Model analysis and catalysts study of CO₂ methanation in fluidized bed reactor

Jia, Chunmiao

2019

Jia, C. (2019). Model analysis and catalysts study of CO₂ methanation in fluidized bed reactor. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/90284>

<https://doi.org/10.32657/10220/48531>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**MODEL ANALYSIS AND CATALYSTS STUDY
OF CO₂ METHANATION IN FLUIDIZED BED
REACTOR**

JIA CHUNMIAO

SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

2019

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STUDY OF CO₂ METHANATION IN
FLUIDIZED BED REACTOR**

JIA CHUNMIAO

SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

A thesis submitted to the Nanyang Technological University

in fulfillment of the requirement for the degree of

Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from 3 paper accepted or published in the following peer-reviewed journals where I was the first author.

Chapter 2 is published as Jia Chunmiao, Gao Jiajian, Dai Yihu, Zhang Jia, Yang Yanhui, The thermodynamics analysis and experimental validation for complicated systems in CO₂ hydrogenation process. Journal of energy chemistry, 2016. 25(6): p.1027-1037.

The contributions of the co-authors are as follows:

- Prof. Yang Yanhui provided the project direction and revised the manuscript drafts.
- Dr. Gao Jiajian helped to obtain the trial version and guided the use of the software CHEMCAD and revised the manuscript draft.
- I conducted the calculations, did the gas solid experiments on the fixed bed, prepared the manuscript drafts.
- The manuscript was revised by Dr. Dai Yihu and Prof. Zhang Jia.

Chapter 3 is accepted as Jia Chunmiao, Dai Yihu, Yang Yanhui, Chew Jia Wei, A fluidized bed modeling study for CO₂ methanation using the NiMgW catalyst. Particuology, 2019. In press.

The contributions of the co-authors are as follows:

- Prof. Chew Jia Wei and Yang Yanhui provided the project direction and revised the manuscript drafts.
- The manuscript was written by Jia Chunmiao and revised by other authors.

Chapter 4 is accepted as Jia Chunmiao, Dai Yihu, Yang Yanhui, Chew Jia Wei, Nickel cobalt catalyst supported on TiO₂-coated SiO₂ spheres for CO₂ methanation in a fluidized bed. International Journal of Hydrogen Energy, 2019, 44(26): 13443-13455.

The contributions of the co-authors are as follows:

- Prof. Chew Jia Wei provided the project direction and revised the manuscript drafts.
- The manuscript was written by Jia Chunmiao and revised by other authors.

29-May-2019

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Acknowledgement

Time goes by so fast, it has been four years since I was enrolled as a PhD student in Jan 2015. During these years, I would like to appreciate my two supervisors Prof. Yang Yanhui and Chew Jiawei most sincerely, for their guidance, encouragement, support and enlightenment. Do scientific research is a hard work for me, however, they always helped me to find the answers of the problems encountered and shared their personal experiences without reservation, and encouraged me to realize my own ideas. During this process, what I learned from them was not only research plan design, problem solving skills, and etc., but also their optimistic attitude and spirit of hard working.

Deep appreciation is also given to all staffs and students in the two research groups and school for their supports and assistances in research and other aspects. Special thanks to Dr. Dai Yihu, Dr. Yan Yong, Mr. Huang Jijiang, Dr. He Chao, Dr. Wang Hou for their insightful discussions with me, and their assistance in the measurements and characterizations.

Finally, I would like to thank my loved parents, husband, and my daughter deeply who have always been encouraging and supporting me out of difficulties.

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Summary

With the increasing greenhouse gas carbon dioxide (CO₂) emission due to the consumption of fossil fuels, various methods have been investigated for the capture and recycle of CO₂. In these processes, catalytic conversion of CO₂ into chemicals and fuels is an alternative to alleviate climate change and ocean acidification. This thesis contains mainly three parts:

Firstly, considering the catalytic reduction of CO₂ by H₂ can lead to the formation of various products: carbon, carbon monoxide, carboxylic acids, aldehydes, alcohols and hydrocarbons, a comprehensive thermodynamics analysis of CO₂ hydrogenation is conducted using the Gibbs free energy minimization method. The results show that CO₂ reduction to CO needs a high temperature and H₂/CO₂ ratio to achieve a high CO₂ conversion. However, synthesis of methanol from CO₂ needs a relatively high pressure and low temperature to minimize the reverse water-gas shift reaction. Direct CO₂ hydrogenation to formic acid or formaldehyde is thermodynamically limited. On the contrary, production of CH₄ from CO₂ hydrogenation is the thermodynamically easiest reaction with nearly 100 % CH₄ yield at moderate conditions. In addition, complex reactions with more than one product are also calculated in this project. The thermodynamic calculations are partially validated with some experimental results, suggesting that the Gibbs free energy minimization method is effective for thermodynamically understanding the reaction network involved in the CO₂ hydrogenation process, which is helpful for the development of high-performance catalysts.

Second, through above thermodynamics analysis, it is known that the reduction of carbon dioxide to methane by hydrogen ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$, termed CO₂ methanation) from renewable energy is a promising process for CO₂ recycling. However, both the development of better catalysts and better reactors for the subsequent implementation are critical for the practical application of CO₂ methanation. Towards large-scale implementation, (i) fluidized beds, which have excellent heat transfer, are promising for the highly exothermic reaction; and (ii) catalysts suitable for long-term use in fluidized beds are needed. This project focused on the former, specifically on

the understanding of the operating parameters affecting CO₂ methanation in the highly efficient fluidized bed reactor. A fluidized bed reactor model was developed based on an earlier one reported for CO methanation. The reaction kinetics of the Ni-Mg-W catalyst, which has been reported to exhibit superior catalytic performance, was experimentally measured. The fluidized bed model results indicated that the Ni-Mg-W was indeed superior to two other catalysts reported earlier in terms of faster depletion of reactants and higher concentrations of product CH₄ throughout the reactor. Moreover, regarding the effect of operating parameters, the overall productivity of CH₄ increases with decreased inlet reactant flow rate, increased temperature, increased H₂/CO₂ ratio, decreased catalyst particle diameter and decreased catalyst particle sphericity. The results presented in this part are expected to be valuable for both the further development of catalysts and of the reactors needed for practical CO₂ methanation processes.

Last part focuses on the catalyst study for carbon dioxide (CO₂) methanation. In this project, a novel Ni-Co bimetal catalyst supported on TiO₂-coated SiO₂ spheres (NiCo/TiO₂@SiO₂) was rationally designed and evaluated for CO₂ methanation in fluidized bed reactor. The results demonstrated that NiCo/TiO₂@SiO₂ exhibited high CO₂ conversion with CH₄ selectivity of greater than 95%. Moreover, the superior performance was sustained for more than 100 hours in the fluidized bed reactor, affirming the long-term stability of the catalyst. Comprehensive characterizations were conducted to understand the relationship between structure and performance. This study is expected to be valuable for the potential implementation of the CO₂ methanation process in fluidized beds.

In all, this thesis would be a useful guidance for the process development of CO₂ utilization through hydrogenation process.

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Chapter 1 Introduction

1.1 Carbon dioxide emissions from fossil fuel

Carbon dioxide (CO₂) emission from fossil fuel (such as coal, oil, and nature gas) have been considered as a serious problem which action must be taken to slow down this process. According to the data from U.S. Department of Energy (Figure 1-1), since 1751 till now, the total amount of carbon released to the atmosphere from the consumption of fossil fuels and cement production have reached 400 billion tons. Moreover, it can be seen from Figure 1-1 that nearly half of these CO₂ emissions from fossil fuel have occurred since the late 1980s. In 2014, the global fossil-fuel carbon emission estimate is 9855 million metric tons, represents an all-time high and a 0.8 % increase over 2013 emissions. In globally, liquid and solid fuels occupied 75 % of the emissions from fossil fuel burning and cement production in 2014 (http://cdiac.ess-dive.lbl.gov/trends/emis/tre_glob_2014.html). Combustion of gas fuels (e.g., natural gas, mainly component is methane (CH₄)) accounted for 18% of the total emissions from fossil fuels in 2014, which reflects a gradually increasing global utilization of natural gas. It should be noted that natural gas is also the main source of today's hydrogen. Emissions from cement production (for example, 568 million metric tons of carbon in 2014) have more than doubled in the last decade and now represent 5.8% of global CO₂ releases from fossil-fuel burning and cement production. During cement production process, the raw material is heated up to 1450 °C. This temperature begins a chemical reaction so called decarbonation, thus, many fossil fuels are consumed in the cement production process.

It is known that the direct concern about CO₂ emission is its global warming effect. Most climate scientists agree the main cause of the current global warming trend is human expansion of the "greenhouse effect" -warming that results when the atmosphere traps heat radiating from Earth toward space. It has been known that certain gases in the atmosphere block heat from escaping. Long-lived gases that remain semi-permanently in the atmosphere and do not respond

physically or chemically to changes in temperature are described as "forcing" climate change. Gases that contribute to the greenhouse effect include water vapor, carbon dioxide, methane, nitrous oxide, and some chlorofluorocarbons (CFCs). In these gases, carbon dioxide (CO₂) is a minor but very important component of the atmosphere. Carbon dioxide is released through natural processes such as respiration and volcano eruptions and can be produced through human activities such as deforestation, land use changes, and burning fossil fuels. Humans have increased atmospheric CO₂ concentration by more than one third since the Industrial Revolution began. This is the most important long-lived "forcing" of climate change. Therefore, various plans such as the capture and utilization of CO₂ have been proposed.

Figure 1-1. Carbon emission from different sources. (Boden, T.A., G. Marland, and R.J. Andres. 2017. Global, Regional, and National Fossil-Fuel CO₂ Emissions. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A. doi 10.3334/CDIAC/00001_V2017)

1.2 Utilization of CO₂ as a chemical feed

To recycle and recuse CO₂, firstly, CO₂ need to be captured from the carbon sources. The

utilization of CO₂ through technological, chemical, or enhanced biological methods may lead to reductions in CO₂ emissions. These innovative processes can substitute for the older technologies and products and impart directly and indirectly benefits on the impact of climate change.

The potential uses of CO₂ in chemical applications are shown in Figure 1-2 [2], where some of the products (such as carboxylates, carbonates, and carbamates in routes A and B) are obtained by incorporation of the entire CO₂ molecule, nearly without the valance state change of carbon. These reactions bearing such products will have a low energy content and may occur at room temperature, or even lower. Processes in which CO₂ is reduced by hydrogen or electrons to other C1 or Cn molecules (routes C and D in Figure 1-2) require an input of energy. The energy can come from the reactant such as H₂, or electrons. Additional energy is usually required to activate the molecules to make the reaction occur even with catalysts and more efficient catalysts would reduce the activation energy needed. It should be noted that, in order to reduce carbon emission, such energy cannot be provided by fossil fuels. This is because if fossil fuels are used as hydrogen source, the total amount of carbon emission would be increased, other than reduced. Therefore, alternative sources must be found, such as solar energy, or other renewable energy are the best candidates. However, these energy sources are still in developing process. Here, the projects in this thesis would mainly deal with catalytic routes. Thus, in the following sections, the route C and D will be discussed in detail. As we know, there are several catalytic types such as heterogeneous catalysis, electro catalysis, and photo catalysis. These three types of catalysis will be introduced by typical examples.

Figure 1-2. The possible applications of CO_2 in chemical syntheses.[2] (Copyright © WILEY-VCH Verlag GmbH & Co. KGaA)

1.2.1 Heterogeneously catalyzed conversion of CO_2

As definition, heterogeneous catalysts act in a different phase than the reactants. In industry, most heterogeneous catalysts are solids with active sites (usually metal or metal oxides) anchored on metal oxides, carbon, or silicon which is known as supports. While the reactants are usually in liquid (like some organic synthesis reactions) or gaseous phase (like ammonia synthesis reaction). Figure 1-3 shows the simple principle of heterogeneous catalysis. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place. For Langmuir-Hinshelwood mechanism, usually both reactants are adsorbed, while in Eley-Rideal mechanism, only one is adsorbed. Moreover, in Mars-van Krevelen mechanism, one reactant reacts with the surface of solid catalysts, then the surface of the catalysts is recovered by another reactant. As can be expected, different reactions may occur with different mechanisms and even same reaction

can proceed through different mechanism over different catalysts or different conditions (such as temperature, pressure, and concentration). There are various heterogeneously catalyzed CO₂ hydrogenation processes which will be discussed later.

Figure 1-3. The principle of heterogeneous catalysis [3]. (Copyright © John Wiley & Sons) Red ball and blue stands for the atoms of reactants.

1.2.2 Electrochemical reduction of CO₂

The electrochemical reduction of carbon dioxide is the process which converts CO₂ to more reduced chemical species such as CO, methane, alcohols, and so on, using electrical energy. [4] The first examples of electrochemical reduction of carbon dioxide are from the 19th century, when CO₂ was reduced to CO using a zinc cathode. Electrochemical methods have gained significant attention due to the following advantages: a) it can occur at ambient pressure and room temperature; b) it can be connected with renewable energy sources; c) it has competitive controllability, modularity and its scale-up is relatively simple. Till now, the electrochemical reduction or electrocatalytic conversion of CO₂ can produce various value-added chemicals such carbon monoxide, methane, ethylene, ethane, alcohols[5], formic acid[6] etc. In general, the obtained products are mainly dependent on the selected catalysts and also the operating potentials.

A typical experimental system for the electrochemical reduction of CO_2 is shown in Figure 1-4.

Figure 1-4. A typical experimental system for the electrochemical reduction of CO_2 . (source:

<http://large.stanford.edu/courses/2016/ph240/liang1/>)

1.2.3 Photocatalytic reduction of CO_2

Photocatalysis is a different process compared with the above two processes. During photocatalysis process, the catalyst can receive light (such as visible light or ultraviolet light) and be promoted to an excited state, and then undergo intersystem crossing with the starting material. After catalytic cycle, the catalyst returns to ground state without being consumed. The excited state of the starting material will then undergo reactions[7]. For example, singlet oxygen is usually produced during photocatalysis process. In CO_2 photocatalysis process, some common reductants, such as H_2 , H_2O (both gaseous and aqueous phases), CH_4 , and CH_3OH are presented. A typical catalysis system is shown in Figure 1-5. During this system, CO_2 was photocatalyzed to CH_4 and H_2O was oxidized to O_2 [8]. TiO_2 was used to adsorb light and generate electrons and holes. MgO was used to adsorb CO_2 and CO_2 was reduced by electrons on Pt to CH_4 .

Figure 1-5. A typical photocatalyst system for CO₂ reduction. [7] (Copyright © THE ROYAL SOCIETY OF CHEMISTRY)

1.3 Thermodynamics of chemical reaction

It is known that chemical thermodynamics deals with the interrelation of heat and works with chemical reactions or with physical changes of state within the confines of the laws of thermodynamics. Given a constant temperature and pressure, the direction of any spontaneous change or chemical reaction is toward a lower Gibbs free energy. Figure 1-6 below shows that during a chemical reaction, the amount of free energy of the system decreases until the reaction reaches the equilibrium state. Here, hydrogenation of CO₂ reactions will be taken as examples to give an explanation.

For case (a) in Figure 1-3, CO₂ methanation is an example. In this process, the Gibbs free energy of the pure products is much lower than pure reactants. As a result, the equilibrium conversion of CO₂ can be close to 100%.

For case (b) in Figure 1-3, CO₂ reduction to CO ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) at high temperatures is a good case. The equilibrium conversion of CO₂ would be close to about 50 %, as Gibbs free energy of the pure products is comparable to that of the pure reactants.

For case (c) in Figure 1-3, hydrogenation of CO₂ to HCOOH is a difficult process, the equilibrium conversion of CO₂ is very low, in some cases, may be less than 1%. A more detailed

analysis of the thermodynamics in CO₂ hydrogenation process will be shown in chapter 2.

It should be noted that there are some factors that can change the equilibrium conversion of the reaction including concentration, temperature, pressure, external energy input, etc. However, catalysts cannot change the equilibrium of reaction but only can accelerate the reaction rate, thus shorten the time to reach equilibrium.

Figure 1-6. Thermodynamics of chemical reaction: (a) $\Delta G_{\text{rxn}} \ll 0$, (b) $\Delta G_{\text{rxn}} \approx 0$, (c) $\Delta G_{\text{rxn}} \gg 0$.

1.4 Catalysts and reaction kinetics

According to the definition of international union of pure and applied chemistry (IUPAC), a catalyst is a substance that increases the rate of reaction without modifying the overall standard Gibbs free energy change in the reaction, the process is called catalysis, and a reaction in which a catalyst is involved is known as a catalyzed reaction. Usually, the catalyst is both one of the reactants and products of the reaction. In other words, a catalyst joined in the reaction process, after completing the reaction cycle at least once, it remained. Figure 1-7 shows the typical catalytic process for CO₂ conversion. With catalysis, the reaction activation energy decreases, however, the overall standard Gibbs free energy change of the reaction is not modified.

In catalysis, the very important Sabatier principle is a qualitative concept named after the French chemist Paul Sabatier. It states that the interactions or adsorption between the catalyst and the reactants or intermediates should be "just right"; that is, neither too strong nor too weak. If the interaction is too weak, the substrate or reactants cannot bind to the catalyst and no reaction will take place. On the other hand, if the interaction or adsorption is too strong, the product fails

to desorb, and the active sites will be blocked. The principle can be shown graphically as shown in Figure 1-8 by plotting the reaction rate against a property such as the heat of adsorption of the reactant by the catalyst. Such plot passes through a maximum reaction rate and are usually called volcano plots because of its shape. In the following parts, the different catalysts for the different CO₂ reduction process will be discussed.

Figure 1-7. Energy levels of carbon dioxide, high energy reactants and low energy products.[1]

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Figure 1-8. The Sabatier principle in catalysis [9]. (Copyright © Elsevier)

(a) Hydrogenation of CO₂ to CO

The reduction of CO₂ to CO ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) also known as the reverse water-gas shift reaction can be used to produce CO, or syngas (CO and H₂ mixture), which can be further used as feedstock for menthol synthesis or Fischer-Tropsch synthesis. It is reported that molybdenum carbide can act as alternative catalysts to precious metals catalyze the hydrogenation of CO₂ to CO[10].

(b) Hydrogenation of CO₂ to CH₄

The hydrogenation of CO₂ to CH₄ ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$) also knows CO₂ methanation, can be used to produce CH₄, which is the mainly components of natural gas. This reaction is highly exothermic and the produced CH₄ can be transported by the mature nature gas network. Recently, catalytic conversion of CO₂ to CH₄ on CoO_x and Ru-doped CoO_x nanorods was studied with ambient pressure XPS.[11] Thus, a direct correlation between catalytic performances and surface chemistry under reaction conditions was obtained. It is found that bimetallic Co–Ru ultrathin film in Ru-CoO_x surface region is the key for its high selectivity of CH₄ compared with CoO_x.

(c) Hydrogenation of CO₂ to methanol

Methanol is a very important industrial chemical which can be used as source for the olefins production (methanol to olefins, MTO process). Recently, various catalysis such as indium oxide[12], Ni-Ga bimetal[13], and copper-ceria and copper-ceria-titanium catalysts[14] were reported as a superior catalyst for methanol synthesis by CO₂ hydrogenation. This reaction can proceed under atmosphere, but its equilibrium conversion of CO₂ is very low (less than 10%).

(d) Hydrogenation of CO₂ to HCOOH

Worldwide demand for formic acid (HCOOH) continues to grow, especially in the context of a renewable energy hydrogen carrier (HCOOH decompose to release hydrogen and CO₂, reverse reaction of hydrogenation of CO₂ to HCOOH), and its production from CO₂

without base via the direct catalytic carbon dioxide hydrogenation is considerably more sustainable than the existing routes. However, direct synthesis of formic acid from carbon dioxide by hydrogenation is limited by thermodynamic in acidic media, therefore, a base is usually added in the reaction system to alter its Gibbs free energy change, thus promote it thermodynamically. In addition, high pressure is usually adopted to increase the conversion of CO₂ since it is a molecular-number-reduced reaction. It is reported that the direct hydrogenation of CO₂ into formic acid can be achieved using a homogeneous ruthenium catalyst in aqueous solution and in dimethyl sulphoxide (DMSO), without any additives[15]. In water, at 40 °C, 0.2 M and 1.9 M formic acid can be obtained under 200 bar at 40 °C in water and DMSO, respectively.

(e) Hydrogenation of CO₂ to olefins

The hydrogenation of CO₂ to lighter olefins (such as ethylene, propylene, butene) is a very attractive process since the high demand of lighter olefins in chemical industry. Recently, this process was investigated over non-supported Fe catalysts.[16] Addition of alkali metal ions to the Fe catalyst can promote CO₂ conversion and the selectivity for olefins. The yield of C₂–C₄ olefins exceeded 10 % over these alkali metal ions modified catalysts. Another method to production olefins through CO₂ hydrogenation is using tandem catalysts with methanol as an intermediate. For example, a bifunctional catalyst composed of a methanol synthesis (In₂O₃/ZrO₂) catalyst and a methanol-to-olefins (SAPO-34) catalyst were reported to be effective for directly converting CO₂ to light olefins.[17]

(f) Hydrogenation of CO₂ to gasoline

The direct production of liquid fuels such as gasoline from CO₂ hydrogenation has attracted enormous interest. Recently, a highly efficient, stable and multifunctional Na–Fe₃O₄/HZSM-5 catalyst was reported. This catalyst system can directly convert CO₂ to gasoline-range (C₅–C₁₁) hydrocarbons with high selectivity up to 78 % of all hydrocarbons at a CO₂ conversion of 22%. Moreover, only 4 % methane were formed under industrial relevant conditions.[18] This

performance is achieved by a multi-functional catalyst providing different active sites, which can catalyze a tandem reaction. This multifunctional catalyst also shows high stability during 1000 h run.

(g) Hydrogenation of CO₂ to aromatics

Selective hydrogenation of CO₂ into aromatics is challenging although it is thermodynamically favorable. This is because of the high unsaturation degree and complex structures of aromatics, resulting that the reaction is difficult to be controlled. Recently, it is reported that a composite catalyst of ZnAlO_x and H-ZSM-5 can yield aromatics with high selectivity of 73.9% with extremely low CH₄ selectivity of 0.4% among the carbon products without CO.[19] During this process methanol (CH₃OH) and dimethyl ether (CH₃OCH₃) are firstly synthesized by hydrogenation of formate species formed on ZnAlO_x surface, then, they are transmitted to H-ZSM-5 zeolites, and subsequently converted into olefins and finally to aromatics in H-ZSM-5.

Reaction kinetics, and mechanism

Till now, a chemical reaction mechanism is usually a theoretical conjecture. It tries to describe in detail what takes place at each stage (or elementary reaction steps) of an overall chemical reaction. In fact, the detailed steps of a reaction in most cases are not observable based on technologies nowadays. The conjectured mechanism is chosen and studied because it is thermodynamically feasible. In addition, it has some experimental support such as observed isolated intermediates or other quantitative and qualitative characteristics of the reaction, such as the reaction order of a specific species. Reaction intermediates are temporary products and/or reactants in the mechanism's reaction steps. They are often free radicals or ions, usually unstable and short-lived, however, sometimes it can be isolated and detected. The reaction kinetics, namely, the relative rates of the reaction steps as well as the rate equation for the overall reaction, are typically explained in terms of the energy needed to convert the reactants to transition states. Information about the mechanism of a chemical reaction is often provided by the use of chemical

kinetics to determine the rate equation and the reaction order in each reactant. Moreover, the recently developed in-situ characterization method can provide more information about the reaction intermediates. Density functional theory (DFT) calculation also can promote the identification of reaction mechanism.

Till now, there are many investigations about the CO₂ hydrogenation reaction process. It can generally be accepted that carbon monoxide (CO) and formate species (COOH, or HCOO, et al.) form on Ni, Ru or Cu catalyst during CO₂ hydrogenation. For carbon monoxide, it can dissociate to be C and O species thus obtain different process. In some cases, CO is suggested to form from formate species (HCOO* to *CO and *OH). In addition, the adsorbed CO can act as an active intermediate (*CO to *C and *O) on Ni and Ru catalysts, thus can be further converted to various products. Carbon monoxide can also form through a parallel or side reverse water gas shift reaction (RWGS, CO₂+H₂ → CO + H₂O) reaction on Cu catalysts. And during this process, it is proposed that formate species are the main intermediates for methanol formation. It is well known that physicochemical properties of the catalyst support can also affect the formation of intermediate species on the active surface of the catalyst, especially on the interface between the active metal and support. In addition, some active supports (such as CeO₂, TiO₂, MgO) are proposed to participate in the activation process. They can promote the formation process of formate species, thus, lead a different coordination geometry to the catalyst surface and make them active for further hydrogenation.[20]

1.5 Fluidized bed Reactor and its modeling

There are different types of reactors for chemical reaction. A fluidized bed reactor is a type of reactor can be used to conduct a variety of multiphase chemical reactions. In fluidized bed reactor, a gas fluid or liquid fluid is passed through a solid granular catalyst material usually shaped as tiny spheres.

Figure 1-9 shows the diagram of a typical fluidized bed reactor. The catalyst in the fluidized bed reactor is typically supported by a porous plate, also known as a gas distributor and the gas

or liquid fluid is forced through the distributor up through the catalysts., The gas or liquid fluid at relatively lower velocities can pass through the voids in the catalysts, thus the catalysts remain in place, in this condition, it is like a packed bed reactor. Further increasing fluid velocity, the force of the fluid on the catalyst will be enough to balance the catalysts' weight. This stage is known as incipient fluidization and the fluid velocity is known as minimum fluidization velocity ($U_{\min}$). Once $U_{\min}$ is surpassed, the contents of the fluidized bed reactor bed begin to expand. They swirl around much like boiling pot of water or an agitated tank. In this stage, the reactor is now a fluidized bed. This process is known as fluidization and this design has some important advantages compared to fixed bed reactor. (a) uniform particle mixing due to the intrinsic fluid-like behavior of the solid material thus allows for a uniform reaction product. (b) relatively uniform temperature gradients, thus local hot or cold spots within the reaction bed which is a problem in fixed packed beds, are avoided in a fluidized bed reactor. (c) the fluidized bed can continuously withdraw product and introduce new reactants into the reaction vessel, thus allows for continuous operation. As a result, the fluidized bed reactor is now used in many industrial applications.

Figure 1-9. A typical sketch of fluidized bed reactor. (source: https://en.wikipedia.org/wiki/Fluidized_bed_reactor)

However, fluidized bed reactor also has some disadvantages: such as increased reactor vessel size due to the expansion of the catalysts, which means more initial capital costs. Moreover, fluidized bed reactor needs pumping and suffer from larger pressure drop compared with fixed bed reactor. Another point includes particle entrainment and powdering. In addition, the full understanding of the catalysts' behavior is limited, thus makes the scale-up difficult.

Chemical reactor modeling is good practice to analyze the behavior of the fluidized bed reactor under different condition. The chemical engineer can benefit from reactor modeling process for the better understanding, design, and control of the reactor. In an industrial problem, selecting the proper reactor is essential for many particular chemical reactions. Additionally, estimating the reactor size and determine the best operating conditions are also necessary. Therefore, the modeling of CO₂ methanation process in fluidized bed reactor is conducted in this thesis.

1.6 Motivation and objective

CO₂ hydrogenation process involves various products but the thermodynamics are still not well investigated. As discussed above, thermodynamics determined the equilibrium conversion which plays a key role in the real application. Thus, this thesis starts with a comprehensive thermodynamic analysis of CO₂ hydrogenation process. We attempted to apply the minimum Gibbs free energy for the analysis, furthermore through varying reaction conditions to know the equilibrium values under specific conditions, aiming to give a guidance for the following research.

Next, as there are very few reports about CO₂ methanation in a fluidized bed reactor. To fill this gap and get understanding about this process, a fluidized bed reactor modeling was conducted. We planned to collaborate the modeling with the reaction, that is to say, the kinetics of certain catalyst should be involved. The objective is to obtain the concentration distribution along the fluidized bed, and also understand the effect of various operation conditions on the catalysis performance.

Then, according to our literature survey, the efficient catalysts used for CO₂ methanation in

fluidized bed reactor still lack, here, we tried to develop a catalyst that exhibits better performance in fluidized bed reactor. As the Geldart B particle is common applied in the industrial fluidized bed and especially our bench scale equipment, the commercial SiO₂ sphere with diameter of 100 μm will act as a basic support, furthermore, in order to increase the activity, the support will be coated by TiO₂ before loading the Ni-Co bimetal as active components.

1.7 Organization of the thesis

The dissertation contains 5 chapters, and is organized as follows:

Chapter 1 provides a general introduction of the topics in this dissertation, including the background and significance of CO₂ emission, conversion, thermodynamics, reaction kinetics, modeling of fluidized bed reactor, and catalysts developments.

In chapter 2, the thermodynamic calculations are validated with experimental results, suggesting that the Gibbs free energy minimization method is effective for thermodynamically understanding the reaction network involved in the CO₂ hydrogenation process, which is helpful for the development of high-performance catalysts.

In chapter 3, a fluidized bed reactor model was developed based on an earlier one reported for CO methanation (Kopyscinski, Schildhauer, & Biollaz, 2010). Firstly, the reaction kinetics of the Ni-Mg-W catalyst, which has been reported to exhibit superior catalytic performance, was experimentally characterized. The results presented here are expected to be valuable for both the further development of catalysts and of the reactors needed for practical CO₂ methanation processes.

In chapter 4, a novel Ni-Co bimetal catalyst supported on TiO₂-coated SiO₂ spheres (NiCo/TiO₂@SiO₂) was rationally designed and evaluated for CO₂ methanation in fluidized bed reactor. This study is expected to be valuable for the potential implementation of the CO₂ methanation process in fluidized beds.

Chapter 5 summarizes a general conclusion of this PhD project, and provides recommendation of directions for future research in the field of CO₂ conversion.

Chapter 2 The thermodynamics analysis of CO₂ hydrogenation process

2.1 Introduction

In recent years, efforts have to be put forth to avoid the climate change and ocean acidification as the atmospheric concentrations of CO₂ greenhouse gas continue to rise [21]. Catalytic conversion of CO₂ into valuable chemicals and fuels is one of the important practical routes to reduce CO₂ emissions while fossil fuels dominate the energy sector [22-24]. CO₂ can be catalytically reduced by H₂ to various products such as hydrocarbons, carbon monoxide, carboxylic acids, aldehydes and alcohols in a homogeneous or heterogeneous way [21-23]. Although catalytic CO₂ hydrogenation has been studied extensively in the last decades [22], it still remains as a challenge to develop highly selective catalyst for large-scale commercialization because CO₂ hydrogenation involves a complex reaction network which is restricted by thermodynamics and kinetics.

Thermodynamics calculation of chemical reactions is helpful in understanding and predicting the complicated catalytic process [25-27]. It provides preliminary information in the chemical process, for instance, the thermodynamics stability of desired chemical species, the yield and selectivity of target product, the reaction heat as well as the impact of reaction parameters such as temperature, pressure, and reactant ratio. The thermodynamics analysis is of benefit to tailor the reaction conditions, and thus improve the conversion of reactants and the selectivity towards the favorable products. Combination of thermodynamics calculation and experimental validation is a useful tool to understand the intrinsic process in CO₂ hydrogenation reaction [28-31]. Gao et al. investigated the thermodynamics of CO₂ methanation reaction and calculated the reaction heats and equilibrium constants of eighteen single CO₂ direct hydrogenation reactions [28]. Xu et al. conducted a thermodynamics analysis of formic acid synthesis from CO₂ hydrogenation [32]. Nonetheless, these works were limited to simple systems

with only a few products. Therefore, a more comprehensive thermodynamics analysis is desirable towards CO₂ hydrogenation.

The Gibbs free energy minimization method is widely employed to deal with complicated reaction systems and obtain the corresponding equilibrium composition [26-28]. Based on the principle that the reaction system processes the minimum total Gibbs free energy at the equilibrium state, it is not necessary to know the accurate equilibrium constant of each reaction step for a multi-steps reaction system. The equilibrium distribution of the product mixture can be established by minimizing the Gibbs free energy function, which is subject to the mass balance constraints if only reactants and products are given in the first place. Herein, systematic thermodynamics analyses of CO₂ hydrogenation reactions were conducted by using the total Gibbs free energy minimization method. The products including carbon, carbon monoxide, carboxylic acids (formic acid, acetic acid, and propionic acid), aldehydes (formaldehyde, acetaldehyde, and propionaldehyde), alcohols (methanol, ethanol, propanols and butanols), alkanes (methane, ethane, propane and butanes), alkenes (ethylene, propylene, and butenes), and alkynes (ethyne, propyne, and butynes) were considered (the isomers were also included if needed). In addition, for given product group, the relations between product distribution and reaction conditions (such as reactant compositions, temperature, and pressure) were also investigated. As the reaction kinetics and the transport phenomena were not involved in thermodynamics calculations, the practical reaction data was obtained on well-designed catalytic experiments. The satisfactory match between thermodynamics calculations and experimental results provided a clear picture on the entire reaction process towards CO₂ hydrogenation reaction.

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2.2 Calculation and Experimental Method

2.2.1 Calculation method

The method was performed on the software ChemCAD (Chemstations, Inc. trail version 7.0). The detailed principles involved in the calculation can be found in the literature [28]. The K-value

models and Enthalpy models determined by the temperature and pressure ranges in the ChemCAD software are listed in Table 2-1.

Table 2-1. Corresponding K-value and Enthalpy models used in ChemCAD software for different reactions. (Copyright © Elsevier)

NO	Reaction Formula	K-value Model	Enthalpy Model
1	$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$	VAP	SRK
2	$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{HCOOH}$	PSRK	MIXH
3	$\text{CO}_2 + 2\text{H}_2 \leftrightarrow \frac{1}{2}\text{CH}_3\text{COOH} + \text{H}_2\text{O}$	PSRK	MIXH
4	$\text{CO}_2 + 2\text{H}_2 \leftrightarrow \text{HCOH} + \text{H}_2\text{O}$	Maurer	Maurer
5	$\text{CO}_2 + \frac{5}{2}\text{H}_2 \leftrightarrow \frac{1}{2}\text{CH}_3\text{CHO} + \frac{3}{2}\text{H}_2\text{O}$	PSRK	MIXH
6	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	PSRK	MIXH
7	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \frac{1}{2}\text{C}_2\text{H}_5\text{OH} + \frac{3}{2}\text{H}_2\text{O}$	PSRK	MIXH
8	$\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	VAP	SRK
9	$\text{CO}_2 + \frac{7}{2}\text{H}_2 \leftrightarrow \frac{1}{2}\text{C}_2\text{H}_6 + 2\text{H}_2\text{O}$	VAP	SRK
10	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \frac{1}{2}\text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$	VAP	SRK
11	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \frac{1}{3}\text{C}_3\text{H}_6 + 2\text{H}_2\text{O}$	SRK	SRK
12	$\text{CO}_2 + 4\text{H}_2 \leftrightarrow x\text{CH}_4 + y\text{CO} + z\text{H}_2\text{O}$	VAP	SRK
13	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow w\text{CH}_3\text{OH} + x\text{CH}_3\text{OCH}_3 + y\text{CO} + z\text{H}_2\text{O}$	PSRK	MIXH
14	$\text{CO}_2 + \frac{5}{2}\text{H}_2 \leftrightarrow \frac{1}{2}\text{C}_2\text{H}_2 + 2\text{H}_2\text{O}$	SRK	SRK
15	$\text{CO}_2 + \frac{8}{3}\text{H}_2 \leftrightarrow \frac{1}{3}\text{C}_3\text{H}_4 + 2\text{H}_2\text{O}$	PSRK	MIXH
16	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \frac{1}{2}\text{CH}_3\text{OCH}_3 + \frac{3}{2}\text{H}_2\text{O}$	PSRK	MIXH
17	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow x\text{CH}_3\text{OH} + y\text{CO} + z\text{H}_2\text{O}$	PSRK	MIXH
18	$\text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_3\text{OH}$	PSRK	SRK
19	$\text{CO}_2 + 2\text{H}_2 \leftrightarrow \text{C} + 2\text{H}_2\text{O}$	SRK	SRK
20	$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{Carboxylic Acids}$	PSRK	MIXH
21	$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{Aldehydes}$	Maurer	Maurer
22	$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{Alcohols}$	PSRK	MIXH
23	$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{lower alkanes}$	SRK	SRK
24	$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{lighter alkenes}$	SRK	SRK
25	$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{lower alkynes}$	PSRK	MIXH

The conversion, selectivity, and yield of species i were defined as follows, respectively:

$$\text{The conversion of species } i: X_i (\%) = \frac{N_{i,in} - N_{i,out}}{N_{i,in}} \times 100\% \quad (2-1)$$

$$\text{The selectivity of species } i: S_i (\%) = \frac{j_i N_{i,out} - j_i N_{i,in}}{N_{CO_2,in} - N_{CO_2,out}} \times 100\% \quad (2-2)$$

$$\text{The yield of species } i: Y_i (\%) = \frac{j_i N_{i,out} - j_i N_{i,in}}{N_{CO_2,in}} \times 100\% \quad (2-3)$$

Among which, $N_{i,in}$ and $N_{i,out}$ is the molar flow rate of species i at the inlet and outlet of the reactor, respectively, while j_i is the number of carbon atoms in species i . It should be noted that as the isomers were considered in the calculation, the selectivity of the species with isomers is the total selectivity of all isomers and the method is also applied in the calculation of yield. (Copyright © Elsevier)

2.2.2 Experimental method

To validate the thermodynamics calculation results, catalytic CO₂ hydrogenation to CO and CH₄ over 10 wt.% Cu/CeO₂ and 10 wt.% Ni/CeO₂ catalysts were carried out. It was reported that copper is an effective catalyst in water-gas shift reaction (CO + H₂O → CO₂ + H₂) [33, 34]. Also, Ni catalysts (10 wt % Ni/CeO₂) have been attempted in CO₂ hydrogenation to CO and CH₄ reaction (CO₂ + 4H₂ ↔ xCH₄ + yCO + zH₂O) by several groups.[35-37]. In this work, both catalysts were prepared by impregnation method and the reactions were carried out in a fixed bed plug flow reactor. A low space velocity was used in order to reach the equilibrium state. Typically, 1.0 g of catalyst diluted with 1.0 g of SiC were loaded and pretreated under purified H₂ at 400 °C for 30 min. The catalyst temperature was monitored by a K-type thermocouple positioned inside the catalyst bed. Flow of CO₂ and H₂ mixture gas with different ratios was controlled using mass flow controller (Alicat Scientific, Inc.) at a total flow rate of 100 mL/min (standard temperature and pressure). The hourly gas space velocity (GSV) was 6000 mL/g/h. The reaction temperature was 200-700 °C at an interval of 50 °C and the ramp rate was 5 °C/min. The concentrations of

CO, CO₂, H₂, CH₄ and N₂ in the inlet and outlet streams were measured by an on-line gas chromatograph (7890B, Agilent Technologies) equipped with TCD and FID detector. CO₂ was separated using a Hayesep Q column while CO, CH₄ and N₂ were separated by a Molsieve 5A column.

In the present work, we focus on the thermodynamic properties of chemical reactions, whereas the reaction kinetics is not considered. Indeed, in real CO₂ conversion process, both thermodynamic reaction control and kinetic control play important roles in determining the composition of a product mixture. Thus, the catalyst morphology, activity and stability will affect the reaction selectivity and yield to some degree. However, the investigation on catalyst effect is out of the scope of this work, hence the detailed discussion is not involved. (Copyright © Elsevier)

2.3 Results and discussion

Considering that the product mixture is usually obtained in a real catalytic process for CO₂ hydrogenation, the products are divided into five groups: carbon monoxide and/or methane, carboxylic acids, aldehydes, alcohols, and hydrocarbons.

2.3.1 Hydrogenation of CO₂ to CO and/or CH₄

Hydrogenation of CO₂ to CO via reverse water-gas shift reaction (RWGS, $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) has been recognized as one of the most promising processes for CO₂ utilization because CO can be used in down-stream Fischer-Tropsch (F-T) reaction and methanol synthesis, etc. The RWGS reaction is also gaining interests in the context of the human missions to Mars primarily for its potential to produce water and oxygen [38]. As shown in Table 2-2, the RWGS reaction is endothermic and the Gibbs free energy change is positive at 1 bar and 25 °C. The equilibrium constant at this condition is extremely low (9.67×10^{-6}). The RWGS reactions with different CO₂/H₂ ratios in the range of 2/1 to 1/10 are performed at 100-800 °C and the corresponding equilibrium values are shown in Figure 2-1a. The effect of pressure can be ignored as the number of molecules does not change in this reaction, which is supported by the overlaps of curves with same CO₂/H₂ ratio but different pressure. However, temperature reveals a critical influence on

the equilibrium CO yield (CO₂ conversion). Within the temperature range, the equilibrium CO yield is increasing with temperature for any feed composition, due to the endothermic characteristics of the RWGS reaction. Moreover, a significant increase in the equilibrium yield of CO is observed with increasing initial H₂ concentration in the feed. When the ratio of CO₂/H₂ is 1/1, the CO yield is obtained nearly 50 % at 800 °C and reaches 90 % when the ratio changes to 1/10 under the same temperature.

Table 2-2. Gibbs free energy changes, enthalpy changes and standard equilibrium constants in hydrogenation reactions of CO₂ to CO or CH₄. (Copyright © Elsevier)

No.	Reaction Formula*	$\Delta G^\ominus(298\text{K})$ (kJ/mol)	$\Delta H^\ominus(298\text{K})$ (kJ/mol)	$K^\ominus(298\text{K})$
1	CO ₂ + H ₂ ↔ CO + H ₂ O	28.6	41.2	9.67×10 ⁻⁶
2	CO ₂ + 4H ₂ ↔ CH ₄ + 2H ₂ O	-113.5	-165.0	7.79×10 ¹⁹

*Note: All the components involved in the reaction formulas in this article are specified as gas state, unless otherwise indicated.

In order to verify the theoretical calculations, the catalytic testing is conducted on Cu/CeO₂, which is a typical selective catalyst for WGS transformation [33, 34] and is probably also active for RWGS reaction. As shown in Figure 2-1b, the comparison results are perfectly matched in the region of medium-high temperature, >350 °C and >400 °C under the ratio of CO₂/H₂ is 1/1 and 1/4, respectively. Namely, reaction remains at the equilibrium state by the thermodynamics limitation, which agrees well with the standpoints from several catalyst systems reported before[39, 40]. However, it cannot reach the equilibrium at relatively low reaction temperature (<350 °C) due to the poor activity of the catalyst.

Frequently, the RWGS reaction exists as a side reaction in CO₂ methanation in both laboratory scale and industrial process, depending on the catalyst and operating parameters. The calculations based on the Gibbs free energy minimization method and catalytic testing over Ni/CeO₂ was

performed to represent the equilibrium values of CO₂ methanation in the presence of CO as a byproduct. The reaction pressure and the CO₂/H₂ ratio in the feed are kept at 1 bar and 1/4, respectively (shown in Figure 2-1c and 2-1d). In accordance with the CO₂ profile of single CO₂ methanation reaction, the CO₂ conversion decreases from 100 to 600 °C, followed by steady increase at high temperatures for CO₂ methanation in the presence of RWGS side reaction. The selectivity studies on CH₄ and CO indicate that CH₄ is the main product below 600 °C; further increase in the temperature leads to the larger percentage of CO because the amount of CH₄ produced reduces rapidly. The 100 % selectivity to CO can be seen at 750 °C, implying that the exothermic CO₂-to-CH₄ reaction dominates at the temperatures below 600 °C, whereas the RWGS reaction is the predominate one above 600 °C. Figure 2-1 shows that the experiment data obtained on Ni/CeO₂ catalyst perfectly fits the calculated values except the CO₂ conversion at the temperature below 300 °C, which is attributed to the poor activity of the catalyst under such a low temperature. The further investigation demonstrates that adding inert gas (N₂) into the reactant stream slightly decreases the CO₂ conversion and the CH₄ selectivity, whereas it increases the selectivity of CO in the temperature range of 450-700 °C (see Figure 2-2).

Figure 2-1. Hydrogenation of CO₂ to CO with different CO₂/H₂ ratios at 1 bar: (a) CO₂ conversion at equilibrium state and (b) comparison of calculated data and experimental data over Cu/CeO₂ catalyst; Hydrogenation of CO₂ to CH₄ and CO at 1 bar: (c) CO₂ conversion, CH₄ and CO selectivity at equilibrium state and (d) comparison of calculated and experimental data over Ni/CeO₂ catalysts. (Copyright © Elsevier)

Figure 2-2. Hydrogenation of CO₂ to CH₄ and CO: (a) effect of inert N₂ and (b) comparison of experimental and calculated data with inert N₂ in the system. (Copyright © Elsevier)

CO₂ can be reduced to carbon according to the following reaction equation: $\text{CO}_2 + 2\text{H}_2 \leftrightarrow \text{C} + 2\text{H}_2\text{O}$. Table 2-3 listed the Gibbs energy, enthalpy changes as well as standard equilibrium constant of CO₂ hydrogenation to carbon at 298 K.

Table 2-3. Gibbs energy changes, enthalpy changes as well as standard equilibrium constant of CO₂ hydrogenation to carbon. (Copyright © Elsevier)

No.	Reaction Formula	$\Delta G^\ominus(298\text{K})$ (kJ/mol)	$\Delta H^\ominus(298\text{K})$ (kJ/mol)	$K^\ominus(298\text{K})$
1	$\text{CO}_2 + 2\text{H}_2 \leftrightarrow \text{C(s)} + 2\text{H}_2\text{O}$	-62.8	-90.1	9.94×10^{10}

The effects of temperature, pressure, H₂/CO₂ molar ratio were studied, and the results are shown in Figure 2-3. It can be seen that low temperature is favorable for the reduction of CO₂ to carbon by H₂. Increasing pressure will increase the conversion of CO₂ since the number of total molecules in reaction is reducing. In addition, higher H₂/CO₂ ratio will also benefit the production of carbon. However, till now, there are still few reports on this reaction.

Figure 2-3. Hydrogenation of CO₂ to carbon with different CO₂:H₂ molar ratios of 1:1, 1:2, and 1:3 at 1, 10, and 100 bar: CO₂ conversion at equilibrium. (Copyright © Elsevier)

2.3.2 Hydrogenation of CO₂ to Carboxylic Acids

It has been reported that CO₂ can be hydrogenated to carboxylic acids, like formic acid [41-43] and acetic acid [44] under certain conditions. Formic acid (HCOOH) has attracted tremendous attention as a safe and convenient hydrogen carrier in fuel cells designed for portable use [42].

As shown in Table 2-4, the hydrogenation of CO₂ to formic acid is an endothermic reaction with a $\Delta H^\ominus$ (298K) of 14.9 kJ/mol and a $\Delta G^\ominus$ of 43.5 kJ/mol at standard condition, as well as the equilibrium constant is very small, only 2.43×10^{-8} at 298 K. However, with the increase of the number of the carbon atoms in carboxylic acids, the reaction process turns to exothermic and the Gibbs free energy turns to negative value. For example, for the CO₂ to acetic acid conversion, $\Delta G^\ominus$ decreases to -21.6 kJ/mol, which is thermodynamically more favorable than the formation of formic acid. Although the thermodynamics prefers the production of higher-carbon acids, it is difficult in the practical catalysis process due to the kinetic constraints in C-C coupling. Very recently, synthesis of acetic acid via methanol hydrocarboxylation with CO₂ and H₂ was reported [45].

Table 2-4. Gibbs free energy, enthalpy changes and standard equilibrium constants for the hydrogenation of CO₂ to formic acid, acetic acid, propionic acid, and butyric acid. (Copyright © Elsevier)

No.	Reaction Formula	$\Delta G^\ominus(298K)$ (kJ/mol)	$\Delta H^\ominus(298K)$ (kJ/mol)	$K^\ominus(298K)$
1	CO ₂ + H ₂ $\leftrightarrow$ HCOOH	43.5	14.9	2.43×10^{-8}
2	CO ₂ (g) + H ₂ (g) + NH ₃ (aq) $\leftrightarrow$ HCO ₂ ⁻ (aq) + NH ₄ ⁺ (aq)	-9.5	-84.3	/
3	CO ₂ (aq) + H ₂ (aq) + NH ₃ (aq) $\leftrightarrow$ HCO ₂ ⁻ (aq) + NH ₄ ⁺ (aq)	-35.4	-59.8	/
4	CO ₂ + 2H ₂ $\leftrightarrow$ $\frac{1}{2}$ CH ₃ COOH + H ₂ O	-21.6	-64.8	6.11×10^3
5	CO ₂ + $\frac{7}{3}$ H ₂ $\leftrightarrow$ $\frac{1}{3}$ C ₂ H ₅ COOH + $\frac{4}{3}$ H ₂ O	-32.6	-80.1	5.17×10^5
6	CO ₂ + $\frac{5}{2}$ H ₂ $\leftrightarrow$ $\frac{1}{4}$ C ₃ H ₇ COOH + $\frac{3}{2}$ H ₂ O	-38.5	-88.2	5.47×10^6

For the simple system of CO₂ hydrogenation to formic acid, the effects of reaction temperature and pressure on CO₂ conversion (same as HCOOH yield) were calculated with the aid of the Gibbs free energy minimization method, as shown in Figure 2-4a. The yield of HCOOH is very low (less than 0.01 %) in a wide temperature (100-400 °C) and pressure (1-300 bar) range. Although the increasing of pressure and temperature can enhance the conversion of CO₂ to HCOOH, the improvement is insignificant. In order to achieve a high yield of HCOOH, the addition of base species in the reaction system is one of the effective strategies [38]. For instance, introducing NH₃ can greatly increase the equilibrium constant (see Table 2-4). Compared with the reaction to produce formic acid, the formation of acetic acid is much more thermodynamically favored with much high CO₂ conversion under the same reaction conditions, as illustrated in Figure 2-4b. Furthermore, we consider a mixed products system, which contains formic acid, acetic acid, and propionic acid, and the selectivity of each product and CO₂ conversion under different temperature and pressure are shown in Figure 2-4c and 2-4d. It can be seen that the higher carbon acid possesses higher selectivity and propionic acid is the dominant product (selectivity > 90 %) under all reaction conditions, indicating that the thermodynamics prefers the formation of the acid with more carbon atoms. This is in accordance with the trends of the three single reactions. In addition, the product distributions vary little at different pressures and CO₂/H₂ molar ratios. However, in practical terms, suitable catalysts for the production of acetic acid or propionic acid are rarely reported and still need further investigations.

Figure 2-4. CO₂ conversions as a function of reaction temperature and pressure for hydrogenation of CO₂ to (a) formic acid and (b) acetic acid. Hydrogenation performance of CO₂ to mixed products of carboxylic acids, products selectivity and CO₂ conversion at (c) CO₂/H₂ ratio of 1/1 and 200 bar and (d) CO₂/H₂ ratio of 1/2 and 50 bar. (Copyright © Elsevier)

2.3.3 Hydrogenation of CO₂ to Aldehydes

Table 2-5 reveals the Gibbs free energy, enthalpy changes and standard equilibrium constants for the hydrogenation of CO₂ to aldehydes such as formaldehyde, acetaldehyde, and propionaldehyde, and butyraldehyde under standard condition. Only the formation of formaldehyde from CO₂ hydrogenation has a positive $\Delta G^\ominus$, whereas the formation processes of higher carbon aldehydes have much smaller values. Moreover, the value of $\Delta G^\ominus$ decreases with the increase of carbon numbers in the aldehydes, and consequently the thermodynamics tends to produce the aldehyde with higher carbon number rather than lower one. This is very similar with the case for CO₂ hydrogenation to carboxylic acids.

Table 2-5. Gibbs free energy, enthalpy change and standard equilibrium constants for the hydrogenation of CO₂ to formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde. (Copyright © Elsevier)

No.	Reaction Formula	$\Delta G^\ominus(298K)$	$\Delta H^\ominus(298K)$	$K^\ominus(298K)$
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		(kJ/mol)	(kJ/mol)	
1	$\text{CO}_2 + 2\text{H}_2 \leftrightarrow \text{HCHO} + \text{H}_2\text{O}$	55.9	35.8	1.63×10^{-10}
2	$\text{CO}_2 + \frac{5}{2}\text{H}_2 \leftrightarrow \frac{1}{2}\text{CH}_3\text{CHO} + \frac{3}{2}\text{H}_2\text{O}$	-12.9	-54.6	1.86×10^2
3	$\text{CO}_2 + \frac{8}{3}\text{H}_2 \leftrightarrow \frac{1}{3}\text{C}_2\text{H}_5\text{CHO} + \frac{5}{3}\text{H}_2\text{O}$	-28.1	-71.6	8.52×10^4
4	$\text{CO}_2 + \frac{11}{4}\text{H}_2 \leftrightarrow \frac{1}{4}\text{n-C}_3\text{H}_7\text{CHO} + \frac{7}{4}\text{H}_2\text{O}$	-34.7	-81.4	1.21×10^6

According to the thermodynamics calculations for hydrogenation of CO_2 to formaldehyde, the CO_2 equilibrium conversion increases monotonically when the reaction temperature or pressure rises, as shown in Figure 2-5a. However, the HCOH yield (CO_2 conversion) is no more than 0.5 % in the temperature range of 200 to 500 °C and pressure range of 1-100 bar, due to the very high and positive Gibbs free energy change value. Higher pressure and temperature will increase the conversion of CO_2 to HCOH since the reaction is an endothermic process with reducing number of molecules. The selective formation of formaldehyde from carbon dioxide and hydrogen ($\text{CO}_2 + 2\text{H}_2 \leftrightarrow \text{HCHO} + \text{H}_2\text{O}$) over PtCu/SiO₂ was reported previously [46]. The experimental results at H_2/CO_2 molar ratio of 20/1 under 150 °C and 6 bar also showed a very low yield of HCHO (estimated to be $\sim 1.5 \times 10^{-5}$) in CO_2 hydrogenation process, which is consistent with our calculation results, due to the thermodynamic limitation.

The single process of CO_2 hydrogenation to acetaldehyde is thermodynamically more likely to occur as compared to formaldehyde production. Figure 2-5b shows the equilibrium values and the effects of temperature and pressure on the CO_2 -to-acetaldehyde process. The results demonstrate that low temperature and high pressure are beneficial to enhance the reaction activity. When the temperature is as low as 200 °C, the conversion of CO_2 to acetaldehyde can reach 20 % and almost 100 % under atmosphere pressure and 100 bar, respectively. Nonetheless, three-carbon propionaldehyde is the main product under given reaction conditions, as shown in Figure 2-5c and 2-5d, if we take a mixed products system including formaldehyde, acetaldehyde, and propionaldehyde into account. In addition, reaction pressure and CO_2/H_2 molar ratio have little

effects on the variation of product selectivity, since propionaldehyde is much more preferred thermodynamically compared with formaldehyde and acetaldehyde. Therefore, from thermodynamic point of view, we expect that aldehyde molecules with longer carbon chains are more facile to be obtained from CO₂ hydrogenation due to negative ΔG values. However, in the real catalysis process, it is difficult to complete the production of those high carbon aldehydes due to the kinetic limitations. Therefore, design of highly efficient catalysts to reach the equilibrium value is still a challenge.

Figure 2-5. The equilibrium values for hydrogenation of CO₂ to (a) formaldehyde and (b) acetaldehyde. Hydrogenation performances of CO₂ to mixture products of aldehydes under (c) CO₂/H₂ ratio of 1/1 at 50 bar and (d) CO₂/H₂ ratio of 1/5 at 200 bar. (Copyright © Elsevier)

2.3.4 Hydrogenation of CO₂ to Alcohols

Recently, the hydrogenation of CO₂ to alcohols has attracted more attention since alcohols are good energy carriers [47-51]. As listed in Table 2-6, CO₂ can be hydrogenated to different alcohols like methanol, ethanol and higher alcohols. In these reactions, the synthesis of methanol from CO₂ hydrogenation is the most direct route and widely investigated one for CO₂ utilization because methanol can be used as fuel additive, fuel substitute and precursor to many commodity chemicals [48-50]. The hydrogenation process of CO₂ to methanol has the $\Delta G^\ominus$ of 3.5 kJ/mol, corresponding to an equilibrium constant of 2.45×10^{-1} at 298 K (Table 4). Figure 2-6a gives the calculation profiles of CO₂ conversion to methanol at different reaction temperatures and pressures. The equilibrium conversion of CO₂ decreases regularly with increasing the temperature because of the exothermic property ($\Delta H^\ominus$ of -49.3 kJ/mol). Higher pressure leads to higher CO₂ conversion at the same reaction temperature as the reaction is a volume reducing reaction. Under the atmosphere condition, CO₂ can be hardly converted (conversion $< 1\%$) in the whole temperature range. However, the CO₂ conversion of $\sim 100\%$ can be achieved under 50 bar at 100 °C and remained at up to 250 °C under both the pressure of 200 and 300 bar. From the thermodynamics analysis, low temperature and high pressure can significantly boost the methanol production. In a typical case of industrial synthesis, CO, H₂ and a small amount of CO₂ could be catalyzed to form methanol efficiently by a Cu/ZnO/Al₂O₃ catalyst between 5-10 MPa at 220-300 °C [52, 53]. In addition, it has been reported that outstanding one-pass CO₂ conversion ($>95\%$) and methanol selectivity ($>98\%$) were accomplished under an optimized reaction conditions (H₂/CO₂ $> 10/1$, 360 bar and 260 °C) [54]. This is generally consistent with the calculated values in Figure 2-6a. For comparison, hydrogenation of CO to methanol was also calculated and revealed similar trends with CO₂-to-methanol process, as given in Figure 2-7.

Table 2-6. Gibbs free energy, enthalpy changes and standard equilibrium constants for the hydrogenation of CO₂ to alcohols including methanol, ethanol, propanols, and butanols, and dimethyl ether. (Copyright © Elsevier)

No.	Reaction Formula	$\Delta G^\ominus(298\text{K})$ (kJ/mol)	$\Delta H^\ominus(298\text{K})$ (kJ/mol)	$K^\ominus(298\text{K})$
1	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	3.5	-49.3	2.45×10^{-1}
2	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \frac{1}{2}\text{C}_2\text{H}_5\text{OH} + \frac{3}{2}\text{H}_2\text{O}$	-32.4	-86.7	4.70×10^5
3	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \frac{1}{3}n\text{-C}_3\text{H}_7\text{OH} + \frac{5}{3}\text{H}_2\text{O}$	-39.9	-94.6	9.82×10^6
4	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \frac{1}{4}n\text{-C}_4\text{H}_9\text{OH} + \frac{7}{4}\text{H}_2\text{O}$	-43.2	-98.3	3.73×10^7
5	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \frac{1}{2}\text{CH}_3\text{OCH}_3 + \frac{3}{2}\text{H}_2\text{O}$	-4.9	-61.3	7.15

The formation of ethanol from CO_2 hydrogenation is more favorable under same reaction conditions from the viewpoint of thermodynamics, and the calculation analysis results are shown in Figure 2-6b. The ethanol yield (CO_2 conversion) of ~85 % can be obtained even at 100 °C and 1 bar, while ~100 % yield can be kept at a temperature as high as 300 °C under reaction pressure of 300 bar. If we consider methanol, ethanol, propanols, and butanols as the possible products in a single system, we can propose the product distributions in Figure 2-6c (CO_2/H_2 ratio of 1/1 at 50 bar) and Figure 2-6d (CO_2/H_2 ratio of 1/5 at 200 bar) according to the thermodynamics calculations. Butanol is the dominant product over a wide range of reaction conditions. A small amount of propanol (1-5 %) is yielded whereas the selectivity of methanol and ethanol is so small that it can be neglected. This trend is in accordance with Gibbs free energy change values in Table 2-6. The calculation results indicate that production of higher alcohol is more thermodynamically favorable.

Figure 2-6. The equilibrium values for hydrogenation of CO₂ to (a) methanol and (b) ethanol. Hydrogenation performances of CO₂ to mixture products of alcohols under (c) CO₂/H₂ ratio of 1/1 at 50 bar and (d) CO₂/H₂ ratio of 1/5 at 200 bar. (Copyright © Elsevier)

Figure 2-7. CO conversion at different temperatures and pressures for CO hydrogenation to

CH₃OH.

To our knowledge, dimethyl ether (CH₃OCH₃) and CO are regarded as common byproducts in the process of CO₂ hydrogenation to methanol [22,25]. Although related thermodynamics investigations have been reported, their calculations were limited to binary product systems, i.e. CH₃OH + CO or CH₃OCH₃ + CO [9]. Therefore, it is necessary to perform the thermodynamics study towards a more complicated ternary product system, which contains CH₃OH, CO, and CH₃OCH₃. The calculation results are shown in Figure 2-8. CO₂ hydrogenation solely to CH₃OCH₃ was also calculated and given in Figure 2-9. The curve of CO₂ conversion to ternary products is a little different from that of single CO₂-to-CH₃OH process. As shown in Figure 2-8a, CO₂ conversion decreases monotonously in the low temperature range and followed by slight increase at higher temperatures. Three reasons may account for such U-shaped curves. (1) The production of CH₃OCH₃ is an exothermic process, and plays a major role at lower temperature. (2) The RWGS reaction of CO₂-to-CO prefers high temperature, which dominates the CO₂ conversion over a high temperature range. (3) Though CH₃OH selectivity reveals a volcano-shaped variation trend, it plays a little role in the entire process. Additionally the thermodynamics profiles towards such system can be verified by the selectivity of the products. In addition, we find that this process is sensitive to pressure. Particularly, a high pressure greatly accelerates the CO₂ conversion and tends to enhance the selectivity for CH₃OH and CH₃OCH₃ but not for CO (Figure 2-8b, c and d). In Figure 2-8b the maximum point of CH₃OH selectivity moves to higher temperature direction with the increasing pressure, due to the joint effects that methanol formation is a volume reducing and exothermic reaction. A high CH₃OCH₃ selectivity can be obtained at low temperature and high pressure and kept in a wide temperature range (Figure 2-8c). In order to reduce CO production, low temperature and high pressure are needed (Figure 2-8d). CH₃OH yield and CH₃OCH₃ yield are given in Figure 2-10. Based on the above analyses, it is recommended that typical CO₂ hydrogenation to CH₃OH process needs lower temperature (<300 °C) and a relatively high pressure (>30 bar).

Figure 2-8. (a) CO₂ conversion, (b) CH₃OH selectivity, (c) CH₃OCH₃ selectivity, and (d) CO selectivity at equilibrium state in hydrogenation of CO₂ to mixture products of CH₃OH, CO and CH₃OCH₃. (Copyright © Elsevier)

Figure 2-9. CO₂ conversion at different temperatures and pressures for CO₂ hydrogenation to

CH₃OCH₃.

Figure 2-10. CH₃OH yield (a), CH₃OCH₃ yield (b), CH₃OCH₃ and CH₃OH selectivity (c) and yield (d) in CO₂ hydrogenation to CH₃OH, CH₃OCH₃ and CO reaction system.

2.3.5 Hydrogenation of CO₂ to Hydrocarbons

Heterogeneous catalytic CO₂ conversion to value-added hydrocarbons has been widely studied in recent years [28, 55-57]. Table 2-7 listed the Gibbs free energy, and enthalpy changes as well as standard equilibrium constants for hydrogenation of CO₂ to hydrocarbons, like methane, ethane, ethylene, and propylene. The $\Delta G^\ominus$ of the formation to CH₄ is much smaller than the other reactions, which means CH₄ is the most favorable product among all the hydrocarbons. The order of production preference for CO₂-to-alkanes conversion in thermodynamics is CH₄ > C₂H₆ > C₃H₈ > C₄H₁₀, as their $\Delta G^\ominus$ values increase along with the increasing of the carbon numbers.

However, the opposite trend is observed for the production of alkenes and alkynes from CO₂ hydrogenation based on the thermodynamics analyses.

Table 2-7. Gibbs free energy, enthalpy changes as well as standard equilibrium constants for hydrogenation of CO₂ to hydrocarbons. (Copyright © Elsevier)

No	Reaction Formula	$\Delta G^\ominus(298\text{K})$ (kJ/mol)	$\Delta H^\ominus(298\text{K})$ (kJ/mol)	$K^\ominus(298\text{K})$
1	$\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-113.5	-165.0	7.79×10^{19}
2	$\text{CO}_2 + \frac{7}{2}\text{H}_2 \leftrightarrow \frac{1}{2}\text{C}_2\text{H}_6 + 2\text{H}_2\text{O}$	-78.7	-132.1	6.26×10^{13}
3	$\text{CO}_2 + \frac{10}{3}\text{H}_2 \leftrightarrow \frac{1}{3}\text{C}_3\text{H}_8 + 2\text{H}_2\text{O}$	-70.9	-125.0	2.64×10^{12}
4	$\text{CO}_2 + \frac{13}{4}\text{H}_2 \leftrightarrow \frac{1}{4}\text{n-C}_4\text{H}_{10} + 2\text{H}_2\text{O}$	-66.9	-121.6	5.28×10^{11}
5	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \frac{1}{2}\text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$	-28.7	-64.0	1.07×10^5
6	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \frac{1}{3}\text{C}_3\text{H}_6 + 2\text{H}_2\text{O}$	-42.1	-83.6	2.34×10^7
7	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \frac{1}{4}\text{1-C}_4\text{H}_8 + 2\text{H}_2\text{O}$	-45.2	-90.3	8.33×10^7
8	$\text{CO}_2 + \frac{5}{2}\text{H}_2 \leftrightarrow \frac{1}{2}\text{C}_2\text{H}_2 + 2\text{H}_2\text{O}$	41.8	23.2	4.69×10^{-8}
9	$\text{CO}_2 + \frac{8}{3}\text{H}_2 \leftrightarrow \frac{1}{3}\text{C}_3\text{H}_4 + 2\text{H}_2\text{O}$	2.0	-28.3	4.39×10^{-1}
10	$\text{CO}_2 + \frac{11}{4}\text{H}_2 \leftrightarrow \frac{1}{4}\text{1-C}_4\text{H}_6 + 2\text{H}_2\text{O}$	-12.2	-48.8	1.38×10^2

The effects of temperature (100-600 °C) and pressure (1-100 bar) on the conversion of CO₂ to CH₄, C₂H₆, C₂H₄, C₃H₆, C₂H₂, and C₃H₄ in each single reaction were calculated, as shown in Figure 2-11. It can be seen that CH₄, C₂H₆, C₂H₄, and C₃H₆ are more favorable to be obtained compared with C₂H₂ and C₃H₄ in thermodynamics. In the following parts, we will discuss the production of alkanes, alkenes, and alkynes as well as their mixture, respectively.

Figure 2-11. Hydrogenation of CO₂ to (a) methane, (b) ethane, (c) ethylene, (d) propylene, (e) C₂H₂ and (f) C₃H₄: CO₂ conversion at different temperatures and pressures.

2.3.5.1 CO₂ hydrogenation to lower alkanes (CH₄, C₂H₆, C₃H₈ and C₄H₁₀)

CO₂ can be hydrogenated to alkanes, such as CH₄, C₂H₆, C₃H₈ and C₄H₁₀. If we consider all these products together in a system, at thermodynamically equilibrium state, CH₄ is most selective with the high selectivity of 99 % under various reaction conditions (CO₂/H₂ molar ratio from 1/1 to 1/5, pressure from 1 to 300 bar, temperature range of 100 to 600 °C, figures are not

shown here)

2.3.5.2 CO₂ hydrogenation to lighter alkenes C₂H₄, C₃H₆, and C₄H₈

The light alkenes are particularly ethylene (C₂H₄), propylene (C₃H₆), and butene (C₄H₈), and they are important intermediates in the manufacture of products such as plastics, solvents, paints, and medicines [58]. For a reaction system of CO₂ hydrogenation to mixed products of C₂H₄, C₃H₆, and C₄H₈, the effects of temperature, pressure and CO₂/H₂ ratio on the equilibrium status were investigated and the results are shown in Figure 2-12.

C₄H₈ is the dominant product over others in the low temperature range; however, its selectivity gradually decreases with the increase of temperature. The temperature is the principal factor for C₄H₈ formation, which prefers a low reaction temperature. In contrast to C₄H₈, a high reaction temperature can facilitate the formation of C₂H₄ and thus increase the selectivity. C₃H₆ production is also sensitive to the reaction temperature. The relation between C₃H₆ selectivity and temperature displays a volcano-shaped curve under 1 bar but linearity under 50 bar. The pressure influences the product distributions for all three alkenes, especially a high pressure is beneficial to improve the formation of C₄H₈ and C₃H₆ but not C₂H₄. For instance, the selectivity to C₄H₈, C₃H₆ and C₂H₄ is varied from 2 %, 15 % and 83 % under 1 bar to 36 %, 44 % and 20 % under 50 bar, respectively, if the temperature is 600 °C and the CO₂/H₂ ratio is 1:1 (Figure 2-12a and 2-12b). In addition, it should be noted that the effect of CO₂/H₂ ratio on product selectivity is inappreciable. The conversion of CO₂ comes from the cooperative effect of the formation processes of three kinds of alkenes, which is simultaneously affected by the temperature, pressure and CO₂/H₂ ratio as well. In particular, CO₂ conversion tends to occur under an optimized reaction condition, which is a lower temperature, a lower CO₂/H₂ ratio and a higher pressure.

Figure 2-12. For CO_2 hydrogenation to C_2H_4 , C_3H_6 , and C_4H_8 , selectivity of products and conversion of CO_2 at different pressure and $CO_2:H_2$ ratio: (a) 1 bar and 1:1, (b) 50 bar and 1:1, (c) 1 bar and 1:5, and (d) 50 bar and 1:5. (Copyright © Elsevier)

2.3.5.3 CO_2 hydrogenation to lower alkynes (C_2H_2 , C_3H_4 , and C_4H_6)

For a reaction system of CO_2 hydrogenation to mixed products of C_2H_2 , C_3H_4 , and C_4H_6 , the effects of temperature, pressure and CO_2/H_2 ratio on the equilibrium status were investigated and the results are shown in Figure 2-13. It can be seen that C_4H_6 nearly achieves 100 % selectivity during lower temperature range. Some C_3H_4 can be found at higher temperature. Pressure and the molar ratio of CO_2/H_2 have some slight effects on the conversion of CO_2 and selectivity of the products.

Figure 2-13. In CO_2 hydrogenation to C_2H_2 , C_3H_4 , and C_4H_6 , selectivity of products and conversion of CO_2 at different pressure and $CO_2:H_2$ ratio: (a) 1 bar and 1:1, (b) 50 bar and 1:1, (c) 1 bar and 1:5, and (d) 50 bar and 1:5. (Copyright © Elsevier)

2.3.5.4 CO_2 hydrogenation to lower alkanes, alkenes and alkynes together

The reaction system considering lower alkanes, alkenes and alkynes together was also calculated and the results reveal that CH_4 selectivity is above 99 % in a wide range of experimental conditions (pressure of 1-300 bar, temperature range of 100-800 $^{\circ}C$, and CO_2/H_2 molar ratio of 1/1 to 1/6, figures are not shown here).

2.4. Conclusion

In summary, we have conducted a systematic thermodynamics analysis towards the hydrogenation of CO_2 to various kinds of products such as CO, hydrocarbons, alcohols, aldehydes and carboxylic acids, by employing the total Gibbs free energy minimization method. Based on

the theoretical calculation results, the information of equilibrium state and the effect of reaction parameters on both reaction systems with single product and multiple products were clearly illustrated. Particularly, for individual RWGS reaction, the reduction of CO₂ to CO needs a high temperature (> 500 °C) and H₂/CO₂ ratio to achieve a high conversion. Lower temperature (< 500 °C) will favor the production of CH₄ if both CO and CH₄ are considered as products. Direct CO₂ hydrogenation to formic acid or formaldehyde is thermodynamically limited unless being disturbed by adding species to the system. According to our thermodynamic calculations, CO₂ tends to convert to the carboxylic acid, aldehyde, alcohol, alkene and alkyne with higher carbon numbers (i.e. propionic acid, propionaldehyde, butanol, butene and butyne in considered cases) at low temperature (e.g. < 200 °C) and high pressure (e.g. > 10 bar). However, it is worth to mention that these reactions are probably limited by kinetics in practice. Thus, designing highly efficient catalysts is critical for further CO₂ conversion studies. As for the CO₂ hydrogenation to alkanes, high H₂/CO₂ ratio in the feed, high pressure and low temperature are beneficial for the enhancement of CO₂ conversion. Moreover, once CH₄ is considered as a kind of product in the mixture of lower alkane, alkenes and alkynes, it will dominate over others, possessing the selectivity of above 90 % under all reaction conditions. In addition, well-designed experiments were also conducted on both RWGS reaction and CO₂ methanation reaction over Cu/CeO₂ and Ni/CeO₂ catalysts, respectively. The good match of the calculation results with the experiment data further proves that the Gibbs free energy minimization approach is significantly effective for the thermodynamics analysis of CO₂ hydrogenation process. Therefore, this work provides a clear thermodynamic picture on the complicated CO₂ conversion process, which is a good reference for the follow-up catalysis research in related areas. In addition, it should be noted that the actual product formation depends, in most cases, significantly more on kinetic factors as opposed to thermodynamic factors. So some of the results may not provide an accurate picture for model reactions and this is the intrinsic limitations of Gibbs free energy minimization analysis.

Considering CO₂ methanation is thermodynamically favorable under relative mild reaction

condition, so the next chapter deal with CO₂ methanation modeling in reactor.

Chapter 3 A fluidized bed modeling study for CO₂ methanation using the Ni-Mg-W catalyst

3.1 Introduction

The production of methane from carbon dioxide (CO₂) hydrogenation, specifically the reduction of carbon dioxide to methane by hydrogen ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$), has received increasing attention, especially over the past decade [20, 59, 60]. This is primarily because (i) the demand for substitute natural gas (SNG) and the need for mitigating the greenhouse effect is escalating; (ii) the availability of hydrogen resource from water-splitting derived by renewable energy makes the CO₂ methanation process more promising; and (iii) CO₂ methanation is the most thermodynamically favorable process among the CO₂ hydrogenation reactions [28]. Tremendous efforts have been devoted to the development of effective and stable catalysts, and the understanding of the reaction mechanisms [59-62]. However, a gap in the knowledge base persists with regards to the practical large-scale implementation of CO₂ hydrogenation.

Notably, the CO₂ methanation reaction is highly exothermic, which means heat removal needs to be highly efficient to avoid the sintering of the catalysts. Compared to the fixed bed, the fluidized bed reactor confers much better heat and mass transfer efficiency [63-65], which makes it more ideal for this application. In particular, the fluidized bed is known to allow for nearly isothermal conditions throughout the particle bed, which minimizes the deactivation of the catalyst because of sintering and coking due to hot spots in the fixed-bed reactor [63-65]. While fluidized bed holds certain advantages over fixed bed, the toxicity of nickel can make it practically challenging to operate such catalysts in fluidized beds while addressing health/safety concerns. To better understand the associated dynamics, the reactor modeling of CO₂ methanation is necessary to rationally design the practical reactor and assess the influence of various operating parameters such as temperature, pressure, gas flow rate, reactor size, etc. [66-70].

Recently, fluidized bed models for carbon monoxide (CO) methanation have been developed that exhibit good agreement with experimental results. Such models provide for a better

understanding of the behavior of the overall reactor and also the reactions, giving comprehensive information for predicting characteristics such as temperature and product distribution profiles within the reactor [66, 71, 72]. However, the corresponding fluidized bed model for CO₂ methanation is not available to date. As CO₂ is more inert than CO, a more effective catalyst is needed to activate this reaction. To this end, previous results have shown that the Ni-Mg-W catalyst is very active and selective for CO₂ methanation [59]. Accordingly, in this work, we further modeled the catalysis behavior of Ni-Mg-W catalyst in the fluidized bed reactor with the kinetics obtained experimentally. Considering that CO can be generated through the reverse water-gas shift (RWGS) reaction (i.e., $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) as a byproduct during the CO₂ methanation process, we also added the RWGS reaction as a side reaction in the modeling process. The influences of different parameters on the CO₂ methanation process in the fluidized bed reactor were systematically studied. The results are expected to provide useful guidance towards the design of the CO₂ methanation fluidized bed reactor. (Copyright © Elsevier)

3.2. Experimental

3.2.1 Kinetics study of the Ni-Mg-W catalyst

The Ni-Mg-W catalyst with the molar ratio of Ni:Mg:W being 1:1:1 was prepared by the homogeneous precipitation method, as reported in an earlier work [59]. A packed-bed quartz-tube reactor with an inner diameter of 6 mm was used to study the kinetics of CO₂ methanation under atmospheric pressure. The bed temperature was monitored by a K-type thermocouple with the tip positioned in the catalyst bed. Before the kinetics test, the Koros-Nowak criterion test was conducted to confirm that the reaction condition was not affected significantly by internal and external diffusions (the experimental details are presented in the Supporting Information) [73].

The Koros-Nowak criterion test was conducted to confirm that the reaction condition was not affected obviously by internal and external diffusions. In detail, the reaction rate was measured over 15 mg of the Ni-Mg-W catalyst mixed with silicon carbide (SiC) of the same mesh size (i.e., 60 - 80 mesh) at mass ratios of 1:6, 1:12 and 1:30. The catalyst was pre-treated under 5% H₂ in

Ar (50 mL/min) at 500 °C for 1 h, then cooled down before the gas was switched to the reaction gas mixture of 20 % CO₂, 6 0% H₂, and 20 % N₂ at a total flow rate of 120 mL/min. The reaction was conducted in the range of 443 to 523 K at temperature intervals of 10 K.

To get the intrinsic kinetics, the Koros-Nowak criterion test was applied to test. Figure 3-1 shows the result. Obviously, we can see that the CO₂ conversion keeps same with different mass ratios of catalyst and SiC at different temperature, indicating that internal and external diffusion together with the heat transfer limitations of Ni-Mg-W catalyst can be ignored.

Figure 3-1. The CO₂ conversion using Ni-Mg-W catalyst under different mass ratios of catalyst and SiC as a function of temperature. (Copyright © Elsevier)

Figure 3-1 shows no obvious difference in the reaction rates with different dilution ratios of the catalyst, demonstrating that the kinetics measurements were generally not affected by diffusion and heat transfer limitations. Then, the kinetics study was conducted by varying the feed gas composition (H₂/CO₂ ratios from 0.29 to 8.3) and the reaction temperatures (453 and 563 K) using the same procedures. The mass ratio of catalyst and silicon carbide was fixed at 1:30. The concentrations of CO₂, H₂, CH₄, H₂O, CO and N₂ in the inlet and outlet streams were measured by an on-line gas chromatograph (7890B, Agilent Technologies) equipped with two thermal

conductivity detector (TCD) and a flame ionization detector (FID) detectors. The CO₂ conversion (X_{CO_2}), CO yield (Y_{CH_4}) and CH₄ yield (Y_{CO}) are calculated as follows:

$$X_{CO_2} (\%) = (F_{CO_2, in} - F_{CO_2, out}) / F_{CO_2, in} \times 100\% \quad (3-1)$$

$$Y_{CH_4} (\%) = F_{CH_4, out} / F_{CO_2, in} \times 100\% \quad (3-2)$$

$$Y_{CO} (\%) = F_{CO, out} / F_{CO_2, in} \times 100\% \quad (3-3)$$

where $F_{i, in}$ and $F_{j, out}$ refers to the molar flow rates (mL/min) of species i and j at the inlet and outlet of the reactor, respectively. The reaction rates for the CO₂ methanation (r_1) and RWGS reaction (r_2) are calculated as follows using the kinetics data:

$$r_1 = \frac{Y_{CH_4} F_{CO_2, in}}{V_m \times m_{catalyst}} \quad (3-4)$$

$$r_2 = \frac{Y_{CO} F_{CO_2, in}}{V_m \times m_{catalyst}} \quad (3-5)$$

where r_1 and r_2 have the same unit of mol/kg·s, and $m_{catalyst}$ is the mass of the Ni-Mg-W catalyst used for the kinetics study with the unit of gram, and V_m is the molar volume under standard temperature and pressure (22.4 L/mol). We used the nonlinear regression method to obtain the correlations for reaction rates as a function of the partial pressure of CO₂ and H₂ in the bed.

3.2.2 Modeling of the fluidized bed reactors

The gas-solid fluidized bed reactor modeled here is a cylinder with height of 0.1 m and diameter of 0.1 m. Recently, Kopyscinski et al. applied a two-phase fluidized-bed model for CO methanation and the results agree well with experimental data [72]. In this study, a similar model was applied for CO₂ methanation over the Ni-Mg-W catalyst. It is assumed that the process is in a steady state and there is no spatial dependence along with x and y directions. We considered five gas species (i) for the CO₂ methanation and RWGS reaction, namely, CO₂, H₂, CH₄, H₂O and CO. Analogous to the model by Kopyscinski [72], the mass balance equations for the bubble and emulsion phases are shown below:

$$\text{Bubble phase: } 0 = -\frac{d\dot{n}_{b,i}}{dz} - K_{G,i} a A (C_{b,i} - C_{e,i}) - \dot{N}_{vc} x_{b,i} \quad (3-6)$$

$$\text{Emulsion phase: } 0 = -\frac{d\dot{n}_{e,i}}{dz} + K_{G,i}aA(C_{b,i} - C_{e,i}) + \dot{N}_{vc}x_{b,i} + (1 - \varepsilon_b)(1 - \varepsilon_{mf})\rho_P AR_i \quad (3-7)$$

where the symbols used are defined in the nomenclature section.

The boundary and initial conditions are

$$\dot{n}_{b,i}|_{z=0} = \dot{n}_{b,i,\text{feed}} \quad \text{and} \quad \dot{n}_{e,i}|_{z=0} = \dot{n}_{e,i,\text{feed}} \quad (3-8)$$

The mass transfer is described by the mass-transfer coefficient (equation is given in Table 3-1) and the concentration difference. Furthermore, the convective mass transfer (equation known as total bulk flow in Table 3-1) is also considered.” The hydrodynamics used for the modeling, such as bubble size and bubble velocity, are listed in Table 3-1 [63, 65, 72]. As in previous studies [63, 65, 74-80], Matlab was used here to obtain the concentration profiles of each component along the fluidized bed.

Table 3-1. Hydrodynamic correlations used for the fluidized-bed model. (Copyright © Elsevier)

Parameters	unit	Correlations and equations
Bubble diameter	m	$d_b = d_{b_0} [1 + 27.2(u - u_{mf})]^{1/3} (1 + 6.84z)^{1.21}$
Theoretical initial bubble diameter	m	$d_{b_0} = 0.00853$
Visible bubble flow	m s ⁻¹	$v_b = 0.69(u - u_{mf})$
Bubble velocity	m s ⁻¹	$u_b = 0.69(u - u_{mf}) + 0.711 \times 0.63 \sqrt{gd_b}$
Bubble phase holdup		$\varepsilon_b = \frac{v_b}{u_b}$
Specific mass-transfer area	m ⁻¹	$a = \frac{6\varepsilon_b}{d_b}$
Mass-transfer coefficient	m s ⁻¹	$K_{G,i} = \frac{u_{mf}}{3} + \sqrt{\frac{4D_{i,m} \varepsilon_{mf} u_b}{\pi d_b}}$
Minimum fluidization velocity	m s ⁻¹	$u_{mf} = \frac{d_p^2 (\rho_P - \rho_g)}{150\eta} \left(\frac{\varepsilon_{mf}^3 \phi_P^2}{1 - \varepsilon_{mf}} \right)$

Total bulk flow	mol.s^{-1} m^{-1}	$\dot{N}_{vc} = \sum_i K_{G,i} a A (c_{b,i} - c_{e,i}) + (1 - \varepsilon_b)(1 - \varepsilon_{mf}) \rho_p A r$
Binary diffusion coefficient of species i and j	$\text{m}^2 \text{s}^{-1}$	$D_{i,j} = 0.01013 \frac{T^{1.75} [(1/M_i) + (1/M_j)]^{1/2}}{p[(\sum \nu_i)^{1/3} + (\sum \nu_j)^{1/3}]^2}$
Molecular diffusion coefficient of species i	$\text{m}^2 \text{s}^{-1}$	$D_{i,mx} = \frac{1 - x_i}{\sum_j (x_j / D_{i,j})}$

3.3 Results and discussion

On top of the Ni-Mg-W catalyst of interest whose kinetics was experimentally studied, two others whose kinetics data are available, namely, Ni/Al₂O₃ and Ni/La₂O₃ [81, 82], were studied.

3.3.1 Experimental results on the reaction kinetics of the Ni-Mg-W catalyst

To determine the correlations for the reaction rates, a series of tests were conducted in the temperature range from 453 K to 563 K over the range of H₂/CO₂ ratios between 0.29 and 8.3. Figure 3-2 shows the CO₂ conversions, and CH₄ and CO yields with respect to temperature under different feed gas compositions. It is clear that CO₂ conversion, and CO and CH₄ yields all increased with temperature and H₂/CO₂ ratio, the trends of which are consistent with past studies [59, 83-87]. These experimental data were used to quantify the reaction rates for both reactions (i.e., CO₂ methanation and RWGS), and then obtain the correlations by the regression method.

Figure 3-2. CO₂ methanation over Ni-Mg-W catalyst from 463 K to 563 K and the H₂/CO₂ ratio from 0.29 to 8.3 under ambient pressure with a total feed gas rate of 100 mL/min: (a) CO₂ conversion, (b) CH₄ yield, and (c) CO yield. (Copyright © Elsevier)

Power law equations were used to best-fit the experimental data based on non-linear regression to describe the kinetics of CO₂ methanation and RWGS reactions, which are expressed respectively as

$$r_1 = A_1 \exp(-E_{a1}/RT) P_{CO_2}^{0.14} P_{H_2}^{0.47} \quad (3-9)$$

$$r_2 = A_2 \exp(-E_{a2}/RT) P_{CO_2}^{0.8} P_{H_2}^{0.2} \quad (3-10)$$

where r_1 and r_2 are respectively the reaction rates (mol.kg_{cat}⁻¹.s⁻¹) for CO₂ methanation and RWGS reaction, P_i is the partial pressure of species i (kPa); R is the ideal gas constant (8.314 J.mol⁻¹.K⁻¹); T is temperature (K); A_1 and A_2 are Arrhenius constants of respectively $1.70 \times 10^7 \frac{\text{mol}}{\text{kg} \cdot \text{s} \cdot \text{kPa}^{0.61}}$ and $1.74 \times 10^3 \frac{\text{mol}}{\text{kg} \cdot \text{s} \cdot \text{kPa}}$, which are consistent with reported values in the literature [20, 62, 86]; and E_{a1} and E_{a2} are activation energies of 104.0 kJ/mol and 72.8 kJ/mol, respectively, which agree with those in literature [20]. The higher activation energy (E_a) of the CO₂ methanation reaction suggests it is more sensitive to temperature. These kinetics parameters were subsequently used to model the CO₂ methanation reaction in a fluidized bed reactor. Figure 3-3 displays the reaction rates for CO₂ methanation and RWGS reactions based on the formation rates of CH₄ and CO, respectively. As per Figure 3-2, higher temperatures led to higher reaction rates, and higher ratios of H₂ to CO₂ benefited both the formation of CH₄ and CO.

Figure 3-3. Reaction rates of (a) CO₂ methanation and (b) RWGS reactions for temperatures between 453 K and 563 K, and H₂/CO₂ ratios between 0.29 and 8.3 under ambient pressure. (Copyright © Elsevier)

3.3.2 Concentration profiles via the fluidized bed model

The comparison among the performance of the three catalysts (namely, Ni-Mg-W, Ni/ γ -Al₂O₃ and Ni/La₂O₃) in a fluidized bed reactor was carried out using the fluidized bed model, based on the kinetics data shown in Figure 3-3 for Ni-Mg-W and from past studies for the other two catalysts [81, 82]. The reactant gas mixture is composed of 20 mol % CO₂, 60 mol % H₂ and 20 mol % N₂. The conditions are superficial gas velocity of 1.1 times of minimum fluidization velocity, temperature of 560 K and ambient pressure (more details are shown in Table 3-2). Figure 3-4a, b and c show respectively the concentrations of CO₂, H₂ and CH₄ along the fluidized bed height for the three catalysts. Consistently, Ni-Mg-W outperformed the other two catalysts in terms of the greatest decrease in the reactants (namely, CO₂ (Figure 3-4a) and H₂ (Figure 3-4b)) and increase in the product CH₄ (Figure 3-4c). For the two different phases (i.e., bubble and emulsion), the reactant (i.e., CO₂ and H₂) concentrations in the bubble are higher than that in the emulsion, whereas the product (i.e., CH₄) concentrations in the emulsion phase are in contrast higher than that in the bubble. This is because the reaction only takes place on the surface of the catalyst, thereby the product concentration is higher in the emulsion phase that is in more intimate contact with the catalyst, while the inlet reactant species in the bubble phase need to diffuse into

the emulsion phase for reacting. Armed with the superior performance of Ni-Mg-W for CO₂ methanation, an overview of the concentrations of the various gas species in both the bubble and emulsion phases with respect to the fluidized bed height is presented in Figure 3-5. Notably, the concentration of CO is consistently low throughout the whole reactor, which is in accordance with the high selectivity for the formation of CH₄ by the Ni-Mg-W catalyst [59]. Also, CO, which is the final product in the RWGS reaction, is known to be an intermediate product during the CO₂ methanation reaction [61, 88], which thereby suppresses the CO measured further. Further sensitivity analyses are discussed in the next section.

Figure 3-4. Comparison of the performance of the three catalysts (namely, Ni-Mg-W, Ni/Al₂O₃ and Ni/La₂O₃) in terms of the concentrations of each gas species along the fluidized bed height: (a) CO₂, (b) H₂ and (c) CH₄. The solid and dotted lines represent respectively the bubble and emulsion phases. (Copyright © Elsevier)

Table 3-2. Conditions used in the fluidized bed model. (Copyright © Elsevier)

Item	Value	Unit
T	560	K
P	101.325	kPa
H ₂ /CO ₂ ratio	4	-
U	$U = 1.1 U_{mf}$	m/s
D	0.1	m
ε_{mf}	0.42	-
d_p	400	μm
ϕ	1	-

Figure 3-5. The concentration profile of each component along the fluidized bed height in the bubble phase (solid line) and emulsion phase (dotted line). (Copyright © Elsevier)

3.3.3 Reaction rate along the fluidized bed height

We further investigate the effect of superficial gas velocity, temperature, H₂/CO₂ ratios, particle diameter and particle sphericity on the reaction rate of CO₂ methanation and reverse water gas shift (RWGS) reaction along the height of the reactor. The results are shown in Figure 3-6. From Figure 3-6a1 and a2, it is clear that both the reaction rates for CO₂ methanation and RWGS

reaction decrease gradually with reactor height as the concentration of the reactants decreases. The reaction rates are positively correlated with the partial pressure of CO_2 and H_2 in the mixture per the results from the kinetics study. Figure 3-6 b1 and b2 show the effect of temperature on the reaction rates. Obviously, higher temperature leads to higher reaction rates of both methanation and RWGS at the beginning. Specifically, at 500 K, the reaction rates for methanation and RWGS are very small. When the temperature rise to 560 K and 600 K, the reaction rate for methanation at the bottom of the reactor is enhanced to 0.07 and 0.3 mol/kg s, respectively. In contrast, the reaction rate of RWGS reaction is enhanced to 0.004 and 0.016 mol/kg.s, respectively. Since the activation energy for CO_2 methanation (104.0 kJ/mol) is higher than that of RWGS (72.8 kJ/mol), the reaction rate of the former is more sensitive to the reaction temperature per the Arrhenius equation, and this is in accordance with the previous results. It is well-known that the feeding ratio of the reactants would affect the reaction rate, so the effect of H_2/CO_2 ratios on the reaction rates are also studied, with the results shown in Figure 3-6 c1 and c2. Here, the partial pressure of CO_2 is kept constant and the ratio of H_2/CO_2 is adjusted by varying the partial pressure of H_2 . As expected, the reaction rate for both reactions show positive correlation with the ratio of H_2/CO_2 . Furthermore, we tested the effect of particle properties including particle diameter (Figure 3-6 d1 and d2), and particle sphericity (Figure 3-6 e1 and e2). All the figures are consistent with the correlations of the reaction rates.

Figure 3-6. The reaction rate along the fluidized bed height under different superficial gas velocities (a1 and a2), different temperatures (b1 and b2), different H₂/CO₂ ratios (c1 and c2), different particle diameters (mm; d1 and d2), and different particle sphericities (e1 and e2).

Finally, some important parameters inside the fluidized bed like the bubble diameter (Figure 3-7a to d), bubble velocity (Figure 3-8a to d), bubble phase holdup (Figure 3-9a to d), and specific mass transfer area (Figure 3-10a to d) under different conditions were also modeled for reference.

Figure 3-7. Effect of the different parameters on the bubble diameter: (a) superficial gas velocity, (b) H_2/CO_2 ratio, (c) particle diameter (mm), and (d) particle sphericity. (Copyright © Elsevier)

Figure 3-8. Effect of the different parameters on the bubble velocity: (a) superficial gas velocity, (b) H_2/CO_2 ratio, (c) particle diameter (mm), and (d) particle sphericity. (Copyright © Elsevier)

Figure 3-9. Effect of the different parameters on the bubble phase holdup: (a) superficial gas velocity, (b) H_2/CO_2 ratio, (c) particle diameter (mm), and (d) particle sphericity. (Copyright © Elsevier)

Figure 3-10. Effect of the different parameters on the specific mass transfer area: (a) superficial gas velocity, (b) H_2/CO_2 ratio, (c) particle diameter (mm), and (d) particle sphericity.

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3.3.4 Sensitivity study

The sensitivity of the fluidized bed reactor performance to the operating conditions, namely, superficial gas velocity, temperature, H_2 to CO_2 molar ratio and particle properties of the Ni-Mg-W catalyst, are further evaluated and the results are discussed as follows.

3.3.4.1 Superficial gas velocity (U)

The increase of the inlet gas flow rate enhances the productivity of the reactor for fast reactions but restricts conversion for slower reactions that requires more contact time, which suggests that the flow rate can be optimized for specific reactions. Figure 3-11 a - d show the effect of varying superficial gas velocities (U) on each of the gas species (namely, CO_2 , H_2 , CH_4 , and CO).

As discussed above, the reactant (CO_2 and H_2) concentrations decrease along the height of the

fluidized bed and are always higher in the bubble phase than that in the emulsion phase. Figure 3-11 a and b indicate that the conversion of the reactants (CO_2 and H_2) decrease as the flow rate increase, which suggest that the reaction rate is rate-determining relative to the flow rate and thereby that the overall productivity can be increased by lowering the flow rate. As the flow rate increases, it is clear that the concentration difference between the bubble and emulsion phases decreases, which is because of the enhanced mass transfer with the faster flow. Analogous observations are made for the product (CH_4 and CO) concentrations in Figure 3-11 c and d. Figure 3-11 e and f further show that the reaction rates for both reactions (CO_2 methanation and RWGS) decrease with height due to the decreasing concentration, but increase with superficial gas velocity due to the enhanced mass transfer evident in the lower concentration difference between the emulsion and bubble phases. Notably, the CO_2 methanation rate (Figure 3-11e) is an order-of-magnitude greater than that of the RWGS reaction rate (Figure 3-11f), because of the selectivity of the Ni-Mg-W catalyst towards the former reaction, as evident in the orders-of-magnitude higher Arrhenius constant for CO_2 methanation ($1.70 \times 10^7 \frac{\text{mol}}{\text{kg} \cdot \text{s} \cdot \text{kPa}^{0.61}}$) relative to that of the RWGS reaction ($1.74 \times 10^3 \frac{\text{mol}}{\text{kg} \cdot \text{s} \cdot \text{kPa}}$).

Figure 3-11. Effect of superficial gas velocity on the species concentration along the fluidized bed height: (a) CO_2 , (b) H_2 , (c) CH_4 and (d) CO ; and the reaction rates for CO_2 methanation (e) and RWGS reaction (f). The operating conditions are 560 K and $H_2/CO_2 = 4$, with Ni-Mg-W catalyst with $d_p = 400 \mu m$ and $\phi = 1$. In (a) – (d), the solid and dotted lines represent respectively the bubble and emulsion phases. (Copyright © Elsevier)

3.3.4.2 Temperature

Since the fluidized bed reactor exhibits excellent heat and mass transfer, near-isothermal conditions are expected throughout the catalyst bed. Figure 3-12 presents the effect of temperature in the range of 500 – 600 K on reactant and product concentrations, and also the reaction rates. Figures. 3-12 a and b show that the conversion of the reactants (i.e., CO_2 and H_2) expectedly increase with temperature per the Arrhenius relationship. As for the products, while the concentration of CH_4 (Figure 3-12c) throughout the fluidized bed height increase monotonically with temperature, the effect of temperature on CO concentration (Figure 3-12d) is not as

straightforward. Specifically, for CO at the highest temperature investigated of 600 K (Figure 3-12d), the concentration increases sharply lower in the bed, then plateaus off quickly by one-fifth of the bed height to a value lesser than that at the lower temperature of 560 K. This is likely because the CO₂ methanation reaction is more dominant vis-à-vis the RWGS reaction at the highest temperature of 600 K because of the larger activation energy (E_{a1}). Consequently, the lower CO concentration in the upper half of the fluidized bed at 600 K relative to 560 K is because of the lower reactant concentrations (Figure 3-12 a and b) due to the higher reaction rates of the former. Regarding the reaction rates of the CO₂ methanation and RWGS reactions, Figs. 6e and f show that they have similar trends with respect to temperature and bed height. Specifically, the reaction rates are uniformly low through the bed at lowest temperature of 500 K, whereas decreases steeply lower in the bed at the higher temperatures. The reaction rates for the highest 600 K temperature are lesser than that at 560 K above approximately mid-height of the bed because of the depletion of the reactants (Figure 3-12 a and b), which implies that a higher inlet reactant concentration would benefit.

Figure 3-12. Effect of temperature on the species concentration along the fluidized bed height: (a) CO₂, (b) H₂, (c) CH₄ and (d) CO; and the reaction rates for CO₂ methanation (e) and RWGS reaction (f). The operating conditions are 560 K and H₂/CO₂ = 4, with Ni-Mg-W catalyst with $d_p = 400 \mu\text{m}$ and $\phi = 1$. In (a) – (d), the solid and dotted lines represent respectively the bubble and emulsion phases. (Copyright © Elsevier)

3.3.4.3 H₂/CO₂ ratio

Another important parameter that influences the performance of the reactor is the composition of the feed mixture. Accordingly, the effect of the H₂/CO₂ ratio on the performance of the fluidized bed reactor is assessed by varying the partial pressure of H₂, as presented in Figure 3-13. Increasing the H₂/CO₂ ratio clearly enhances the conversion of CO₂ (Figure 3-13a) and the formation of CH₄ (Figure 3-13c), which indicates that the increase in the composition of H₂ favors the CO₂ methanation reaction. On the other hand, the relationship between the H₂/CO₂ ratio and CO formation is non-monotonic, specifically in that, as the H₂/CO₂ ratio increases from 1 to 4,

the CO formed increases then decreases. The underlying reason is that, CO concentration increases as the H_2/CO_2 ratio increases from 1 to 2 because of the excess H_2 present, then decreases as the H_2/CO_2 ratio further increases to 4 because the increased preference to form CH_4 (Figure 3-13c) suppresses the formation of CO. Figure 3-13e and f reflect the reaction rates of CO_2 methanation and RWGS with respect to fluidized bed height, indicating that higher rates are obtained at higher H_2/CO_2 ratios particularly lower in the bed, but the difference among the H_2/CO_2 ratios diminishes at higher bed height due to the reduced reactant concentrations (Figure 3-13a and b).

Figure 3-13. Effect of H_2/CO_2 ratios on the species concentration along the fluidized bed height: (a) CO_2 , (b) H_2 , (c) CH_4 and (d) CO ; and the reaction rates for CO_2 methanation (e) and RWGS reaction (f). The operating conditions are 560 K and $H_2/CO_2 = 4$, with Ni-Mg-W catalyst with $d_p = 400 \mu m$ and $\phi = 1$. In (a) – (d), the solid and dotted lines represent respectively the bubble and emulsion phases. (Copyright © Elsevier)

3.3.4.4 Diameter and sphericity of the catalyst particle

Particle diameters in the range of $300 \mu m$ - $600 \mu m$ were modelled to assess the effect of catalyst particle size on the catalysis performance. As the minimum fluidization velocity (U_{mf}) is a function of particle diameter, keeping the superficial gas velocity at 1.1 times U_{mf} means that the inlet gas velocities are different for the four particle diameters investigated. Figure 3-14 gives the concentration profiles of the reactants and products along the reactor. Clearly, the smaller particle diameter results in the greater conversion, due to the increased surface area per unit volume of particles. This indicates that the catalyst amount is limiting in this case, which implies that a taller fluidized bed and/or even smaller particle diameters would enhance the conversion.

Figure 3-14. Effect of particle diameter on the species concentration along the fluidized bed height: (a) CO_2 , (b) H_2 , (c) CH_4 and (d) CO . The operating conditions are 560 K and $\text{H}_2/\text{CO}_2 = 4$, with Ni-Mg-W catalyst with $\phi = 1$. The solid and dotted lines represent respectively the bubble and emulsion phases. (Copyright © Elsevier)

As particle sphericity is an important particle property that affects the fluidized bed reactor performance [63, 89], the effect of three different particle sphericity values (ϕ ; namely, 0.6, 0.8 and 1.0) was assessed, as depicted in Figure 3-15. Interestingly, Figure 3-15 a – b show that, as the particle sphericity decreases, the extent of reactant depletion increases, with the CO_2 in the emulsion completely depleted at the lower sphericities of 0.6 and 0.8. As for the product CH_4 (Figure 3-15c), the trends are consistent with the reactant depletion, specifically in that the CH_4 concentration increases as the particle sphericity (ϕ) decreases. On the other hand, for the product of the RWGS reaction, CO (Figure 3-15d), the relationship between particle sphericity and CO

concentration is non-monotonic because of the increasing depletion of the reactants for the lowest particle sphericity of 0.6. Therefore, it can be concluded that non-spherical Ni-Mg-W catalysts are advantageous for this application.

Figure 3-15. Effect of particle diameter on the species concentration along the fluidized bed height: (a) CO₂, (b) H₂, (c) CH₄ and (d) CO. The operating conditions are 560 K and H₂/CO₂ = 4, with Ni-Mg-W catalyst of $d_p = 400 \mu\text{m}$. The solid and dotted lines represent respectively the bubble and emulsion phases. (Copyright © Elsevier)

3.4 Conclusion

This study focused on the evaluation of the performance of the Ni-Mg-W catalyst, which has been shown to be superior in terms of faster kinetics and selectivity for CO₂ methanation [59] in a fluidized bed reactor.

The reaction kinetics parameters, namely, the Arrhenius constant and activation energy, of

the Ni-Mg-W catalyst for CO₂ methanation and RWGS reactions were first experimentally characterized. Then, the performance of two other catalysts that catalyze the same reactions were compared to that of the Ni-Mg-W catalyst using the fluidized bed model developed based on that earlier reported for CO methanation [72]. Both the concentrations in the bubble and emulsion phases were revealed. The model results indicate that the Ni-Mg-W catalyst leads to faster depletion of the reactants and consequently higher concentrations of the product CH₄.

Subsequently, the sensitivity of the performance of the Ni-Mg-W catalyst in a fluidized bed reactor to the various operating parameters, including superficial gas velocity, temperature, reactant ratio (i.e., H₂/CO₂) and catalyst particle properties, was assessed. The overall productivity of CH₄ increases with decreased inlet reactant flow rate, increased temperature, increased H₂/CO₂ ratio, decreased catalyst particle diameter and decreased catalyst particle sphericity.

The results presented here are expected to provide useful guidance for the development of a CO₂ methanation fluidized bed reactor.

In the next chapter, a methanation catalysts suitable for fluidized bed reactor will be studied to advance the CO₂ methanation topic. (Copyright © Elsevier)

Chapter 4 Nickel-Cobalt catalyst supported on TiO₂-coated SiO₂ spheres for CO₂ methanation in a fluidized bed

4.1 Introduction

With the potential availability of hydrogen from water-splitting derived by renewable energy[90, 91], the conversion of carbon dioxide (CO₂) to valuable products by hydrogen reduction has received more attention in recent years.[92-94] Among the various CO₂ hydrogenation reactions, CO₂ methanation ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$) is the most thermodynamically favorable process, which makes it attractive for addressing the increasing demand for substitute natural gas (SNG) in some countries.[95, 96] Tremendous efforts have been devoted to develop effective and stable catalysts, and also to understand the reaction mechanisms.[61, 97] However, the practical large-scale implementation of CO₂ methanation remains unfeasible, primarily because the CO₂ methanation reaction is highly exothermic. When the heat is not efficiently dissipated, problems that arise include (i) “hot spots” resulting in the sintering of the active metal nanoparticles in the catalysts [98, 99]; and (ii) promotion of the side reverse water gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) by the higher temperature, which decreases the selectivity of CH₄. [95, 100] For efficient heat transfer, the fluidized bed reactor is much more superior than the fixed bed, allowing for nearly isothermal conditions throughout the particle bed that makes it ideal for CO₂ methanation.[101-103] Towards the large-scale CO₂ methanation, two gaps in the knowledge base has to be bridged, namely, (a) enhanced understanding of the performance of CO₂ methanation catalysts in a fluidized bed reactor, and (b) better catalysts with improved catalytic activity. The current study targeted at addressing both.

For supported catalysts, both the support and the active metal affect the catalytic performance. Among the various supports (e.g., Al₂O₃, SiO₂, TiO₂, CeO₂, et al), SiO₂ spheres have been reported to be suitable for use in a fluidized bed reactor to maintain good fluidization

quality, [97] so SiO₂ supports were used here. Unfortunately, SiO₂-supported catalysts are acknowledged to exhibit relatively lower activity compared with those supported by TiO₂, ZrO₂ or CeO₂. [97, 100, 104-107] Accordingly, in this study, mesoporous SiO₂ spheres with diameters of about 100 - 200 μm were also coated with TiO₂ (TiO₂@SiO₂) to attempt to improve the activity. As for the metal constituent, although noble metals such as ruthenium [108, 109], rhodium [110] and palladium [111] are reported to be highly active for CO₂ hydrogenation, nickel (Ni) is a better choice for industrial large-scale application based on the trade-off between cost and activity. In addition, considering bimetals (i.e., coupling of two metals) are known to increase the activity due to synergistic effects [111-113], the nickel-cobalt (NiCo) bimetal was dispersed onto TiO₂@SiO₂ too to evaluate the benefits. The performance of the novel, rationally designed catalysts for CO₂ methanation were evaluated in both a fixed bed and a fluidized bed. The objective of this chapter is to develop a high-performance catalyst that can be used in fluidized bed reactor for CO₂ methanation. (Copyright © Elsevier)

4.2 Experimental section

4.2.1 Catalyst preparation

Silicon dioxide (SiO₂) spheres (75 - 200 μm), titanium isopropoxide (98%), nickel nitrate hexahydrate (98%), cobalt nitrate hexahydrate (98%), ammonia solution (25 wt%) and isopropanol (99.9%, anhydrous) were purchased from Sigma-Aldrich and used directly. Deionized (DI) water was obtained from the Millipore water purification system (Milli-Q® Integral).

The coating of titanium dioxide (TiO₂) on the SiO₂ spheres was carried out as follows. Firstly, the targeted amount of SiO₂ spheres were calcined at 400 °C for 2 h in the box furnace (1200X, MTI) under static air. Then, 10 g of the obtained SiO₂ spheres were dispersed in 150 mL of isopropanol and 2 mL of ammonia solution (25 wt%) at 60 °C under magnetic stirring. Then, 5 mL of titanium isopropoxide (98%) was added dropwise into the stirred suspension over about 30 min. After all the titanium isopropoxide was added, the obtained suspension was further stirred

at a temperature of 60 °C until all the isopropanol evaporated. Then, the solid was calcined at 700 °C for 5 h to obtain TiO₂-coated SiO₂ (TiO₂@SiO₂). Bare SiO₂ was also calcined at 700 °C for 5 h to serve as a benchmark for comparison.

The catalysts were prepared by impregnation method. Taking NiCo/TiO₂@SiO₂ (with Ni and Co content of 15 wt% and 5 wt%, respectively) as an example, 7.43 g nickel nitrate hexahydrate and 2.47 g cobalt nitrate hexahydrate was first dissolved in DI water. Then, 8 g of TiO₂@SiO₂ was added under stirring, following which the obtained suspension was heated to 80 °C until all the water was evaporated. After that, the obtained solid was dried and then calcined at 400 °C for 2 h in the box furnace under static air, resulting in the catalyst NiOCoO/TiO₂@SiO₂. After reduction in H₂ at 500 °C for 2 h, NiCo/TiO₂@SiO₂ was obtained. Similarly, other unreduced catalysts, namely, NiO/SiO₂ (i.e., 20 wt % Ni on SiO₂), NiOCoO/SiO₂ (i.e., 15 wt% Ni and 5 wt% Co on SiO₂) and NiO/TiO₂@SiO₂ (20 wt% Ni on TiO₂-coated SiO₂), were obtained, which became respectively Ni/SiO₂, NiCo/SiO₂ and Ni/TiO₂@SiO₂ after reduction at the same condition in H₂ at 500 °C for 2 h.

4.2.2 Characterizations

Powder X-ray diffraction (XRD) analysis was carried out on a Bruker D2 Phaser using Cu Ka radiation ($\lambda = 0.15418$ nm) with a LYNXEYE detector at 30 kV and 10 mA. The Scherrer equation was applied to calculate the crystal size of the metal nanoparticles in the samples. The surface area and pore size distributions of catalysts and support were measured by nitrogen adsorption and desorption using Brunauer–Emmett–Teller (BET) method and BJH method respectively on BET-AS6. The morphologies of the support and catalysts were observed via scanning electron microscopy (SEM; JEOL JSM 6700F, Japan) and transmission electron microscopy (TEM; JEOL 2010 HR & UHR). To make the TEM observations of the H₂-reduced catalysts, the samples were firstly reduced in a fixed bed quartz tube reactor in H₂ flow at 600 °C for 2 h, then cooled down to room temperature in H₂ flow. The surface chemical composition of the samples was determined by X-ray photoelectron spectroscopy (XPS) on a ESCALAB 250Xi

instrument (Thermo Fisher Scientific, America) using a monochromatized Al K α source ($h\nu=1486.6$ eV) at 150 W. The binding energies of all spectra were calibrated against the C(1s) peak, which was fixed at a binding energy of 284.8 eV. Temperature-programmed H₂ reduction (H₂-TPR), temperature-programmed H₂ desorption (H₂-TPD), and temperature-programmed CO₂ desorption (CO₂-TPD) were carried out on a Quantachrome automated chemisorption analyzer (chemBET pulsar TPR/TPD). For H₂-TPR, 0.1 g samples were loaded in a quartz U-tube and heated from room temperature to 300 °C at the heating rate of 10 °C·min⁻¹ and maintained for 2 h in Ar flow. Then, the samples were cooled down to room temperature, followed by heating to 900 °C in a 5.0 vol % H₂/Ar flow at the flow rate of 30 mL·min⁻¹. The H₂ consumption in H₂-TPR process was continuously monitored as a function of increasing temperature using a thermal conductivity detector (TCD). As for H₂-TPD, the catalysts were first reduced by H₂ at 600 °C and then cooled down to room temperature in H₂ flow, the H₂ adsorption were conducted at room temperature under flowing H₂ for 30 min, then the sample was purged by He to remove H₂ in the tube until the TCD signal become stable. Then the sample was heated to 700 °C at a ramp rate of 20 °C/min. The desorbed H₂ was detected by TCD. The adsorption amount of hydrogen was used to determine the nickel metal dispersion and surface averaged nickel metal diameter according to reported formula.[114] Finally for CO₂-TPD, the catalysts were also reduced at the same condition as described above. The CO₂-TPD process is the same as that for H₂-TPD except CO₂ was used instead of H₂ in the adsorption process at room temperature.

4.2.3 Catalytic performance of the prepared catalysts

The CO₂ methanation reaction was firstly conducted in a packed-bed quartz-tube reactor with an inner diameter of 6 mm under atmospheric pressure to compare the activity of the four catalysts. A K-type thermocouple with the tip positioned in the catalyst bed was used to monitor the bed temperature. The concentrations of CO₂, H₂, CH₄, H₂O, CO and N₂ in the inlet and outlet streams were measured by an on-line gas chromatograph (7890B, Agilent Technologies) equipped with two thermal conductivity detector (TCD) and a flame ionization detector (FID) detectors. The

reaction rates were calculated according to the data obtained from the GC. The CO₂ conversion (X_{CO_2}), CO yield (Y_{CH_4}) and CH₄ yield (Y_{CO}) were calculated as follows:

$$X_{CO_2} (\%) = (F_{CO_2, in} - F_{CO_2, out}) / F_{CO_2, in} \times 100\% \quad (4-1)$$

$$Y_{CH_4} (\%) = F_{CH_4, out} / F_{CO_2, in} \times 100\% \quad (4-2)$$

$$Y_{CO} (\%) = F_{CO, out} / F_{CO_2, in} \times 100\% \quad (4-3)$$

where $F_{i, in}$ and $F_{j, out}$ are respectively the molar flow rates (L/h) of species i and j , and the subscripts in and out refer to respectively the inlet and outlet of the reactor.

The Koros-Nowak criterion was applied to confirm the proper reaction condition. The catalysts were tested at different mass ratios of catalyst to silicon carbide (SiC), and the reaction rates were measured at different temperatures. [73] The results shown in Figure 4-1 indicate that the different mass ratios of catalyst to SiC gave similar trends.

Figure 4-1. Koros-Nowak criterion test results.

The turnover frequency (TOF) quantifies the specific activity of a catalytic center by the number of molecular produced (here is CO and CH₄) occurring at an active site per unit time. It is assumed that all the surface Ni atoms (determined by H₂-TPD with H:Ni molar ration of 1) are the active sites. Here, the reaction rate at 280 °C was chosen to limit the conversion of CO₂ less

than 5 %, thus effectively reduce the possible concentration and temperature gradients.

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For the activity test in a fluidized bed reactor, a bench-scale reactor was used, with the dimensions of the quartz tube shown in Figure 4-2. For the experiments, the quartz tube was positioned in a tubular electric furnace (inner diameter of 22 mm and length of 1 m). Three thermocouples measured the temperatures of the outer wall at different heights (namely, 15 cm, 30 cm and 45 cm above the porous plate) along the quartz tube. Data were recorded 30 min after reaching the desired reaction temperature to collect only steady-state data. The experimental protocol was as follows. 9 g of catalyst was added into the quartz tube to be reduced with a H₂ flow of 10 L/h and N₂ gas of 20 L/h at 600 °C for 2 h, then the temperature was decreased to 180 °C, after which the inlet gas was switched to a mixture of H₂ and CO₂ at a ratio of 4:1 and total flow rate of 25 L/h, and finally the temperature was increased to 400 °C to obtain the performance of catalyst. Finally, longer-term stability tests were conducted at 260 °C at the H₂/CO₂ ratio of 4 under ambient pressure for 120 hours.

Figure 4-2. The schematic diagram of the quartz tube reactor, which served as the fluidized bed reactor in this study. The tube had three different diameters, namely, 12 mm, 20 mm and 40 mm. At the mid-length of the tube was a porous quartz plate where the catalysts were loaded. (Copyright © Elsevier)

4.3 Results and discussion

4.3.1 Catalyst characterization

The morphology of the SiO_2 support is shown in Figure 4-3a, which reflects that the diameter range of the spheres was between 100 and 200 μm . The crystal structures of four catalysts (namely, Ni/SiO_2 , NiCo/SiO_2 , $\text{Ni/TiO}_2\text{@SiO}_2$ and $\text{NiCo/TiO}_2\text{@SiO}_2$) were analyzed by XRD and displayed in Figure 4-3b. The peaks corresponding to Ni metal appeared in all the four catalysts

at 2θ values of 44° and 52° for respectively the (111) and (200) planes. Note that the diffraction peaks of Co and Ni are at the same position. The mean crystal sizes of Ni or Co calculated by the Scherer formula [115] for the four catalysts, namely, Ni/SiO₂, NiCo/SiO₂, Ni/TiO₂@SiO₂ and NiCo/TiO₂@SiO₂ were approximately similar at 6.0, 7.0, 5.4 and 8.0 nm, respectively.

Figure 4-3. SEM image of the SiO₂ support (a) and XRD patterns of the four reduced catalysts (b). (Copyright © Elsevier)

Considering the specific surface areas and pore structures of the catalysts are critical parameters that affect the catalyst performance, the SiO₂ support and five catalysts were analyzed by N₂ adsorption and desorption. Figure 4-4a reflects that (i) the pure SiO₂ support exhibited the typical type IV behavior characteristic of mesoporous materials, with the isotherm displaying hysteresis in the pressure range of 0.7~0.9, and had a specific surface area of 297 m²/g (Table 4-1), and (ii) all five catalysts exhibited similar isotherm trends as and lower specific surface areas (in the range of 196 - 272 m²/g) than that of SiO₂. Furthermore, Figure 4-4b indicates that (i) the pore size of pure SiO₂ was centered at 12 nm and had a specific pore volume of 0.91 m³/g, and (ii) the mean pore size and specific pore volume for all five catalysts were in the respective ranges of 10 - 11 nm and 0.42 – 0.77 m³/g, which are lower than that of SiO₂. Therefore, Figure 4-4 indicates that, while the catalysts retained the mesoporous characteristics of the SiO₂ support, the porosity reduced.

Figure 4-4. N₂ adsorption-desorption isotherm curves (a) and pores size distributions (b) of the reduced catalysts and SiO₂ support. (Copyright © Elsevier)

Table 4-1. The surface area, pore size and total pore volume of the support and catalysts. (Copyright © Elsevier)

Samples	BET surface area /(m ² /g)	Total pore volume /(cm ³ /g)	Mean pore size /(nm)
SiO ₂	296.8	0.91	12.0
TiO ₂ @SiO ₂	272.0	0.77	11.3
Ni/SiO ₂	251.0	0.60	11.4
NiCo/SiO ₂	234.7	0.56	11.2
Ni/TiO ₂ @SiO ₂	197.9	0.47	10.0
NiCo/TiO ₂ @SiO ₂	196.1	0.42	10.3

The reduction of the nickel oxides and cobalt oxides on the catalysts were investigated by

H₂-TPR. It can be seen from Figure 4-5a that the reduction of nickel oxides in NiO/SiO₂ started from about 200 °C and ended at about 650 °C. The temperature range was similar for the other three catalysts, namely, NiOCoO/SiO₂, NiO/TiO₂@SiO₂ and NiOCoO/TiO₂@SiO₂. To reduce the active metal species of the catalyst as much as possible, and avoid the sintering of the active metal nanoparticles at higher temperatures, the reduction temperature was set at 600 °C and maintained for 2 h. Considering that the adsorption of CO₂ and H₂ on the catalyst surface plays an important role in the catalysis performance, CO₂ and H₂ temperature-programmed desorptions were conducted to investigate the adsorption amount and strength on the four reduced catalysts. It can be seen from Figure 4-5b that all the four reduced catalysts exhibited two desorption peaks at about 150 and 600 °C. The lower-temperature peak is generally attributed to the desorbed H₂ from the exposed metallic Ni atoms, while the higher-temperature peak to the H₂ adsorbed in the subsurface layers of Ni atoms and/or to the spillover H₂. [116, 117] The adsorption amount of H₂ were listed in Table 4-2. For Ni/SiO₂ and NiCo/SiO₂, very similar peak positions and total adsorption amounts (133.0 and 159.6 μmol/g_{cat}, respectively) were observed. After the SiO₂ support was coated with TiO₂, the adsorption amount and strength of H₂ were increased for Ni/TiO₂@SiO₂ (245.1 μmol/g_{cat}) and NiCo/TiO₂@SiO₂ (315.4 μmol/g_{cat}). This is likely due to the electronic effect of TiO₂ to the active metal or the different metal-support interaction compared with SiO₂ support, thus lead a higher Ni dispersion as calculated in Table 1. In addition, the magnitude of the higher-temperature peak was higher for NiCo/TiO₂@SiO₂ (17.4 μmol/g_{cat}) than Ni/TiO₂@SiO₂ (12.5 μmol/g_{cat}), which can be attributed to the interaction between Co and Ni in the former. The surface averaged Ni diameter for Ni/SiO₂ and NiCo/SiO₂ is larger than that of Ni/TiO₂@SiO₂ and NiCo/TiO₂@SiO₂, suggesting that the interaction between TiO₂ and Ni could promote the dispersion of Ni compared with pure SiO₂ support. For CO₂-TPD (Fig. 3c), only one peak at about 200 °C was present for all the four catalysts. Ni/SiO₂ and NiCo/SiO₂ had similar and relatively lower adsorption (102.5 μmol/g_{cat}) compared with that on Ni/TiO₂@SiO₂ and NiCo/TiO₂@SiO₂ (106.5 μmol/g_{cat}). In short, the coating of TiO₂ increased the adsorption

amount of CO₂ and H₂, while the addition of Co increased the adsorption of H₂. This agrees with previous results that show that TiO₂-supported catalysts and bimetal catalysts usually exhibit higher activity[97].

Figure 4-5. H₂-TPR (a), H₂-TPD (b) and CO₂-TPD (c) of the four reduced catalysts. (Copyright © Elsevier)

The presence of Ni and Co in the reduced catalysts was verified using TEM. Figure 4-6a and b shows that the SiO₂ support was particulates of about 10 nm. Regarding TiO₂@SiO₂, Figure 4-6 c and d confirms that the coated TiO₂ was of the rutile phase. As for NiCo/TiO₂@SiO₂, Figure 4-6e shows the appearance of Ni and/or Co as particulates of about 20-30 nm, while Figure 4-6 f indicates that Ni or Co and Ti were present. The TEM images of the other three reduced catalysts (namely, Ni/SiO₂, NiCo/SiO₂ and Ni/TiO₂@SiO₂) are shown in Figure 4-7 and the observed metal particles size are listed in Table 4-2. The metal particles size observed by TEM is distributed but mainly in 20-40 nm range. In addition, the size observed by TEM is larger than the mean crystal

size calculated by XRD (Table 4-21), suggesting that the particles are aggregated grains. The surface averaged nickel diameter is even larger than the one seen by TEM, this may due to some particles are gathered together.

Table 4-2. The adsorption amount of H₂ and CO₂ calculated by TPD and the dispersion, estimated diameter of Ni (Co) in the catalysts. (Copyright © Elsevier)

Catalysts	H ₂ adsorption amount ($\mu\text{mol/g}_{\text{cat}}$)			CO ₂ Adsorption amount ($\mu\text{mol/g}_{\text{cat}}$)	Ni (Co) dispersion	Surface averaged diameter of Ni (nm)	Mean crystal size of Ni by XRD (nm)	Particle size observed by TEM (nm)
	Weak adsorption (25~500 °C)	Strong adsorption (500~700 °C)	Total					
Ni/SiO ₂	129.7	3.3	133.0	39.2	8.4	115	6.0	20~40
Ni/TiO ₂ @SiO ₂	232.6	12.5	245.1	102.5	15.1	64	7.0	20~40
NiCo/SiO ₂	154.0	5.6	159.6	41.3	10.0	97	5.4	20~30
NiCo/TiO ₂ @SiO ₂	301.0	17.4	318.4	106.5	19.6	50	8.0	20~30

Figure 4-6. TEM images at different magnifications of the SiO₂ support ((a) and (b)); TiO₂@SiO₂ ((c) and (d)); and NiCo/TiO₂@SiO₂ ((e) and (f)). (Copyright © Elsevier)

Figure 4-7. TEM images of Ni/SiO₂ (a and b), NiCo/SiO₂ (c and d), and Ni/TiO₂@SiO₂ (e and f). (Copyright © Elsevier)

The valence states of all the elements in the unreduced and reduced catalysts were analyzed by XPS. Figure 4-8 shows the XPS spectra of Ni 2p and Co 2p of the reduced catalysts. Figure 4-8a indicates that Ni in all the four reduced catalysts (i.e., NiCo/TiO₂@SiO₂, Ni/TiO₂@SiO₂, NiCo@SiO₂ and Ni@SiO₂) was mainly of the valence state of +2 (i.e.), while some existed as Ni⁰ in Ni/TiO₂@SiO₂ and Ni/SiO₂. Considering the catalysts were reduced in H₂ at 600 °C for 2 h, the Ni in the reduced catalysts should be in the Ni⁰ rather than Ni²⁺ state. Therefore, the dominance of Ni²⁺ and disappearance of Ni⁰ indicates the high activity of the metals, which were readily oxidized upon exposure to air. Accordingly, it can be deduced that the Ni in NiCo/TiO₂@SiO₂ and NiCo/SiO₂ was more active than that in Ni/TiO₂@SiO₂ and Ni/SiO₂. The

Ni 2p spectra of the unreduced catalysts are given in Figure 4-9a, which indicates the lack of Ni^0 . Similarly, Figure 4-8b shows that the Co species in reduced $\text{NiCo/TiO}_2\text{@SiO}_2$ and NiCo/SiO_2 was also mainly composed of Co^{2+} due to oxidation in air, which is very similar with the unreduced catalysts (Figure 4-9b). The XPS spectra of Si and Ti of the catalysts are shown in Figure 4-8c and d, which indicates similar valence states among all the catalysts. This suggests the states of Si and Ti did not change with H_2 reduction.

Figure 4-8. XPS spectra of Ni 2p (a), Co 2p (b), Si 2p (c) and Ti 2p (d) of the catalysts.

Figure 4-9. XPS spectra of Ni 2p (a) and Co 2p (b) of the reduced catalysts. (Copyright © Elsevier)

4.3.2 Activity in the fixed bed reactor

Figure 4-10 shows the reaction rates over the prepared catalysts under the H_2/CO_2 ratio of 4 in the temperature range of 473-773 K. Fig. 6a shows that the CO_2 conversion rates for all the catalysts increased rapidly with increasing temperature. The highest activity was conferred by $\text{NiCo}/\text{TiO}_2@\text{SiO}_2$, followed by NiCo/SiO_2 , $\text{Ni}/\text{TiO}_2@\text{SiO}_2$ and then Ni/SiO_2 . This implies that (i) coating with TiO_2 improved the catalytic performance relative to that without, and (ii) the coupled NiCo performed better than Ni alone. Figure 4-10b shows the CH_4 production rate with respect to temperature, which shows similar trends as Figure 4-10a, and thereby similarly that TiO_2 and NiCo were beneficial. In addition, Figure 4-10c shows the CO formation rates, which is much smaller compared with the CH_4 formation rates (Figure 4-10b), suggesting that all the four catalysts were more selective to CH_4 . This is because CO was an intermediate product that can be further hydrogenated to CH_4 . From the H_2 -TPD and CO_2 -TPD results, it is clear that the TiO_2 coat increased the adsorption amount and strength of H_2 and CO_2 onto the catalysts, thus promoting the reaction rate. In addition, the increased adsorption strength of H_2 by TiO_2 further hydrogenated CO to CH_4 , thus increasing its selectivity, as depicted in Figure 4-10d. Among the

four catalysts, NiCo/TiO₂@SiO₂ exhibited the highest activity for CO₂ methanation. TOF value calculated by the reaction rate at 280 °C and the number of surface Ni atoms in catalysts (determined by H₂ adsorption, see method section for details) are shown in Fig. 4-10e. The TOF value of CH₄ formation over Ni/SiO₂ and Ni/TiO₂/SiO₂ is comparable which TOF of CO formation decreased in the later. Namely, the increased apparent rate in Figure 4-10b is mainly due to the increased dispersion of Ni in Ni/TiO₂@SiO₂. As discussed above, the different interaction between Ni-TiO₂ and Ni-SiO₂ should be main reason for the increased dispersion. Moreover, the TOF over the two bimetal catalysts (NiCo/SiO₂ and NiCo/TiO₂@SiO₂) increased obviously compared with the single Ni catalysts, suggesting cobalt did promote the intrinsic activity through synergistic effect. Together with the Ni dispersion promoted by TiO₂ support, thus, the NiCo/TiO₂@SiO₂ shows the highest apparent activity.

Figure 4-10. CO₂ methanation in the fixed bed reactor under the condition of H₂/CO₂ ratio of 4 and ambient pressure: (a) CO₂ reaction rate, (b) CH₄ formation rate, (c) CO formation rate, (d) CH₄ selectivity. and (e) TOF values of CH₄ and CO formation over the four catalysts at 280 °C. (Copyright © Elsevier)

4.3.3 Activity and stability in the fluidized bed

The methanation performance of the four catalysts in the fluidized bed reactor under ambient pressure in the temperature range between 180 and 400 °C is shown in Figure 4-11. As has been observed in the fixed bed reactor, the same relative activity among the four catalysts persisted in the fluidized bed reactor. Compared to the fixed bed (Figure 4-10d), the CH₄ selectivity of all the four catalysts in the fluidized bed reactor all increased (Figure 4-11b) to nearly 100% because of the larger amount of catalyst used, which can further hydrogenate CO to CH₄. In addition, the heat released during the reaction process would lead temperature increase in the whole fluidized bed, thus further accelerate the reaction rate. Therefore, this kind of positive feedback leads larger difference in activity in the fluidized bed reactor compared with the activity results in Fig.6, thus lead the NiCo/TiO₂@SiO₂ exhibit much higher conversion of CO₂ compared with other three catalysts. It should be noted that the conversion of CO₂ at temperature higher than 300 °C here is mainly controlled by the transport process due to concentration gradient caused by the high reaction rate, thus the performance difference of the four catalysts is not so significant compared with the low temperature range (200~280 °C). Considering stability test should be carried out at

conversion far away from equilibrium conversion and free of mass transfer effect. Therefore, the catalytic stability test of NiCo/TiO₂@SiO₂ was carried out at 260 °C and H₂/CO₂ ratio of 4 under ambient pressure over 120 h. Figure 4-11c shows that the CO₂ conversion hovered around 52 % and CH₄ selectivity around 97 %, affirming the long-term stability of the catalytic performance. Some methods to further increase the conversion is: increasing pressure, increasing the loading amount, decreasing the gas flow rate, et al.

Figure 4-11. Activity in the fluidized bed at the H₂/CO₂ ratio of 4 under ambient pressure: (a) CO₂ conversion, (b) CH₄ selectivity, and (c) stability test of NiCo/TiO₂@SiO₂ at 260 °C. (Copyright © Elsevier)

4.4 Conclusion

In summary, novel catalysts based on rational design for CO₂ methanation have been successfully synthesized and tested in both a fixed bed and a fluidized bed reactor, the latter of

which is promising for the highly exothermic reaction due to excellent heat transfer characteristics. The SiO_2 spheres were suitable support particles. Compared with SiO_2 -supported catalysts, additionally coating with TiO_2 dramatically increased the activity of the Ni catalysts due to the electronic effect of TiO_2 , thereby promoting the adsorption of CO_2 and H_2 . Furthermore, compared to a single metal Ni, a bimetal coupling of Co with Ni further increased the catalytic activity through synergistic effects. Therefore, among the catalysts, $\text{NiCo/TiO}_2@\text{SiO}_2$ exhibited the highest activity, selectivity and stability for CO_2 methanation, which makes it promise for large-scale application in fluidized bed reactors. (Copyright © Elsevier)

Chapter 5 Conclusions and outlook

This thesis focusses on the CO₂ hydrogenation process, including thermodynamics analysis, kinetics and catalyst study, and reactor modeling.

Firstly, in thermodynamics section. a comprehensive thermodynamics analysis of CO₂ hydrogenation is conducted using the Gibbs free energy minimization method. The results show that CO₂ reduction to CO needs a high temperature and H₂/CO₂ ratio to achieve a high equilibrium CO₂ conversion. However, synthesis of methanol from CO₂ needs a relatively high pressure and low temperature to minimize the reverse water-gas shift reaction, thus a suitable yield of methanol can be reached. Direct CO₂ hydrogenation to formic acid or formaldehyde is thermodynamically limited, thus some alkaline compounds can be added to adjust the Gibbs energy change. On the contrary, production of CH₄ from CO₂ hydrogenation is the thermodynamically easiest reaction with nearly 100 % CH₄ yield at moderate conditions (1 atm, 200~300 °C). In addition, complex reactions with more than one product are also calculated in this work. Among the considered carboxylic acids (HCOOH, CH₃COOH and C₂H₅COOH), propionic acid dominates in the product stream (selectivity above 90 %). However, it should be noted that here the conclusion will change if other higher carboxylic acids are considered in the system, thus the results obtained here can only be used as a reference. The same trend can also be found in the hydrogenation of CO₂ to aldehydes and alcohols with the major product of propionaldehyde and butanol, respectively. Once again, it should be pointed out that the conclusion will change if some other alcohols or aldehydes are added in the system for consideration. In the process of CO₂ hydrogenation to alkenes, low temperature, high pressure, and high H₂ partial pressure favor the CO₂ conversion. C₄H₆ is the most thermodynamically favorable among all considered alkynes under different temperatures and pressures. Here, the limitation discussed before also holds in alkenes system. The thermodynamic calculations are validated with experimental results, suggesting that the Gibbs free energy minimization method is effective for thermodynamically understanding the

reaction network involved in the CO₂ hydrogenation process, which is helpful for the development of high-performance catalysts. It should be emphasized that thermodynamics analysis does not consider the effect of catalysts. Therefore, although some reactions may be thermodynamically favorable, effective catalysts for these reactions may lack. In addition, in catalysis research process, most cases are far away from the equilibrium, the real conversion can be smaller or larger than the equilibrium conversion. The latter case (conversion higher than equilibrium conversion) may be considered as the reverse reaction has not reached equilibrium conversion. Thus, attention is needed when comparing the experimental conversion with the equilibrium conversion.

In the second section of this thesis, efforts are put on the understanding of the operating parameters affecting CO₂ methanation in the highly efficient fluidized bed reactor. Firstly, the reaction kinetics of the Ni-Mg-W catalyst, was experimentally characterized. Then, a fluidized bed reactor model was developed. Modeling analysis indicated that the Ni-Mg-W was indeed superior to two other catalysts reported earlier in terms of faster depletion of reactants and higher concentrations of product CH₄ throughout the reactor. Regarding the effect of operating parameters, the overall productivity of CH₄ increases with decreased inlet reactant flow rate, increased temperature, increased H₂/CO₂ ratio, decreased catalyst particle diameter and decreased catalyst particle sphericity. The results presented here are expected to be valuable for both the further development of catalysts and of the reactors needed for practical CO₂ methanation processes. The limitations here are the simplicity of the model and lack of heat balance consideration. Future work may adopt more complicated models and include the heat transfer and balance calculation to get more solid results.

In the last project, a Ni-Co bimetal catalyst supported on TiO₂-coated SiO₂ spheres (NiCo/TiO₂@SiO₂) was rationally designed and evaluated for CO₂ methanation in fluidized bed reactor. The results demonstrate that NiCo/TiO₂@SiO₂ exhibited high CO₂ conversion with CH₄ selectivity of greater than 95%. Moreover, the superior performance was sustained for more than

100 h in the fluidized bed reactor, affirming the long-term stability of the catalyst. Comprehensive characterizations were conducted to understand the relationship between structure and performance. This study is expected to be valuable for the potential implementation of the CO₂ methanation process in fluidized beds. The limitation here is the mechanical strength of the catalysts which is also an important aspect for a catalyst applied in fluidized bed reactor are not studied. Some binders can be added to promote the strength in future study if the present strength is not high enough.

In all, conversion of CO₂ by H₂ is under the base that H₂ is obtained from renewable energy other than fossil resource. The hydrogenation of CO₂ can make various products depending on the catalysts and reaction condition applied. Many effects affect the real application of these processes, and the cooperation of chemist, engineer, and even government is needed. This thesis would be a useful guidance for the process development of CO₂ utilization.

References

1. Alper, E. and O. Yuksel Orhan, *CO₂ utilization: Developments in conversion processes*. Petroleum, 2017. **3**(1): p. 109-126.
2. Aresta, M., *Carbon dioxide as chemical feedstock*. 2010, Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA. 11.
3. Ertl, G., *Principles of heterogeneous catalysis*, in *Reactions at Solid Surfaces*. 2010, John Wiley & Sons, Inc. p. 103-121.
4. Qiao, J., et al., *A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels*. Chemical Society Reviews, 2014. **43**(2): p. 631-75.
5. Li, H., et al., *Integrated electromicrobial conversion of CO₂ to higher alcohols*. Science, 2012. **335**(6076): p. 1596.
6. Zhu, Q., et al., *Efficient reduction of CO₂ into formic acid on a lead or tin electrode using an ionic liquid catholyte mixture*. Angewandte Chemie International Edition, 2016. **55**(31): p. 9012-6.
7. Karamian, E. and S. Sharifnia, *On the general mechanism of photocatalytic reduction of CO₂*. Journal of CO₂ Utilization, 2016. **16**: p. 194-203.
8. Xie, S., et al., *Photocatalytic reduction of CO₂ with H₂O: significant enhancement of the activity of Pt-TiO₂ in CH₄ formation by addition of MgO*. Chem Commun (Camb) Chemical Communications, 2013. **49**(24): p. 2451-3.
9. Medford, A.J., et al., *From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis*. Journal of Catalysis, 2015. **328**: p. 36-42.
10. Porosoff, M.D., et al., *Molybdenum carbide as alternative catalysts to precious metals for highly selective reduction of CO₂ to CO*. Angewandte Chemie International Edition, 2014. **126**(26): p. 6823-6827.

11. Zhu, Y., et al., *Catalytic conversion of carbon dioxide to methane on ruthenium–cobalt bimetallic nanocatalysts and correlation between surface chemistry of catalysts under reaction conditions and catalytic performances*. ACS Catalysis, 2012. **2**(11): p. 2403-2408.
12. Martin, O., et al., *Indium oxide as a superior catalyst for methanol synthesis by CO₂ hydrogenation*. Angewandte Chemie International Edition, 2016. **55**(21): p. 6261-6265.
13. Studt, F., et al., *Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol*. Nature Chemistry, 2014. **6**: p. 320.
14. Graciani, J., et al., *Highly active copper-ceria and copper-ceria-titania catalysts for methanol synthesis from CO₂*. Science, 2014. **345**(6196): p. 546-550.
15. Moret, S., P.J. Dyson, and G. Laurenczy, *Direct synthesis of formic acid from carbon dioxide by hydrogenation in acidic media*. Nature Communications, 2014. **5**: p. 4017.
16. You, Z., et al., *Hydrogenation of carbon dioxide to light olefins over non-supported iron catalyst*. Chinese Journal of Catalysis, 2013. **34**(5): p. 956-963.
17. Gao, J.J., C.M. Jia, and B. Liu, *Direct and selective hydrogenation of CO₂ to ethylene and propene by bifunctional catalysts*. Catalysis Science & Technology, 2017. **7**(23): p. 5602-5607.
18. Wei, J., et al., *Directly converting CO₂ into a gasoline fuel*. Nature Communications, 2017. **8**: p. 15174.
19. Ni, Y., et al., *Selective conversion of CO₂ and H₂ into aromatics*. Nature Communications, 2018. **9**(1): p. 3457.
20. Jalama, K., *Carbon dioxide hydrogenation over nickel-, ruthenium-, and copper-based catalysts: Review of kinetics and mechanism*. Catalysis Reviews, 2017. **59**(2): p. 95-164.
21. Aresta, M., A. Dibenedetto, and A. Angelini, *Catalysis for the valorization of exhaust carbon: from CO₂ to chemicals, materials, and fuels. technological use of CO₂*. Chemical Reviews, 2014. **114**(3): p. 1709-42.

22. Porosoff, M.D., B. Yan, and J.G. Chen, *Catalytic reduction of CO₂ by H₂ for synthesis of CO, methanol and hydrocarbons: challenges and opportunities*. Energy & Environmental Science, 2016. **9**(1): p. 62-73.
23. Wang, W.H., et al., *CO₂ hydrogenation to formate and methanol as an alternative to photo- and electrochemical CO₂ reduction*. Chemical Reviews, 2015. **115**(23): p. 12936-73.
24. Sakakura, T., J.C. Choi, and H. Yasuda, *Transformation of carbon dioxide*. Chemical Reviews, 2007. **107**(6): p. 2365-87.
25. Jarunthammachote, S. and A. Dutta, *Equilibrium modeling of gasification: Gibbs free energy minimization approach and its application to spouted bed and spout-fluid bed gasifiers*. Energy Conversion and Management, 2008. **49**(6): p. 1345-1356.
26. Tang, H. and K. Kitagawa, *Supercritical water gasification of biomass: thermodynamic analysis with direct Gibbs free energy minimization*. Chemical Engineering Journal, 2005. **106**(3): p. 261-267.
27. Lima da Silva, A., C.d.F. Malfatti, and I.L. Müller, *Thermodynamic analysis of ethanol steam reforming using Gibbs energy minimization method: A detailed study of the conditions of carbon deposition*. International Journal of Hydrogen Energy, 2009. **34**(10): p. 4321-4330.
28. Gao, J., et al., *A thermodynamic analysis of methanation reactions of carbon oxides for the production of synthetic natural gas*. RSC Advances, 2012. **2**(6): p. 2358.
29. Cao, F., et al., *Thermodynamic analysis of CO₂ direct hydrogenation reactions*. Journal of Natural Gas chemistry, 2001. **10**(1): p. 24-33.
30. Shen, W.J., et al., *Thermodynamic investigation of methanol and dimethyl ether synthesis from CO₂ hydrogenation*. Korean Journal of Chemical Engineering, 2000. **17**(2): p. 210-216.

31. Swapnesh, A., V.C. Srivastava, and I.D. Mall, *Comparative study on thermodynamic analysis of CO₂ utilization reactions*. Chemical Engineering & Technology, 2014. **37**(10): p. 1765-1777.
32. Xu, W., et al. *Thermodynamic analysis of formic acid synthesis from CO₂ hydrogenation*. in *Materials for Renewable Energy & Environment (ICMREE), 2011 International Conference*. 2011.
33. Wang, X., et al., *In situ studies of the active sites for the water gas shift reaction over Cu–CeO₂ catalysts: Complex interaction between metallic copper and oxygen vacancies of ceria*. The Journal of Physical Chemistry B, 2006. **110**(1): p. 428-434.
34. Si, R., et al., *Structure sensitivity of the low-temperature water-gas shift reaction on Cu–CeO₂ catalysts*. Catalysis Today, 2012. **180**(1): p. 68-80.
35. Su, X., et al., *Catalytic carbon dioxide hydrogenation to methane: A review of recent studies*. Journal of Energy Chemistry, 2016. **25**(4): p. 553-565.
36. He, L., et al., *Unique catalysis of Ni-Al hydrotalcite derived catalyst in CO₂ methanation: cooperative effect between Ni nanoparticles and a basic support*. Journal of Energy Chemistry, 2014. **23**(5): p. 587-592.
37. Fan, Z., et al., *Improved activity of Ni/MgAl₂O₄ for CO₂ methanation by the plasma decomposition*. Journal of Energy Chemistry, 2015. **24**(5): p. 655-659.
38. Whitlow, J.E. and C.F. Parrish, *Operation, Modeling and Analysis of the Reverse Water Gas Shift Process*. AIP Conference Proceedings, 2003. **654**(1): p. 1116-1123.
39. Chen, C.S., W.H. Cheng, and S.S. Lin, *Study of reverse water gas shift reaction by TPD, TPR and CO₂ hydrogenation over potassium-promoted Cu/SiO₂ catalyst*. Applied Catalysis A: General, 2003. **238**(1): p. 55-67.
40. Porosoff, M.D., et al., *Molybdenum carbide as alternative catalysts to precious metals for highly selective reduction of CO₂ to CO*. Angewandte Chemie International Edition, 2014. **53**(26): p. 6705-9.

41. Jessop, P.G., et al., *Homogeneous Catalysis in Supercritical Fluids: Hydrogenation of Supercritical Carbon Dioxide to Formic Acid, Alkyl Formates, and Formamides*. Journal of the American Chemical Society, 1996. **118**(2): p. 344-355.
42. Moret, S., P.J. Dyson, and G. Laurenczy, *Direct synthesis of formic acid from carbon dioxide by hydrogenation in acidic media*. Nature Communication, 2014. **5**: p. 4017.
43. Srivastava, V., *In Situ Generation of Ru Nanoparticles to Catalyze CO₂ Hydrogenation to Formic Acid*. Catalysis Letters, 2014. **144**(10): p. 1745-1750.
44. Ikehara, N., et al., *Unique temperature dependence of acetic acid formation in CO₂ hydrogenation on Ag-promoted Rh/SiO₂ catalyst*. Chemistry Letters, 1994(2): p. 263-264.
45. Qian, Q., et al., *Synthesis of acetic acid via methanol hydrocarboxylation with CO₂ and H₂*. Nature Communication, 2016. **7**: p. 11481.
46. Lee, D.K., D.S. Kim, and S.W. Kim, *Selective formation of formaldehyde from carbon dioxide and hydrogen over PtCu/SiO₂*. Applied Organometallic Chemistry, 2001. **15**(2): p. 148-150.
47. He, Z., et al., *Water-Enhanced Synthesis of Higher Alcohols from CO₂ Hydrogenation over a Pt/Co₃O₄ Catalyst under Milder Conditions*. Angewandte Chemie International Edition, 2016. **55**(2): p. 737-41.
48. Studt, F., et al., *Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol*. Nature Chemistry, 2014. **6**(4): p. 320-4.
49. Díez-Ramírez, J., et al., *CO₂ Hydrogenation to Methanol at Atmospheric Pressure: Influence of the Preparation Method of Pd/ZnO Catalysts*. Catalysis Letters, 2015. **146**(2): p. 373-382.
50. Ashley, A.E., A.L. Thompson, and D. O'Hare, *Non-metal-mediated homogeneous hydrogenation of CO₂ to CH₃OH*. Angewandte Chemie International Edition, 2009. **48**(52): p. 9839-43.

51. Li, C.S., et al., *High-performance hybrid oxide catalyst of manganese and cobalt for low-pressure methanol synthesis*. Nature Communication, 2015. **6**: p. 6538.
52. Behrens, M., et al., *The Active Site of Methanol Synthesis over Cu/ZnO/Al₂O₃ Industrial Catalysts*. Science, 2012. **336**(6083): p. 893-897.
53. Dong, X., et al., *Highly Active CNT-Promoted Cu–ZnO–Al₂O₃ Catalyst for Methanol Synthesis from H₂/CO/CO₂*. Catalysis Letters, 2003. **85**(3): p. 237-246.
54. Bansode, A. and A. Urakawa, *Towards full one-pass conversion of carbon dioxide to methanol and methanol-derived products*. Journal of Catalysis, 2014. **309**: p. 66-70.
55. Dorner, R.W., et al., *Heterogeneous catalytic CO₂ conversion to value-added hydrocarbons*. Energy & Environmental Science, 2010. **3**(7): p. 884.
56. Fischer, N., et al., *Hydrocarbons via CO₂ Hydrogenation Over Iron Catalysts: The Effect of Potassium on Structure and Performance*. Catalysis Letters, 2015. **146**(2): p. 509-517.
57. Mattia, D., et al., *Towards Carbon-Neutral CO₂ Conversion to Hydrocarbons*. ChemSusChem, 2015. **8**(23): p. 4064-72.
58. Jiao, F., et al., *Selective conversion of syngas to light olefins*. Science, 2016. **351**(6277): p. 1065-1068.
59. Yan, Y., et al., *A novel W-doped Ni-Mg mixed oxide catalyst for CO₂ methanation*. Applied Catalysis B: Environmental, 2016. **196**: p. 108-116.
60. Wang, W., et al., *Recent advances in catalytic hydrogenation of carbon dioxide*. Chemical Society Reviews, 2011. **40**(7): p. 3703-3727.
61. Wei, W. and G. Jinlong, *Methanation of carbon dioxide: an overview*. Frontiers of Chemical Science and Engineering, 2011. **5**(1): p. 2-10.
62. Lu, B., et al., *Grafting Ni particles onto SBA-15, and their enhanced performance for CO₂ methanation*. RSC Advances, 2015. **5**(70): p. 56444-56454.
63. Kunii, D. and O. Levenspiel, *Fluidization engineering*. 2013: Elsevier.

64. Kopyscinski, J., *Production of synthetic natural gas in a fluidized bed reactor*. 2010.
65. Werther, J., *Fluidized - Bed Reactors*. 1992: Wiley Online Library.
66. Kopyscinski, J., T.J. Schildhauer, and S.M.A. Biollaz, *Methanation in a fluidized bed reactor with high initial CO partial pressure: Part II—Modeling and sensitivity study*. Chemical Engineering Science, 2011. **66**(8): p. 1612-1621.
67. Thompson, M.L., H. Bi, and J.R. Grace, *A generalized bubbling/turbulent fluidized-bed reactor model*. Chemical Engineering Science, 1999. **54**(13): p. 2175-2185.
68. Cobb Jr, J.T. and R.C. Streeter, *Evaluation of fluidized-bed methanation catalysts and reactor modeling*. Industrial & Engineering Chemistry Process Design and Development, 1979. **18**(4): p. 672-679.
69. Kunii, D. and O. Levenspiel, *Bubbling bed model for kinetic processes in fluidized beds. Gas-solid mass and heat transfer and catalytic reactions*. Industrial & Engineering Chemistry Process Design and Development, 1968. **7**(4): p. 481-492.
70. Kunii, D. and O. Levenspiel, *Bubbling bed model. Model for flow of gas through a fluidized bed*. Industrial & Engineering Chemistry Fundamentals, 1968. **7**(3): p. 446-452.
71. Kopyscinski, J., T.J. Schildhauer, and S.M.A. Biollaz, *Methanation in a fluidized bed reactor with high initial CO partial pressure: Part I—Experimental investigation of hydrodynamics, mass transfer effects, and carbon deposition*. Chemical Engineering Science, 2011. **66**(5): p. 924-934.
72. Kopyscinski, J., T.J. Schildhauer, and S.M.A. Biollaz, *Fluidized-Bed methanation: Interaction between kinetics and mass transfer*. Industrial & Engineering Chemistry Research, 2010. **50**(5): p. 2781-2790.
73. Koros, R. and E. Nowak, *A diagnostic test of the kinetic regime in a packed bed reactor*. Chemical Engineering Science, 1967. **22**(3): p. 470.

74. Wen, C.Y. and Y.H. Yu, *A generalized method for predicting the minimum fluidization velocity*. AIChE Journal, 1966. **12**(3): p. 610-612.
75. Fuller, E.N., P.D. Schettler, and J.C. Giddings, *New method for prediction of binary gas-phase diffusion coefficients*. Industrial & Engineering Chemistry, 1966. **58**(5): p. 18-27.
76. Wilke, C.R. and C.Y. Lee, *Estimation of diffusion coefficients for gases and vapors*. Industrial & Engineering Chemistry, 1955. **47**(6): p. 1253-1257.
77. Wilke, C.R. and P. Chang, *Correlation of diffusion coefficients in dilute solutions*. AIChE Journal, 1955. **1**(2): p. 264-270.
78. Taghipour, F., N. Ellis, and C. Wong, *Experimental and computational study of gas-solid fluidized bed hydrodynamics*. Chemical Engineering Science, 2005. **60**(24): p. 6857-6867.
79. Sit, S.P. and J.R. Grace, *Effect of bubble interaction on interphase mass transfer in gas fluidized beds*. Chemical Engineering Science, 1981. **36**(2): p. 327-335.
80. Fuller, E.N., K. Ensley, and J.C. Giddings, *Diffusion of halogenated hydrocarbons in helium. The effect of structure on collision cross sections*. The Journal of Physical Chemistry, 1969. **73**(11): p. 3679-3685.
81. Lim, J.Y., et al., *Kinetic studies of CO₂ methanation over a Ni/ γ -Al₂O₃ catalyst using a batch reactor*. Chemical Engineering Science, 2016. **141**: p. 28-45.
82. Kai, T., T. Takahashi, and S. Furusaki, *Kinetics of the methanation of carbon dioxide over a supported Ni - La₂O₃ catalyst*. The Canadian Journal of Chemical Engineering, 1988. **66**(2): p. 343-347.
83. Rahmani, S. and M. Rezaei, *A comparative study on the kinetics of carbon dioxide methanation over bimetallic and monometallic catalysts*. Iranian Journal of Hydrogen & Fuel Cell, 2016. **3**(1): p. 59-71.
84. Lim, J.Y., et al., *Kinetic studies of CO₂ methanation over a Ni/ γ -Al₂O₃ catalyst using a batch reactor*. Chemical Engineering Science, 2016. **141**: p. 28-45.

85. Li, T., et al., *Synthesis of g-C₃N₄/SmVO₄ composite photocatalyst with improved visible light photocatalytic activities in RhB degradation*. Applied Catalysis B: Environmental, 2013. **129**: p. 255-263.
86. Chiang, J.H. and J.R. Hopper, *Kinetics of the hydrogenation of carbon dioxide over supported nickel*. Industrial & Engineering Chemistry Product Research and Development, 1983. **22**(2): p. 225-228.
87. Van Herwijnen, T., H. Van Doesburg, and W.A. De Jong, *Kinetics of the methanation of CO and CO₂ on a nickel catalyst*. Journal of Catalysis, 1973. **28**(3): p. 391-402.
88. Weatherbee, G.D. and C.H. Bartholomew, *Hydrogenation of CO₂ on group VIII metals: II. Kinetics and mechanism of CO₂ hydrogenation on nickel*. Journal of Catalysis, 1982. **77**(2): p. 460-472.
89. Liu, L., et al., *Effect of particle properties on the flowability of ibuprofen powders*. International Journal of Pharmaceutics, 2008. **362**(1-2): p. 109-117.
90. Ni, M., et al., *A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production*. Renewable and Sustainable Energy Reviews, 2007. **11**(3): p. 401-425.
91. Peharz, G., F. Dimroth, and U. Wittstadt, *Solar hydrogen production by water splitting with a conversion efficiency of 18%*. International Journal of Hydrogen Energy, 2007. **32**(15): p. 3248-3252.
92. Liu, B., et al., *Doping high-surface-area mesoporous TiO₂ microspheres with carbonate for visible light hydrogen production*. Energy & Environmental Science, 2014. **7**(8): p. 2592-2597.
93. Wang, X., et al., *A metal-free polymeric photocatalyst for hydrogen production from water under visible light*. Nature materials, 2009. **8**(1): p. 76.
94. Turner, J.A., *Sustainable hydrogen production*. Science, 2004. **305**(5686): p. 972-974.

95. Jia, C., et al., *The thermodynamics analysis and experimental validation for complicated systems in CO₂ hydrogenation process*. Journal of Energy Chemistry, 2016. **25**(6): p. 1027-1037.
96. Rönsch, S., et al., *Review on methanation—From fundamentals to current projects*. Fuel, 2016. **166**: p. 276-296.
97. Frontera, P., et al., *Supported catalysts for CO₂ methanation: a review*. Catalysts, 2017. **7**(2): p. 59.
98. Ghaib, K., K. Nitz, and F.Z. Ben - Fares, *Chemical methanation of CO₂: a review*. ChemBioEng Reviews, 2016. **3**(6): p. 266-275.
99. Duyar, M.S., et al., *Kinetics of CO₂ methanation over Ru/ γ -Al₂O₃ and implications for renewable energy storage applications*. Journal of CO₂ Utilization, 2015. **12**: p. 27-33.
100. Lu, H., et al., *Metal (Fe, Co, Ce or La) doped nickel catalyst supported on ZrO₂ modified mesoporous clays for CO and CO₂ methanation*. Fuel, 2016. **183**: p. 335-344.
101. Liu, B. and S. Ji, *Comparative study of fluidized-bed and fixed-bed reactor for syngas methanation over Ni-W/TiO₂-SiO₂ catalyst*. Journal of Energy Chemistry, 2013. **22**(5): p. 740-746.
102. Liu, J., et al., *Syngas methanation for substitute natural gas over Ni-Mg/Al₂O₃ catalyst in fixed and fluidized bed reactors*. Catalysis Communications, 2013. **38**: p. 35-39.
103. Kai, T., S. furusaki, and K. yamamoto, *Methanation of carbon monoxide by a fluidized catalyst bed*. Journal of Chemical Engineering of Japan, 1984. **17**(3): p. 280-285.
104. Zhou, R., et al., *Effect of the structure of Ni/TiO₂ catalyst on CO₂ methanation*. International Journal of Hydrogen Energy, 2016. **41**(47): p. 22017-22025.
105. Deleitenburg, C. and A. Trovarelli, *Metal-support interactions in Rh/CeO₂, Rh/TiO₂, and Rh/Nb₂O₅ catalysts as inferred from CO₂ methanation activity*. Journal of Catalysis, 1995. **156**(1): p. 171-174.

106. Guo, M. and G.X. Lu, *The effect of impregnation strategy on structural characters and CO₂ methanation properties over MgO modified Ni/SiO₂ catalysts*. Catalysis Communications, 2014. **54**: p. 55-60.
107. Tada, S., et al., *Ni/CeO₂ catalysts with high CO₂ methanation activity and high CH₄ selectivity at low temperatures*. International Journal of Hydrogen Energy, 2012. **37**(7): p. 5527-5531.
108. Sharma, S., et al., *CO₂ methanation on Ru-doped ceria*. Journal of Catalysis, 2011. **278**(2): p. 297-309.
109. Wang, F., et al., *Active Site Dependent Reaction Mechanism over Ru/CeO₂ Catalyst toward CO₂ Methanation*. Journal of the American Chemical Society, 2016. **138**(19): p. 6298-305.
110. Trovarelli, A., et al., *Co₂ methanation under transient and steady-state conditions over Rh/CeO₂ and CeO₂-promoted Rh/SiO₂ - the role of surface and bulk ceria*. Journal of Catalysis, 1995. **151**(1): p. 111-124.
111. Karelovic, A. and P. Ruiz, *Improving the hydrogenation function of Pd/ γ -Al₂O₃ catalyst by Rh/ γ -Al₂O₃ addition in CO₂ methanation at low temperature*. ACS Catalysis, 2013. **3**(12): p. 2799-2812.
112. Ren, J., et al., *Methanation of carbon dioxide over Ni-M/ZrO₂ (M= Fe, Co, Cu) catalysts: Effect of addition of a second metal*. Fuel Processing Technology, 2015. **137**: p. 204-211.
113. Park, J.-N. and E.W. McFarland, *A highly dispersed Pd-Mg/SiO₂ catalyst active for methanation of CO₂*. Journal of Catalysis, 2009. **266**(1): p. 92-97.
114. Mustard, D.G. and C.H. Bartholomew, *Determination of metal crystallite size and morphology in supported nickel catalysts*. Journal of Catalysis, 1981. **67**(1): p. 186-206.
115. Cullity, B.D. and S.R. Stock, *Elements of X-Ray Diffraction*. 2001, Prentice-Hall Inc. p. p 167-171.

116. Velu, S. and S.K. Gangwal, *Synthesis of alumina supported nickel nanoparticle catalysts and evaluation of nickel metal dispersions by temperature programmed desorption*. Solid State Ionics, 2006. **177**(7-8): p. 803-811.
117. Gao, J., et al., *Effect of nickel nanoparticle size in Ni/ α -Al₂O₃ on CO methanation reaction for the production of synthetic natural gas*. Catalysis Science & Technology, 2013. **3**(8).

Publication list

- (1) Chunmiao Jia, Yihu Dai, Yanhui Yang, Jia Wei Chew*. Nickel-Cobalt catalyst supported on TiO₂-coated SiO₂ spheres for CO₂ methanation in a fluidized bed. *International Journal of Hydrogen Energy*, 2019, 44(26): 13443-13455.
- (2) Chunmiao Jia, Yihu Dai, Yanhui Yang, Jia Wei Chew*. A fluidized bed modeling study for CO₂ methanation using the Ni-Mg-W catalyst. *Particuology*, 2019, *In press*.
- (3) Chunmiao Jia, Jiajian Gao, Yihu Dai, Jia Zhang, Yanhui Yang*. The thermodynamics analysis and experimental validation for complicated systems in CO₂ hydrogenation process. *Journal of Energy Chemistry*, 2016, 25(6): 1027-1037.
- (4) Jiajian Gao, Chunmiao Jia, Liping Zhang, Hongming Wang, Yanhui Yang, Sung-Fu Hung, Ying-Ya Hsu, Bin Liu*. Tuning chemical bonding of MnO₂ through transition-metal doping for enhanced CO oxidation. *Journal of Catalysis*, 2016, 341: 82-90.
- (5) Jiajian Gao, Chunmiao Jia, Bin Liu, Direct and selective hydrogenation of CO₂ to ethylene and propene by bifunctional catalysts. *Catalysis Science & Technology*, 2017, 7: 5602-5607.