled reactants.

Scheme 6.1 Proposed reaction pathway of CO_2 methanation over $\text{Ru}/\text{Al}_2\text{O}_3$.

Combining with the DFT calculation results, the observance in the isotope-labeled experiments was the result of the substitution of the ^{16}O at the periphery of Ru clusters by new $\text{Ru}-^{18}\text{O}-\text{Al}$ structures, the O^{18} in which was then incorporated into H_2^{18}O during the subsequent exposure to C^{16}O_2 and H_2 . This

active participation of peripheral O species in the activation process of CO₂ agreed well with our DFT calculations. Thus, based on the experimental results and theoretical calculations, the reaction mechanism of CO₂ hydrogenation at ambient pressure on Ru/Al₂O₃ is proposed (Scheme 6.1). Over the top sites of Ru multilayer clusters, CH₄ reaction channel is preferentially favored. In contrast, CO₂ that is adsorbed on Ru sites that directly connect to the support follows the RWGS pathway to form CO. Noticeably, the dissociation of CO₂ on the Ru sites that adjacent to the periphery of the metal leaves an active O* that further bridges with Al site of the support to form a ‘new’ interface Ru-O-Al bond, by which the dissociative products are effectively stabilized. As a consequence, the interfacial O at the periphery of Ru clusters not only plays a significant role in the reaction selectivity but also dynamically participates in the activation process of CO₂.

6.3.3 Quantification of peripheral O

The same MS experiment was performed over pure Al₂O₃, 1% Ru/Al₂O₃ and 2% Ru/Al₂O₃ (Figure 6.16). Not surprisingly, no traceable formation of H₂¹⁸O was observed over pure Al₂O₃ when exposing to H₂ and C¹⁶O₂ after 90 min reaction in H₂ and C¹⁸O₂. To quantitatively compare the incorporation amount of the peripheral O in the final products, the peak area under the signal of $m/z=20$ obtained over the three catalysts was integrated to show the amount of the H₂¹⁸O formed, which further correlated to the interchangeable peripheral O atoms, as listed in Table 6.3.

Table 6.3 Physical properties and MS experiment results of Ru/Al₂O₃ with different Ru loadings.

Sample	Area under MS signals ^a	Periphery Ru sites ^b
1% Ru/Al ₂ O ₃	3.86×10^{-11}	2.63×10^{18}
2% Ru/Al ₂ O ₃	5.81×10^{-11}	4.01×10^{18}
3% Ru/Al ₂ O ₃	7.22×10^{-11}	4.80×10^{18}

^a Integrated area under MS signals of H₂¹⁸O ($m/z=20$) and normalized by catalyst weight.

^b The amount of periphery was obtained on the basis of H₂-O₂ titrations and IRAS of CO adsorptions.

Figure 6.16 Comparison of MS signals of $m/z=20$ as a function of time when H₂ was added into the feed gas of C¹⁶O₂/He over Ru/Al₂O₃ of different loadings at 350 °C after being exposed to C¹⁸O₂ and H₂.

Figure 6.17 MS signals as a function of time when H_2 was added into the feed gas of $\text{C}^{16}\text{O}_2/\text{He}$ over 1% $\text{Ru}/\text{Al}_2\text{O}_3$ (top) and 2% $\text{Ru}/\text{Al}_2\text{O}_3$ (bottom) at 350 °C, which is previously exposed to C^{18}O_2 and H_2 for 90 min at 350 °C and then treated in 10% H_2/He for 60 min and purged in He for 60 min at 500 °C.

Figure 6.18 Correlations between the amount of periphery Ru sites and the area under $m/z=20$ during MS experiments.

The amount of periphery Ru sites was calculated based on the total available surface Ru sites by $\text{H}_2\text{-O}_2$ titration and the ratio of interfacial Ru sites at the periphery that determined by IRAS of CO adsorption. A linear correlation was observed between these two values (Figure 6.18), a strong quantitative consolidation of the involvement of the metal-support interface during the activation process of CO_2 by H_2 under atmospheric pressure.

6.4 Summary

EXAFS, $\text{H}_2\text{-O}_2$ titration and CO adsorption accompanied by IRAS were

employed to explore the structure of metal particles over Ru/Al₂O₃. A model of Ru multilayers has been applied, by which the abundance of Ru monolayers on 1% Ru/Al₂O₃ and the prevailing presence of 3D Ru nanoclusters on 2% and 3% Ru/Al₂O₃ was recognized. Combined experimental data and theoretical calculations, we identified the active sites for RWGS and methanation of CO₂ over Ru/Al₂O₃ catalysts, the Ru sites with direct contact with the support and the Ru top sites of multilayer Ru clusters, respectively. The dissociative adsorption of CO₂ at the Ru sites close to the periphery leaves O* at an adjacent Ru site to facilitate bridge with the surface Al site from the support, resulting in the formation of new Ru-O-Al structures, which stabilizes the transitional state, contributing to the effective activation of CO₂. Further evidence of isotope-exchange mass spectrometry experiments using C¹⁸O₂ revealed the dynamic participation of the O atoms of periphery Ru-O-Al bonds in the hydrogenation of CO₂.

Chapter 7 Conclusions and future perspectives

7.1 Conclusions

In this thesis, Ni-based catalysts with improved catalytic performance have been synthesized for CO₂ methanation. Besides, the structure sensitive reaction mechanism for CO₂ hydrogenation at ambient pressure has been comprehensively studied over prototype Ru/Al₂O₃ catalysts. The merits and discoveries are summarized as following.

Ni/Y₂O₃ catalysts showed excellent catalytic performance for CO₂ methanation. When solids obtained from the hydrothermal treatment of Y₂(NO₃)₃ solutions with the addition of urea, Y₄O(OH)₉(NO₃), was used as the precursor for preparation of Ni/Y₂O₃ catalysts, the CO₂ methanation activity has been significantly improved. CO₂-TPD was carried out to study the surface basicity of the as-prepared catalysts, the results of which revealed an enrichment of basic sites over the catalysts prepared from Y₄O(OH)₉(NO₃), especially those of medium basicity that played a significant role in CO₂ activations. Noticeably, over Ni/Y₂O₃ with higher metal loadings than 10%, strong basic sites were presented, which was accompanied by inferior stability and high sensitivity to coke formation. DRIFTS studies have been performed to explore the reaction mechanism of CO₂ methanation over Y₂O₃ supported Ni catalysts. Resulted spectra revealed that CO₂ adsorption led to the formation of carbonates species, which further reacted with H species to form surface formate species. Subsequently, formates were

hydrogenated into CH_4 , which probably served as the rate-determining step. Interestingly, the adoption of different support precursor during the preparation altered the reactivity of formate species toward H , which was likely to be responsible for the improved activity for CO_2 methanation over $\text{Ni/Y}_2\text{O}_3$ catalysts prepared from $\text{Y}_4\text{O}(\text{OH})_9(\text{NO}_3)$.

Modifications of conventional Ni/MgO catalysts by a third dopant via a homogeneous precipitation method were carried out. Compare to the one obtained via traditional impregnation, much improved catalytic performance was achieved on the one prepared by the homogeneous precipitation method. W, Mo, Fe, Co, Mn and Cu were incorporated into the mixed oxide catalysts, among which NiWMgO_x demonstrated both superior activity and great selectivity to CH_4 . Besides, promoted anti-sintering stability and an anti-CO-poisoning ability were obtained after W addition. XRD and HRTEM-EDX results suggested that W has highly dispersed in the Ni-Mg solid solution. Mechanism studies by *in situ* DRIFTS experiments revealed that monodentate formate species was more active towards H_2 to yield CH_4 if compared to bidentate formate species. W addition has significantly promoted the formation of active monodentate formate species during CO_2 methanation. Besides, CO_2 -TPD results reflected that W additions greatly promoted the formation of stable surface basic sites. H_2 -TPR profiles exhibited that Ni species in NiWMgO_x diffused into deep lattice of Ni-Mg solutions in contrast to that most of the Ni species was located at the first few layers in

NiMgO_x. This caused a difference in the amount of anchoring sites for the active reduced Ni species.

Combined results of chapter 4 and chapter 5, a fine tune of the interaction between Ni and the supports was required for the realization of both superior methanation activity and robust stability. An interaction that was too weak probably led to unpredictable sintering of Ni particles during the high-demanding industrial running, also interpreted as being vulnerable to elongated high temperature exposure. Conversely, if the interaction between Ni species and the support was too strong to break, the pretreatment by H₂ reduction cannot create an adequate amount of surface metallic species, which resulted in the inferior catalytic performance. Ideally, the metal-support interaction should be strong enough to offer enough anchor sites for the highly dispersed surface active sites, however not too strong to prevent the Ni²⁺ from being reduced to active metallic form. In this thesis, the variation of metal support interaction has been explored by either applying different precursors or adding dopants.

Besides from the development of effective Ni-based catalysts systems for CO₂ methanation, mechanistic studies on Ru/Al₂O₃ as a targeted catalyst system were carried out. Activity results demonstrated that a high yield of CO was presented on Ru/Al₂O₃ with Ru loadings as low as 1% while on 2% and 3% Ru/Al₂O₃ CH₄ was preferentially formed. Further kinetic measurements revealed a counter dependence on Ru loadings for CO and CH₄ formation rates, along with

a variation in the activation energy for both products when Ru loadings changed. Characterization on the surface metal structures by EXAFS, $\text{H}_2\text{-O}_2$ titration and IRAS of CO adsorption identified that Ru monolayers were abundant over 1% Ru/ Al_2O_3 while most Ru sites were presented as 3D multilayers nanoclusters over 2% Ru/ Al_2O_3 and 3% Ru/ Al_2O_3 . DFT calculations were performed on two model catalysts system of Ru₉/ Al_2O_3 and Ru₃₅/ Al_2O_3 , as the representative structures for Ru monolayers supported on Al_2O_3 and the representative structures for 3D Ru nanoclusters supported on Al_2O_3 , respectively. Computational results revealed that a lower activation energy for CO formation than that for CH_4 formation on Ru sites of monolayers directly connecting to the support. In contrast, on the top sites of 3D Ru nanocluster, the CH_4 reaction pathway exhibited a lower activation energy than the CO reaction pathway, which agreed well with the experimental results. An important reaction process of the incorporation of interfacial O at the peripimeters of Ru particles into the final products of CO_2 hydrogenation has been predicted, which was further verified by isotop-exchange MS experiments.

7.2 Future perspectives

On the basis of the above-mentioning results, some research topics are proposed for further studies. In chapter 4, we demonstrated the significant effects of different precursors for the support of Ni/ Y_2O_3 on their catalytic performance of CO_2 methanation. More candidates can be explored to offer a conclusive result. Characterization included XRD, BET, TPR and TPD gave a structural evidence to

interpret the difference in activity results. Further evidence can be found in metal dispersions, electron states, morphologies and so on, which are available by H₂-O₂ titration, chemisorption, XPS, EXAFS, TEM and SEM. Moreover, a tentative mechanism was proposed based on *in situ* DRIFTS spectra involving carbonates and formates. Isotope experiments can be carried out to trace the reaction passage for key intermediates.

In chapter 5, a novel Ni-W-Mg catalyst was prepared for CO₂ methanation. The structural properties responsible for the improved activity and stability were studied. Besides, a key intermediate, monodentate formate species has been identified, which was favorably formed after W addition. DFT calculations can be carried out to study the structural changes after W adding in the Ni-Mg solid solution and the role of W in the reaction process. Furthermore, the special role of W doping in the catalysts has also been reported in other systems, raising a question about the unique properties that distinguish W element from the others on an atomic and electronic perspective. The Cu doped catalysts showed an obviously different reaction pattern from other catalysts, with high selectivity for CO formation. Thus, the doping content should be varied to examine how the catalytic behaviors changed from methanation to RWGS by monitoring the surface species and studying the structural parameters. Last but not the least, more candidates for doping can be considered .

Reaction mechanisms over Ru/Al₂O₃ with different dominant metal structures

were studied in chapter 6. Kinetic measurements and DFT calculations exhibited that CO formation and CH₄ formation was favored over supported monolayers and 3D nanoclusters, respectively, which was attributed to the altering of Ru electron environments by the direct connection to the support. Different support precursors such as AlOOH, Al₂O₃ and Al(OH)₃ can be applied to prepare Al₂O₃-related catalysts in order to tune the formation of the metal support interface [198], which shall be explored in Ru/Al₂O₃ system. Besides, a formation of new Ru-O-Al interfaces was verified as a spontaneous process accompanying the RWGS at the perimeters of Ru particles by theoretical calculations and mass spectrometry experiments. As a consequence, a disintegration of Ru particles can be expected as the result of weakening of Ru-Ru bonds [81, 172].

References

- [1] Dlugokencky E., in, National Oceanic & Atmospheric Administration, Earth System Research Laboratory, 2016.
- [2] Broecker W.S., *Science*, 278 (1997) 1582.
- [3] Clark P.U., Pisias N.G., Stocker T.F., Weaver A.J., *Nature*, 415 (2002) 863.
- [4] Ruhlemann C., Mulitza S., Muller P.J., Wefer G., Zahn R., *Nature*, 402 (1999) 511.
- [5] Wunsch C., *Science*, 298 (2002) 1179.
- [6] Stocker T.F., Schmittner A., *Nature*, 388 (1997) 862.
- [7] Stouffer R.J., Yin J., Gregory J.M., Dixon K.W., Spelman M.J., Hurlin W., Weaver A.J., Eby M., Flato G.M., Hasumi H., Hu A., Jungclaus J.H., Kamenkovich I.V., Levermann A., Montoya M., Murakami S., Nawrath S., Oka A., Peltier W.R., Robitaille D.Y., Sokolov A., Vettoretti G., Weber S.L., *Journal of Climate*, 19 (2006) 1365.
- [8] Wood R.A., Keen A.B., Mitchell J.F.B., Gregory J.M., *Nature*, 399 (1999) 572.
- [9] Rao A.B., Rubin E.S., *Environmental Science & Technology*, 36 (2002) 4467.
- [10] Jacobson M.Z., *Journal of Geophysical Research: Atmospheres*, 107 (2002) ACH 16.
- [11] Wang W., Wang S.P., Ma X.B., Gong J.L., *Chem. Soc. Rev.*, 40 (2011) 3703.

- [12] Cheng D.J., Negreiros F.R., Apra E., Fortunelli A., *Chemsuschem*, 6 (2013) 944.
- [13] Peters M., Kohler B., Kuckshinrichs W., Leitner W., Markewitz P., Muller T.E., *Chemsuschem*, 4 (2011) 1216.
- [14] State Plastic And Paper Bag Legislation, N.C.o.S. Legislatures, <http://www.ncsl.org/research/environment-and-natural-resources/plastic-bag-legislation.aspx>
- [15] United Nations Framework Convention on Climate Change, t.U. Nations, <http://unfccc.int/2860.php>
- [16] Goeppert A., Czaun M., Prakash G.K.S., Olah G.A., *Energ. Environ. Sci.*, 5 (2012) 7833.
- [17] Liu L., Zhao C., Xu J., Li Y., *Appl. Catal. B: Environ.*, 179 (2015) 489.
- [18] Wang S.P., Yan S.L., Ma X.B., Gong J.L., *Energ. Environ. Sci.*, 4 (2011) 3805.
- [19] Rochelle G.T., *Science*, 325 (2009) 1652.
- [20] Banerjee R., Phan A., Wang B., Knobler C., Furukawa H., O'Keeffe M., Yaghi O.M., *Science*, 319 (2008) 939.
- [21] Hamidipour M., Mostoufi N., Sotudeh-Gharebagh R., *Chem. Eng. J.*, 106 (2005) 249.
- [22] Kudo A., Miseki Y., *Chem. Soc. Rev.*, 38 (2009) 253.
- [23] Liu Z., Hou W., Pavaskar P., Aykol M., Cronin S.B., *Nano Letters*, 11 (2011) 1111.

- [24] Khan S.U.M., Al-Shahry M., Ingler W.B., *Science*, 297 (2002) 2243.
- [25] Osterloh F.E., *Chem. Soc. Rev.*, 42 (2013) 2294.
- [26] Abdel-Mageed A.M., Widmann D., Olesen S.E., Chorkendorff I., Biskupek J., Behm R.J., *ACS Catal.*, (2015) 6753.
- [27] Munnik P., Velthoen M.E.Z., de Jongh P.E., de Jong K.P., Gommers C.J., *Angew. Chem. Int. Ed.*, 53 (2014) 9493.
- [28] Kelley R.D., Madey T.E., Yates Jr J.T., *J. Catal.*, 50 (1977) 301.
- [29] Sharma S., Hu Z.P., Zhang P., McFarland E.W., Metiu H., *J. Catal.*, 278 (2011) 297.
- [30] Roiaz M., Monachino E., Dri C., Greiner M., Knop-Gericke A., Schlögl R., Comelli G., Vesselli E., *J. Am. Chem. Soc.*, 138 (2016) 4146.
- [31] Wang F., He S., Chen H., Wang B., Zheng L., Wei M., Evans D.G., Duan X., *J. Am. Chem. Soc.*, (2016)
- [32] Thampi K.R., Kiwi J., Gratzel M., *Nature*, 327 (1987) 506.
- [33] Kim D.H., Park J.L., Park E.J., Kim Y.D., Uhm S., *ACS Catal.*, 4 (2014) 3117.
- [34] Kim S.S., Lee H.H., Hong S.C., *Appl. Catal. B: Environ.*, 119 (2012) 100.
- [35] Goguet A., Meunier F., Breen J.P., Burch R., Petch M.I., Faur Ghenciu A., *J. Catal.*, 226 (2004) 382.
- [36] Fujita S.-I., Usui M., Takezawa N., *J. Catal.*, 134 (1992) 220.
- [37] Boccuzzi F., Chiorino A., Manzoli M., Andreeva D., Tabakova T., *J. Catal.*, 188 (1999) 176.

- [38] Sloczynski J., Grabowski R., Kozłowska A., Olszewski P., Stoch J., Skrzypek J., Lachowska M., *Appl. Catal. A: Gen.*, 278 (2004) 11.
- [39] Sa S., Silva H., Brandao L., Sousa J.M., Mendes A., *Appl. Catal. B: Environ.*, 99 (2010) 43.
- [40] Ye J., Liu C.-j., Mei D., Ge Q., *J. Catal.*, 317 (2014) 44.
- [41] Kattel S., Yan B., Yang Y., Chen J.G., Liu P., *J. Am. Chem. Soc.*, 138 (2016) 12440.
- [42] Studt F., Sharafutdinov I., Abild-Pedersen F., Elkjær C.F., Hummelshøj J.S., Dahl S., Chorkendorff I., Nørskov J.K., *Nature Chemistry*, 6 (2014) 320.
- [43] Behrens M., Studt F., Kasatkin I., Kuhl S., Havecker M., Abild-Pedersen F., Zander S., Girgsdies F., Kurr P., Knief B.L., Tovar M., Fischer R.W., Nørskov J.K., Schlogl R., *Science*, 336 (2012) 893.
- [44] Zhang Z., Hu S., Song J., Li W., Yang G., Han B., *ChemSusChem*, 2 (2009) 234.
- [45] Johnson T.C., Morris D.J., Wills M., *Chem. Soc. Rev.*, 39 (2010) 81.
- [46] Jessop P.G., Hsiao Y., Ikariya T., Noyori R., *J. Am. Chem. Soc.*, 118 (1996) 344.
- [47] Munshi P., Main A.D., Linehan J.C., Tai C.-C., Jessop P.G., *J. Am. Chem. Soc.*, 124 (2002) 7963.
- [48] Sun K., Lu W., Wang M., Xu X., *Catal. Commun.*, 5 (2004) 367.
- [49] Aguayo A.T., Ereña J., Sierra I., Olazar M., Bilbao J., *Catal. Today*, 106 (2005)

265.

- [50] Takeguchi T., Yanagisawa K.-i., Inui T., Inoue M., *Appl. Catal. A: Gen.*, 192 (2000) 201.
- [51] Izumi Y., Kurakata H., Aika K.-i., *J. Catal.*, 175 (1998) 236.
- [52] Kurakata H., Izumi Y., Aika K.-i., *Chem. Commun.*, (1996) 389.
- [53] Kusama H., Okabe K., Sayama K., Arakawa H., *Catal. Today*, 28 (1996) 261.
- [54] Inui T., Yamamoto T., *Catal. Today*, 45 (1998) 209.
- [55] Cao Z., Guo L., Liu N., Zheng X., Li W., Shi Y., Guo J., Xi Y., *RSC Adv.*, 6 (2016) 108270.
- [56] Ro I., Sener C., Stadelman T.M., Ball M.R., Venegas J.M., Burt S.P., Hermans I., Dumesic J.A., Huber G.W., *J. Catal.*, 344 (2016) 784.
- [57] Fichtl M.B., Schumann J., Kasatkin I., Jacobsen N., Behrens M., Schlögl R., Muhler M., Hinrichsen O., *Angew. Chem. Int. Ed.*, 53 (2014) 7043.
- [58] Vidal A.B., Feria L., Evans J., Takahashi Y., Liu P., Nakamura K., Illas F., Rodriguez J.A., *Phys. Chem. Lett.*, 3 (2012) 2275.
- [59] Yang Y., White M.G., Liu P., *J. Phys. Chem. C*, 116 (2012) 248.
- [60] Rodriguez J.A., Liu P., Stacchiola D.J., Senanayake S.D., White M.G., Chen J.G., *ACS Catal.*, 5 (2015) 6696.
- [61] Tsai J.C., Nicholas K.M., *J. Am. Chem. Soc.*, 114 (1992) 5117.
- [62] Leitner W., *Angew. Chem. Int. Ed.*, 34 (1995) 2207.
- [63] Federsel C., Boddien A., Jackstell R., Jennerjahn R., Dyson P.J., Scopelliti R.,

- Laurenczy G., Beller M., *Angew. Chem. Int. Ed.*, 49 (2010) 9777.
- [64] Huff C.A., Sanford M.S., *ACS Catal.*, 3 (2013) 2412.
- [65] Schaub T., Paciello R.A., *Angew. Chem. Int. Ed.*, 50 (2011) 7278.
- [66] Wang S., Mao D., Guo X., Wu G., Lu G., *Catal. Commun.*, 10 (2009) 1367.
- [67] Zhang Q., Zuo Y.-Z., Han M.-H., Wang J.-F., Jin Y., Wei F., *Catal. Today*, 150 (2010) 55.
- [68] Zha F., Ding J., Chang Y., Ding J., Wang J., Ma J., *Industrial & Engineering Chemistry Research*, 51 (2012) 345.
- [69] Aguayo A.T., Ereña J., Mier D., Arandes J.M., Olazar M., Bilbao J., *Industrial & Engineering Chemistry Research*, 46 (2007) 5522.
- [70] Inoue T., Iizuka T., Tanabe K., *Appl. Catal.*, 46 (1989) 1.
- [71] Spivey J.J., Egbebi A., *Chem. Soc. Rev.*, 36 (2007) 1514.
- [72] Zhen W., Li B., Lu G., Ma J., *Chem. Commun.*, 51 (2015) 1728.
- [73] Zhi G.J., Guo X.N., Wang Y.Y., Jin G.Q., Guo X.Y., *Catal. Commun.*, 16 (2011) 56.
- [74] VanderWiel D. P., Zilka-Marco J. L., Wang Y., Tonkovich A. Y., S. W.R., in: Spring National Meeting, AIChE, Atlanta, 2000.
- [75] Brooks K.P., Hu J., Zhu H., Kee R.J., *Chem. Eng. Sci.*, 62 (2007) 1161.
- [76] Lunde P.J., Kester F.L., *Ind. Eng. Chem. Process Des. Dev.*, 13 (1974) 27.
- [77] Tada S., Ochieng O.J., Kikuchi R., Haneda T., Kameyama H., *Int. J. Hydrogen Energ.*, 39 (2014) 10090.

- [78] Wang X., Hong Y., Shi H., Szanyi J., *J. Catal.*, 343 (2016) 185.
- [79] Panagiotopoulou P., Kondarides D.I., Verykios X.E., *J. Phys. Chem. C*, 115 (2011) 1220.
- [80] Eckle S., Augustin M., Anfang H.G., Behm R.J., *Catal. Today*, 181 (2012) 40.
- [81] Abdel-Mageed A.M., Eckle S., Widmann D., Behm R.J., *J. Catal.*, 335 (2016) 79.
- [82] Sabatier P., Senderens J.B., *CR Acad. Sci.*, 134 (1902) 689.
- [83] Garbarino G., Bellotti D., Riani P., Magistri L., Busca G., *Int. J. Hydrogen Energ.*, (2015)
- [84] Solymosi F., Erdohelyi A., Kocsis M., *J. Chem. Soc., Faraday Trans.*, 77 (1981) 1003.
- [85] Abe T., Tanizawa M., Watanabe K., Taguchi A., *Energ. Environ. Sci.*, 2 (2009) 315.
- [86] Upham D.C., Derk A.R., Sharma S., Metiu H., McFarland E.W., *Catal. Sci. Tech.*, 5 (2015) 1783.
- [87] Beuls A., Swalus C., Jacquemin M., Heyen G., Karelovic A., Ruiz P., *Appl. Catal. B: Environ.*, 113 (2012) 2.
- [88] Swalus C., Jacquemin M., Poleunis C., Bertrand P., Ruiz P., *Appl. Catal. B: Environ.*, 125 (2012) 41.
- [89] Karelovic A., Ruiz P., *J. Catal.*, 301 (2013) 141.
- [90] Karelovic A., Ruiz P., *ACS Catal.*, 3 (2013) 2799.

- [91] Park J.N., McFarland E.W., *J. Catal.*, 266 (2009) 92.
- [92] Kim H.Y., Lee H.M., Park J.-N., *J. Phys. Chem. C*, 114 (2010) 7128.
- [93] Erdohelyi A., Pasztor M., Solymosi F., *J. Catal.*, 98 (1986) 166.
- [94] Luengo C.A., Cabrera A.L., MacKay H.B., Maple M.B., *J. Catal.*, 47 (1977) 1.
- [95] Falconer J.L., Zagli A.E., *J. Catal.*, 62 (1980) 280.
- [96] B. Kester K., Zagli E., L. Falconer J., *Appl. Catal.*, 22 (1986) 311.
- [97] Takezawa N., Terunuma H., Shimokawabe M., Kobayashib H., *Appl. Catal.*, 23 (1986) 291.
- [98] Tada S., Shimizu T., Kameyama H., Haneda T., Kikuchi R., *Int. J. Hydrogen Energ.*, 37 (2012) 5527.
- [99] Pan Q., Peng J., Sun T., Gao D., Wang S., Wang S., *Fuel Process. Technol.*, 123 (2014) 166.
- [100] Iizuka T., Tanaka Y., Tanabe K., *J. Catal.*, 76 (1982) 1.
- [101] Iizuka T., Tanaka Y., Tanabe K., *J. Mol. Catal.*, 17 (1982) 381.
- [102] Kattel S., Yan B., Chen J.G., Liu P., *J. Catal.*, 343 (2016) 115.
- [103] Prairie M.R., Renken A., Highfield J.G., Thampi K.R., Gratzel M., *J. Catal.*, 129 (1991) 130.
- [104] Scire S., Crisafulli C., Maggiore R., Minico S., Galvagno S., *Catal. Lett.*, 51 (1998) 41.
- [105] Kowalczyk Z., Stolecki K., Rarog-Pilecka W., Miskiewicz E., Wilczkowska

- E., Karpinski Z., *Appl. Catal. A: Gen.*, 342 (2008) 35.
- [106] Traa Y., Weitkamp J., *Chem. Eng. Sci.*, 22 (1999) 291.
- [107] Garbarino G., Riani P., Magistri L., Busca G., *Int. J. Hydrogen Energ.*, 39 (2014) 11557.
- [108] Garbarino G., Valsamakis I., Riani P., Busca G., *Catal. Commun.*, 51 (2014) 37.
- [109] Muroyama H., Tsuda Y., Asakoshi T., Masitah H., Okanishi T., Matsui T., Eguchi K., *J. Catal.*, 343 (2016) 178.
- [110] Aziz M.A.A., Jalil A.A., Triwahyono S., Mukti R.R., Taufiq-Yap Y.H., Sazegar M.R., *Appl. Catal. B: Environ.*, 147 (2014) 359.
- [111] Aziz M.A.A., Jalil A.A., Triwahyono S., Sidik S.M., *Appl. Catal. A: Gen.*, 486 (2014) 115.
- [112] Ocampo F., Louis B., Kiwi-Minsker L., Roger A.-C., *Appl. Catal. A: Gen.*, 392 (2011) 36.
- [113] Pan Q., Peng J., Wang S., Wang S., *Catal. Sci. Tech.*, 4 (2014) 502.
- [114] Liu J., Bing W., Xue X., Wang F., Wang B., He S., Zhang Y., Wei M., *Catal. Sci. Tech.*, (2016)
- [115] Westermann A., Azambre B., Bacariza M.C., Graça I., Ribeiro M.F., Lopes J.M., Henriques C., *Appl. Catal. B: Environ.*, 174–175 (2015) 120.
- [116] Du G.A., Lim S., Yang Y.H., Wang C., Pfefferle L., Haller G.L., *J. Catal.*, 249 (2007) 370.

- [117] Karelovic A., Ruiz P., *Appl. Catal. B: Environ.*, 113 (2012) 237.
- [118] Kusmierz M., *Catal. Today*, 137 (2008) 429.
- [119] Kwak J.H., Kovarik L., Szanyi J., *ACS Catal.*, 3 (2013) 2449.
- [120] Kwak J.H., Kovarik L., Szanyi J., *ACS Catal.*, 3 (2013) 2094.
- [121] Wang X., Shi H., Kwak J.-H., Szanyi J., *ACS Catal.*, (2015)
- [122] Matsubu J.C., Yang V.N., Christopher P., *J. Am. Chem. Soc.*, 137 (2015) 3076.
- [123] Ma S., Song W., Liu B., Zheng H., Deng J., Zhong W., Liu J., Gong X.-Q., Zhao Z., *Catal. Sci. Tech.*, (2016)
- [124] Yin A.X., Liu W.C., Ke J., Zhu W., Gu J., Zhang Y.W., Yan C.H., *J. Am. Chem. Soc.*, 134 (2012) 20479.
- [125] Aksoylu A.E., Akin A.N., Onsan Z.I., Trimm D.L., *Appl. Catal. A: Gen.*, 145 (1996) 185.
- [126] Liu J., Li C., Wang F., He S., Chen H., Zhao Y., Wei M., Evans D.G., Duan X., *Catal. Sci. Tech.*, 3 (2013) 2627.
- [127] Wu H.C., Chang Y.C., Wu J.H., Lin J.H., Lin I.K., Chen C.S., *Catal. Sci. Tech.*, 5 (2015) 4154.
- [128] Rynkowski J.M., Paryjczak T., Lewicki A., Szyrkowska M.I., Maniecki T.P., Jóźwiak W.K., *React. Kinet. Catal. Lett.*, 71 (2000) 55.
- [129] Aika K., Shimazaki K., Hattori Y., Ohya A., Ohshima S., Shirota K., Ozaki A., *J. Catal.*, 92 (1985) 296.

- [130] Zhang Z.L., Kladi A., Verykios X.E., *J. Catal.*, 156 (1995) 37.
- [131] Tada S., Kikuchi R., Takagaki A., Sugawara T., Oyama S.T., Urasaki K., Satokawa S., *Appl. Catal. B: Environ.*, 140–141 (2013) 258.
- [132] Büchel R., Baiker A., Pratsinis S.E., *Appl. Catal. A: Gen.*, 477 (2014) 93.
- [133] Heyl D., Rodemerck U., Bentrup U., *ACS Catal.*, (2016)
- [134] Bando K.K., Ichikuni N., Soga K., Kunimori K., Arakawa H., Asakura K., *J. Catal.*, 194 (2000) 91.
- [135] Zhu Y., Zhang S.R., Ye Y.C., Zhang X.Q., Wang L., Zhu W., Cheng F., Tao F., *ACS Catal.*, 2 (2012) 2403.
- [136] Beaumont S.K., Alayoglu S., Specht C., Michalak W.D., Pushkarev V.V., Guo J., Kruse N., Somorjai G.A., *J. Am. Chem. Soc.*, 136 (2014) 9898.
- [137] Xavier K.O., Sreekala R., Rashid K.K.A., Yusuff K.K.M., Sen B., *Catal. Today*, 49 (1999) 17.
- [138] Guo M., Lu G., *React. Kinet. Mech. Catal.*, 113 (2014) 101.
- [139] Cai M., Wen J., Chu W., Cheng X., Li Z., *J. Nat. Gas Chem.*, 20 (2011) 318.
- [140] Guo M., Lu G., *RSC Adv.*, 4 (2014) 58171.
- [141] Guo M., Lu G., *Catal. Commun.*, 54 (2014) 55.
- [142] Kattel S., Yu W., Yang X., Yan B., Huang Y., Wan W., Liu P., Chen J.G., *Angew. Chem. Int. Ed.*, 128 (2016) 8100.
- [143] Vaarkamp M., Modica F.S., Miller J.T., Koningsberger D.C., *J. Catal.*, 144 (1993) 611.

- [144] Lopez T., Gomez R., Novaro O., Ramirezsolis A., Sanchezmora E., Castillo S., Poulain E., Martinezmagadan J.M., *J. Catal.*, 141 (1993) 114.
- [145] Li D., Ichikuni N., Shimazu S., Uematsu T., *Appl. Catal. A: Gen.*, 172 (1998) 351.
- [146] Li D., Ichikuni N., Shimazu S., Uematsu T., *Appl. Catal. A: Gen.*, 180 (1999) 227.
- [147] Li C.M., Zhang S.T., Zhang B.S., Su D.S., He S., Zhao Y.F., Liu J., Wang F., Wei M., Evans D.G., Duan X., *J. Mater. Chem. A*, 1 (2013) 2461.
- [148] Li Y., Lu G., Ma J., *RSC Adv.*, 4 (2014) 17420.
- [149] Zhen W., Li B., Lu G., Ma J., *RSC Adv.*, 4 (2014) 16472.
- [150] Nakayama T., Ichikuni N., Sato S., Nozaki F., *Appl. Catal. A: Gen.*, 158 (1997) 185.
- [151] Takenaka S., Sato S., Takahashi R., Sodesawa T., *Phys. Chem. Chem. Phys.*, 5 (2003) 4968.
- [152] He S., Li C., Chen H., Su D., Zhang B., Cao X., Wang B., Wei M., Evans D.G., Duan X., *Chem. Mater.*, 25 (2013) 1040.
- [153] Jacquemin M., Beuls A., Ruiz P., *Catal. Today*, 157 (2010) 462.
- [154] Carencio S., Sassoie C., Faustini M., Eloy P., Debecker D.P., Bluhm H., Salmeron M., *J. Phys. Chem. C*, (2016)
- [155] Hwang C.P., Yeh C.T., Zhu Q.M., *Catal. Today*, 51 (1999) 93.
- [156] Komvokis V.G., Marnellos G.E., Vasalos I.A., Triantafyllidis K.S., *Appl.*

- Catal. B: Environ.*, 89 (2009) 627.
- [157] Gupta N.M., Kamble V.S., Kartha V.B., Iyer R.M., Thampi K.R., Gratzel M.,
J. Catal., 146 (1994) 173.
- [158] Zhang Z.L., Kladi A., Verykios X.E., *J. Catal.*, 148 (1994) 737.
- [159] Fisher I.A., Bell A.T., *J. Catal.*, 162 (1996) 54.
- [160] Fujita S.I., Takezawa N., *Chem. Eng. J.*, 68 (1997) 63.
- [161] Marwood M., Doepper R., Renken A., *Appl. Catal. A: Gen.*, 151 (1997) 223.
- [162] Akamaru S., Shimazaki T., Kubo M., Abe T., *Appl. Catal. A: Gen.*, 470
(2014) 405.
- [163] Avanesian T., Gusmão G.S., Christopher P., *J. Catal.*, 343 (2016) 86.
- [164] Fujita S., Nakamura M., Doi T., Takezawa N., *Appl. Catal. A: Gen.*, 104
(1993) 87.
- [165] Weatherbee G.D., Bartholomew C.H., *J. Catal.*, 77 (1982) 460.
- [166] Pan Q.S., Peng J.X., Sun T.J., Wang S., Wang S.D., *Catal. Commun.*, 45
(2014) 74.
- [167] Silaghi M.-C., Comas-Vives A., Copéret C., *ACS Catal.*, 6 (2016) 4501.
- [168] Pan Y.X., Liu C.J., Ge Q.F., *J. Catal.*, 272 (2010) 227.
- [169] Zhang R., Liu H., Wang B., Ling L., *Appl. Catal. B: Environ.*, 126 (2012)
108.
- [170] Vesselli E., De Rogatis L., Ding X.L., Baraldi A., Savio L., Vattuone L.,
Rocca M., Fornasiero P., Peressi M., Baldereschi A., Rosei R., Comelli G., *J.*

- Am. Chem. Soc.*, 130 (2008) 11417.
- [171] Abdel-Mageed A.M., Eckle S., Behm R.J., *J. Am. Chem. Soc.*, 137 (2015) 8672.
- [172] Abdel-Mageed A.M., Widmann D., Eckle S., Behm R.J., *ChemSusChem*, 8 (2015) 3869.
- [173] Agnelli M., Kolb M., Mirodatos C., *J. Catal.*, 148 (1994) 9.
- [174] Djinoovic P., Galletti C., Specchia S., Specchia V., *Top. Catal.*, 54 (2011) 1042.
- [175] Lin B.Y., Wang R., Lin J.X., Ni J., Wei K.M., *Catal. Lett.*, 141 (2011) 1557.
- [176] Bragg W.L., *Nature*, 90 (1912) 410.
- [177] Brunauer S., Emmett P.H., Teller E., *J. Am. Chem. Soc.*, 60 (1938) 309.
- [178] Bartholomew C.H., Pannell R.B., *J. Catal.*, 65 (1980) 390.
- [179] Shastri A.G., Schwank J., *J. Catal.*, 95 (1985) 271.
- [180] Ashley C.A., Doniach S., *Phys. Rev. B*, 11 (1975) 1279.
- [181] Vuurman M.A., Wachs I.E., *J. Phys. Chem.*, 96 (1992) 5008.
- [182] Velu S., Suzuki K., Vijayaraj M., Barman S., Gopinath C.S., *Appl. Catal. B: Environ.*, 55 (2005) 287.
- [183] Russo T.V., Martin R.L., Hay P.J., *J. Phys. Chem.*, 99 (1995) 17085.
- [184] Kresse G., Hafner J., *Phys. Rev. B*, 48 (1993) 13115.
- [185] Kresse G., Furthmüller J., *Phys. Rev. B*, 54 (1996) 11169.
- [186] Kresse G., Joubert D., *Phys. Rev. B*, 59 (1999) 1758.

- [187] Shan W.P., Liu F.D., He H., Shi X.Y., Zhang C.B., *Chem. Commun.*, 47 (2011) 8046.
- [188] Xia W., Wang F., Mu X., Chen K., Takahashi A., Nakamura I., Fujitani T., *Catal. Commun.*, 90 (2017) 10.
- [189] Gao P., Zhong L., Zhang L., Wang H., Zhao N., Wei W., Sun Y., *Catal. Sci. Tech.*, 5 (2015) 4365.
- [190] Cao Y., Feng X., Xu H., Lan L., Gong M., Chen Y., *Catal. Commun.*, 76 (2016) 33.
- [191] Sun L., Tan Y., Zhang Q., Xie H., Song F., Han Y., *Int. J. Hydrogen Energ.*, 38 (2013) 1892.
- [192] Sun G.B., Hidajat K., Wu X.S., Kawi S., *Appl. Catal. B: Environ.*, 81 (2008) 303.
- [193] Sun J., Qiu X.-P., Wu F., Zhu W.-T., *Int. J. Hydrogen Energ.*, 30 (2005) 437.
- [194] Oemar U., Hidajat K., Kawi S., *Int. J. Hydrogen Energ.*, 40 (2015) 12227.
- [195] Wijaya H.W., Kojima T., Hara T., Ichikuni N., Shimazu S., *ChemCatChem*, (2017) n/a.
- [196] Aldana P.A.U., Ocampo F., Kobl K., Louis B., Thibault-Starzyk F., Daturi M., Bazin P., Thomas S., Roger A.C., *Catal. Today*, 215 (2013) 201.
- [197] Liu H., He D., *Int. J. Hydrogen Energ.*, 36 (2011) 14447.
- [198] Zhang R.D., Kaliaguine S., *Appl. Catal. B: Environ.*, 78 (2008) 275.
- [199] Yu Y.B., Zhao J.J., Yan Y., Han X., He H., *Appl. Catal. B: Environ.*, 136

- (2013) 103.
- [200] Tao M., Meng X., Xin Z., Bian Z., Lv Y., Gu J., *Appl. Catal. A: Gen.*, (2016)
- [201] Zhao F.Z., Liu Z.Y., Xu W.Q., Yao S.Y., Kubacka A., Johnston-Peck A.C., Senanayake S.D., Zhang A.Q., Stach E.A., Fernandez-Garcia M., Rodriguez J.A., *J. Phys. Chem. C*, 118 (2014) 2528.
- [202] Tan M., Wang X., Wang X., Zou X., Ding W., Lu X., *J. Catal.*, 329 (2015) 151.
- [203] Arena F., Horrell B.A., Cocke D.L., Parmaliana A., Giordano N., *J. Catal.*, 132 (1991) 58.
- [204] Parmaliana A., Arena F., Frusteri F., Coluccia S., Marchese L., Martra G., Chuvilin A.L., *J. Catal.*, 141 (1993) 34.
- [205] Shen W.M., Dumesic J.A., Hill Jr C.G., *J. Catal.*, 68 (1981) 152.
- [206] Liu J., Yu J., Su F., Xu G., *Catal. Sci. Tech.*, 4 (2014) 472.
- [207] Wang Y.-H., Liu H.-M., Xu B.-Q., *J. Mol. Catal. A: Chem.*, 299 (2009) 44.
- [208] Zhu H., Razzaq R., Li C., Muhmmad Y., Zhang S., *AIChE J.*, 59 (2013) 2567.
- [209] Liu Z., Xu W., Yao S., Johnson-Peck A.C., Zhao F., Michorczyk P., Kubacka A., Stach E.A., Fernández-García M., Senanayake S.D., Rodriguez J.A., *J. Catal.*, 321 (2015) 90.
- [210] Aziz M.A.A., Jalil A.A., Triwahyono S., Ahmad A., *Green Chem.*, 17 (2015) 2647.

- [211] Hu G., Zhu L.I.N., Jia A., Hu X.I.N., Xie G., Lu J., Luo M., *Appl. Spectrosc.*, 66 (2012) 122.
- [212] Cornu D., Guesmi H., Krafft J.-M., Lauron-Pernot H., *J. Phys. Chem. C*, 116 (2012) 6645.
- [213] Dantas S.C., Escritori J.C., Soares R.R., Hori C.E., *Chem. Eng. J*, 156 (2010) 380.
- [214] Parmaliana A., Arena F., Frusteri F., Giordano N., *J. Chem. Soc., Faraday Trans.*, 86 (1990) 2663.
- [215] Liu Q., Gao J., Zhang M., Li H., Gu F., Xu G., Zhong Z., Su F., *RSC Adv.*, 4 (2014) 16094.
- [216] Southmayd D.W., Contescu C., Schwarz J.A., *J. Chem. Soc., Faraday Trans.*, 89 (1993) 2075.
- [217] Yan Y., Dai Y., He H., Yu Y., Yang Y., *Appl. Catal. B: Environ.*, 196 (2016) 108.
- [218] Abdel-Mageed A.M., Eckle S., Anfang H.G., Behm R.J., *J. Catal.*, 298 (2013) 148.
- [219] Saavedra J., Doan H.A., Pursell C.J., Grabow L.C., Chandler B.D., *Science*, 345 (2014) 1599.
- [220] Cargnello M., Doan-Nguyen V.V.T., Gordon T.R., Diaz R.E., Stach E.A., Gorte R.J., Fornasiero P., Murray C.B., *Science*, 341 (2013) 771.
- [221] Chen G.X., Zhao Y., Fu G., Duchesne P.N., Gu L., Zheng Y.P., Weng X.F.,

- Chen M.S., Zhang P., Pao C.W., Lee J.F., Zheng N.F., *Science*, 344 (2014) 495.
- [222] Tada S., Kikuchi R., *Catal. Sci. Tech.*, 5 (2015) 3061.
- [223] Karim A.M., Prasad V., Mpourmpakis G., Lonergan W.W., Frenkel A.I., Chen J.G., Vlachos D.G., *J. Am. Chem. Soc.*, 131 (2009) 12230.
- [224] Diao W., Tengco J.M.M., Regalbuto J.R., Monnier J.R., *ACS Catal.*, 5 (2015) 5123.
- [225] Chen M., Kumar D., Yi C.-W., Goodman D.W., *Science*, 310 (2005) 291.
- [226] Altmann J., Löffler E., Birkner A., Muhler M., *Catal. Today*, 85 (2003) 235.
- [227] Eckle S., Denkwitz Y., Behm R.J., *J. Catal.*, 269 (2010) 255.
- [228] Pfnür H., Menzel D., Hoffmann F.M., Ortega A., Bradshaw A.M., *Surf. Sci.*, 93 (1980) 431.
- [229] Brown M.F., Gonzalez R.D., *J. Phys. Chem.*, 80 (1976) 1731.
- [230] Yokomizo G.H., Louis C., Bell A.T., *J. Catal.*, 120 (1989) 1.
- [231] Winslow P., Bell A.T., *J. Catal.*, 86 (1984) 158.
- [232] Ye J., Liu C., Mei D., Ge Q., *ACS Catal.*, 3 (2013) 1296.
- [233] Yang Y., Evans J., Rodriguez J.A., White M.G., Liu P., *Phys. Chem. Chem. Phys.*, 12 (2010) 9909.
- [234] Fujitani T., Nakamura I., Akita T., Okumura M., Haruta M., *Angew. Chem. Int. Ed.*, 121 (2009) 9679.
- [235] Boronat M., Illas F., Corma A., *The Journal of Physical Chemistry A*, 113

(2009) 3750.

[236] Fernández C., Bion N., Gaigneaux E.M., Duprez D., Ruiz P., *J. Catal.*, 344

(2016) 16.

[237] Bhatia S., Engelke F., Pruski M., Gerstein B.C., King T.S., *J. Catal.*, 147

(1994) 455.

Appendix

List of abbreviations

3D	Three Dimensions
BET	Brunauer Emmett Teller
DFT	Density Functional Theory
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
EDX	Energy-dispersive X-ray
EXAFS	Extended X-ray Absorption Fine Structure
FTIR	Fourier Transform Infrared Spectroscopy
HRTEM	High-Resolution Transmission Electron Microscopy
ICP-EOS	Inductively Coupled Plasma Atomic Emission Spectroscopy
IRAS	Infrared Reflection Absorption Spectroscopy
MCT	Mercury Cadmium Telluride
MS	Mass Spectrometer
RWGS	Reversed Water Gas Shift
SEM	Scanning Electron Microscopy
TCD	Thermal Conductivity Detector
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TOF	Turnover Frequency
TPD	Temperature-Programmed Desorption

TPR	Temperature-Programmed Reduction
XAS	X-ray Absorption Spectroscopy
XANE	X-ray Absorption Near Edge Structure
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

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