CHEMICAL UTILIZATION OF CO_2

–Thermodynamics and catalysts

Esa Turpeinen

Environmental and Chemical Engineering Research group

1. INTRODUCTION

Carbon dioxide (CO_2) can be considered a carbon source rather than just a greenhouse gas (GHG) that needs to be mitigated. The strategies of CO_2 utilization should concentrate on the use of CO_2 for the environmentally benign processes, the production of industrially useful chemicals from CO_2, and the CO_2 recycling involving renewable energy to conserve primary carbon sources. Unfortunately, the use of CO_2 as a chemical reactant is limited to a few industrial processes. High stability, inert property and low reactivity of CO_2 molecule are the major reasons why this compound is not widely used in the industry.

In recent years, much research has been devoted to find out reaction systems, which are technically and economically feasible. Among them, hydrogenation and reforming of CO_2 are attractive approaches. The products of CO_2 hydrogenation such as methanol and hydrocarbons are excellent fuels in internal combustion engines and easy for storage and transportation. Furthermore, syngas, methanol and formic acid are important raw materials and intermediates for many chemical syntheses.

In this research, the viability of selected CO_2 utilizing reactions is analyzed by thermodynamic calculations (effect of temperature, pressure and feed ratio). Moreover, typical catalytic systems used in those reactions are listed. The reactions chosen for this research are dry reforming, methanol synthesis, synthetic natural gas synthesis, reverse water gas shift reaction, formic acid synthesis and dimethyl carbonate synthesis. These reactions have been under investigation at University of Oulu during CCS programme.

1.1 Catalysts

Being thermodynamically stable molecule, substantial energy input, active catalysts, and optimum reaction conditions are necessary for successful and viable CO_2 conversion. The main part of the CO_2 related R&D work has especially been focused on catalyst development for various reaction routes converting CO_2 into valuable chemicals and fuels. Both homogeneous and heterogeneous catalysts have advantages and shortcomings. Normally, homogeneous catalytic systems show higher catalytic activity than their heterogeneous counterparts do. Nevertheless, heterogeneous catalysts can offer technical advantages related to stability, separation, handling, and reuse of catalysts as well as reactor design (Ma et al. 2009). In industrial processes, production cost can be reduced significantly if a heterogeneous catalyst of high efficiency is deployed (Dai et al. 2009).

1.2 Thermodynamics of CO_2 conversion processes

Carbon dioxide is a stable molecule (ΔG_f = -396 kJ/mol) and, with water, the product of any combustion of materials containing carbon and hydrogen, thus laying in a potential-energy well (Fig.1). From the energetic point of view, the conversion of CO_2 will require an amount of energy that depends on the downwards steps of the oxidation state of carbon from +4 in CO_2 to that of the target product. In general, if CO_2 is incorporated as the entire moiety into a compound the energetic

of the process is around to be favorable, while if one reduces carbon, energy is required (Aresta et al. 2013). As carbon in CO_2 is in the oxidized form, many of the CO_2 utilizing reactions are reductions.

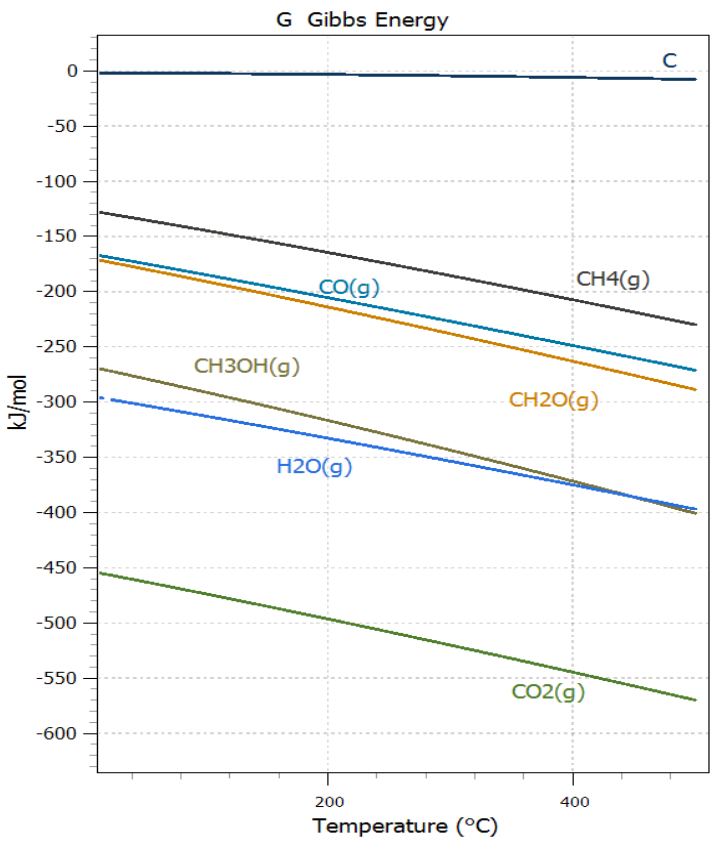

Figure 1. Free-energy of formation for CO2, H2O and various C1 species.

2. DRY REFORMING

Dry reforming of methane (DRM, Eq. 1) for the production of syngas (mixture of hydrogen (H_2) and carbon monoxide (CO)) has attracted much attention from both industrial and environmental aspects. It offers removal of GHG (methane and carbon dioxide), biogas utilization (Lucredio et al. 2012) and conversion of natural gas with a high carbon dioxide content to valuable syngas (Lunsford 2000, Bradford and Vannice 1999), which is an important compound in chemical industry. Dry reforming of methane yields a low syngas ratio (H_2/CO_2 = 1), which is suitable for the synthesis of oxygenated chemicals (Wurzel et al. 2000) and hydrocarbons via Fischer-Tropsch synthesis (Fujimoto et al. 1992).

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad \Delta H_{25°C} = 247.0 \text{ kJ/mol}, \quad \Delta G_{25°C} = 170.5 \text{ kJ/mol} \qquad (1)$$

2.1 Thermodynamics

Dry reforming of methane is an extremely endothermic reaction (high enthalpy value) and thus it requires extremely high temperatures to attain high equilibrium conversions of feedstocks to syngas. The effect of temperature on the product distribution is illustrated in Figure 1.

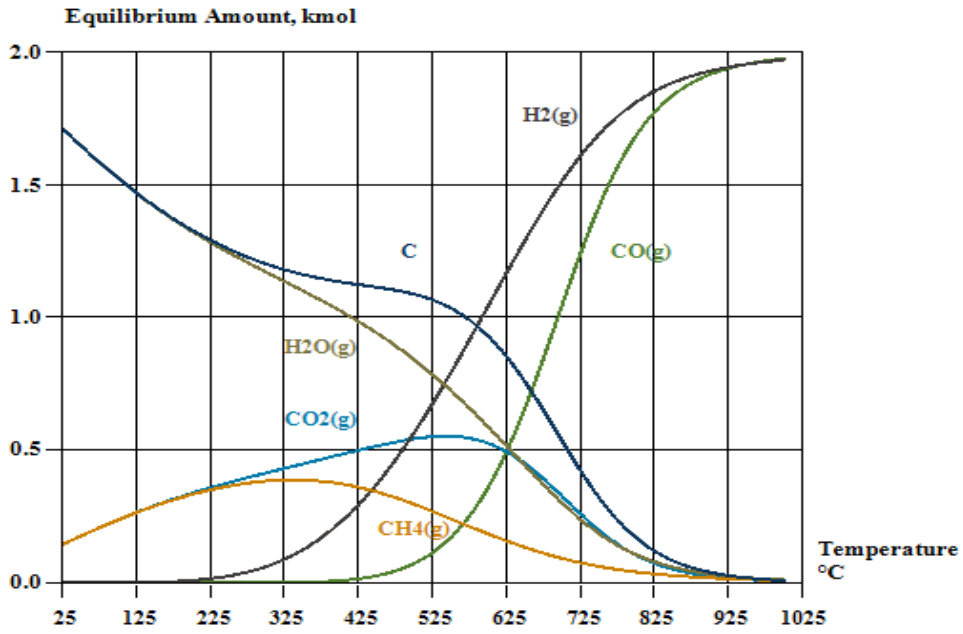

Figure 1. Equilibrium composition as a function of temperature in dry reforming (feed: CO_2/CH_4 = 1, P = 1 bar)

Thermodynamic calculations show that high temperature favors the dry reforming reaction. In order to attain high conversions of reactants and syngas yield a temperature of 900 °C is needed. At that temperature the conversions are almost complete. Catalyst deactivation due to carbon formation has found to be a severe problem in dry reforming. As calculations show there is a solid carbon formation phenomenon. The formation decreases when temperature increases but there is a possibility for that even at high temperatures.

The effect of pressure on the product distribution is illustrated in Figure 2.

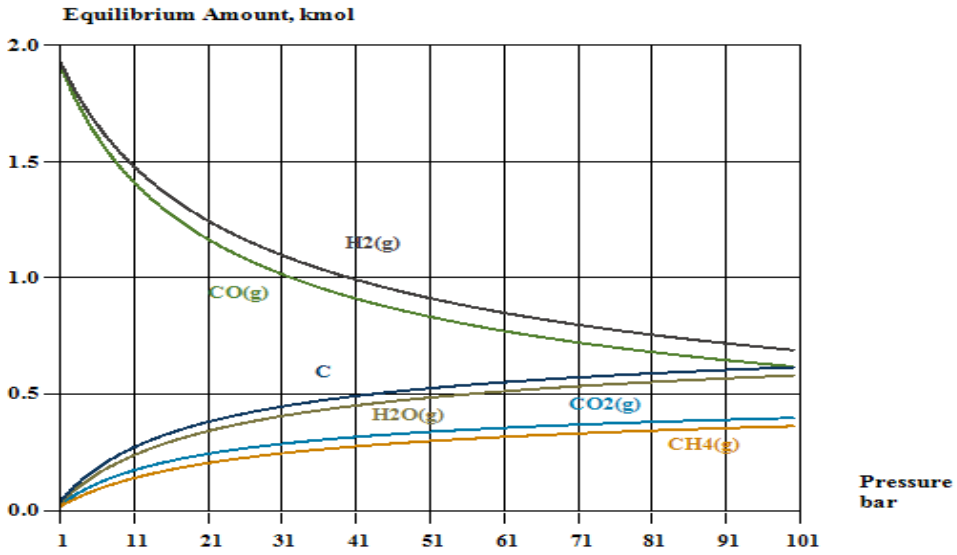

Figure 2. Equilibrium composition as a function of pressure in dry reforming (feed: CO_2/CH_4 = 1, T = 900 °C).

The conversions of CH_4 and CO_2 and the H_2 and CO yields drop significantly with increasing operating pressure. Thus, it is essential to operate at low pressures to achieve high conversions and high H_2 + CO yields.

The effect of feed ratio on the product distribution is presented in Figure 3.

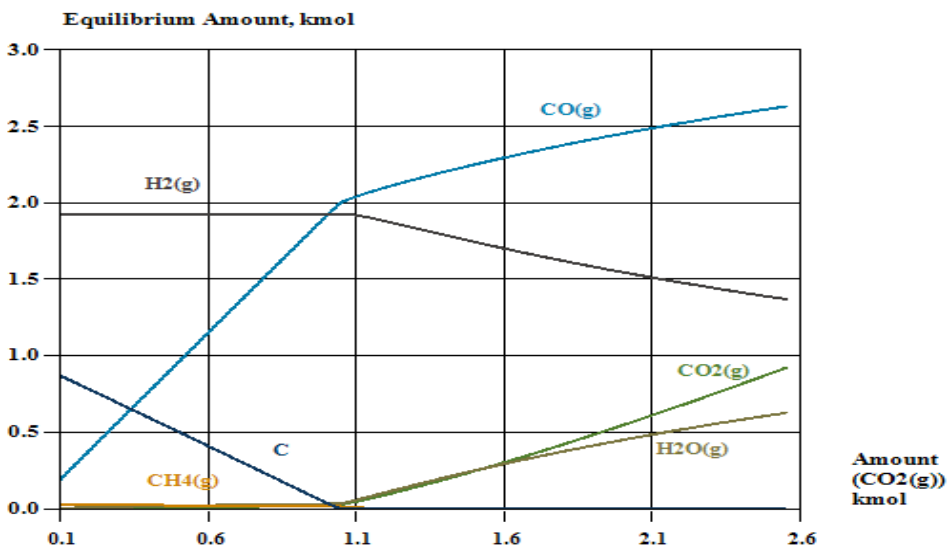

Figure 3. Equilibrium composition as a function of feedstock in dry reforming (feed: T= 900 °C, P = 1 bar).

Below stoichiometric feed ratio (CO_2:CH_4 =1) carbon formation is dominant feature in dry reforming reaction. When the input CO_2 amount is above stoichiometric ratio, proportion of CO_2 remains

unreacted and H_2 amount starts to decrease. The results show that high temperature, low pressure and near stoichiometric feed ratio are the most optimal conditions for dry reforming reaction.

2.2 Catalysts

During the past decades, the process of carbon dioxide reforming of methane has received attention, and efforts have focused on development of catalysts which show high activity towards synthesis gas formation, and are also resistant to coking, thus ensuring stable long-term operation. Numerous supported metal catalysts have been developed and tested for this reaction. Among them, nickel-based catalysts and supported noble metal catalysts (e.g. Rh and Ru) give promising catalytic performance in terms of feedstock conversion and selectivity to synthesis gas (Usman et al. 2015). Generally, most of the group VIII metals (Rh, Ru, Ni, Pt, Pd, Ir, Co, Fe) except Os are more or less effective catalysts for the dry reforming reaction (Wang and Lu 1996). Nickel catalysts have been long accepted as proper catalysts for dry and reforming reactions because of their (a) high activity, (b) reasonable stability, and (c) reasonable cost and availability (Shah & Gardner 2014).

Noble metals like Rh, Ru and Pt are highly active towards DRM and are more resistant to carbon formation than other transition metals, especially nickel, but they are expensive (Kehres et al.2000, Ferreira-Aparicio et al. 1999, Carrara et al. 2008, Zhang et al. 1996) Considering the high cost and limited availability of noble metals, it is more profitable to develop a Ni-based catalyst, which is resistant to coke accumulation and exhibits long-term stability. Bimetallic (Ni-Pt, Ni-Rh, Ni-Ce, Ni-Mo and Ni-Co) catalysts appear to be a promising alternative to high-cost monometallic noble metal catalysts (Usman et al. 2015). Suitable supports have to be resistant to the high temperature applied and they have to provide surface area and to maintain the metal dispersion of the catalyst during operation (Guo et al. 2004).

3. REVERSE WATER GAS SHIFT REACTION

Catalytic conversion of CO_2 to CO via reverse water shift gas (RWGS) reaction is one process for CO_2 conversions.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_{25°C} = 41.1 \text{ kJ/mol}, \quad \Delta G_{25°C} = 28.6 \text{ kJ/mol} \qquad (2)$$

The reverse water shift reaction (and water gas shift (WGS)) reaction occurs in many processes, wherever CO_2 and H_2 are present in a reaction mixture. Due to the importance of this reaction from both fundamental and practical points of view, the design and characterization of RWGS catalysts have attracted considerable attention. This reaction is mildly endothermic and will occur at elevated temperatures. RWGS reaction is an endothermic reaction, and thus high temperature would facilitate the formation of CO. However, the RWGS reaction will only be commercially interesting as a source for syngas if an appropriate and sustainable source of hydrogen and thermal energy at the appropriate temperature level is provided.

3.1 Thermodynamics

The effect of temperature on the product distribution is illustrated in Figure 4.

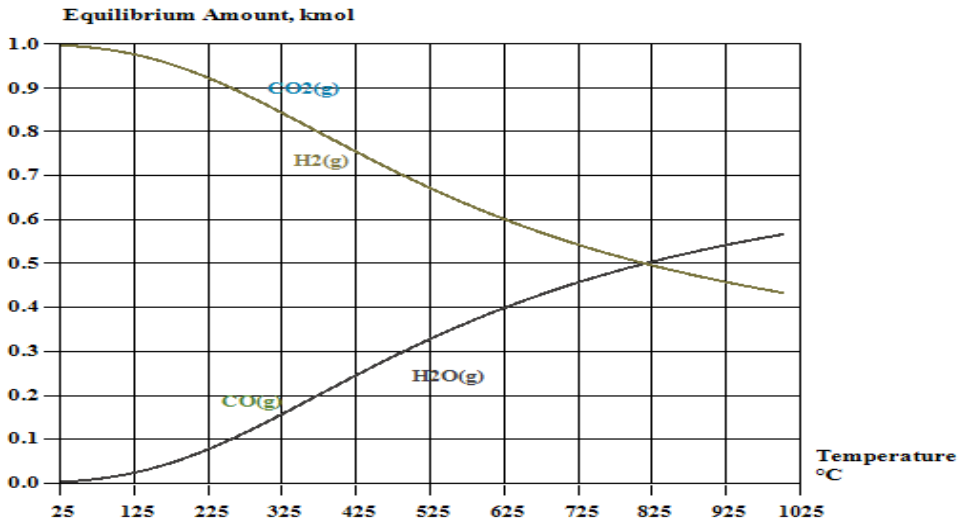

Figure 4. Equilibrium composition as a function of temperature in reverse water shift gas reaction (feed: CO_2/H_2 = 1, P = 1 bar).

RWGS reaction is an endothermic reaction, and thus high temperature facilitates the conversion of CO_2. Based on the thermodynamic equilibrium, temperatures above 700 °C are necessary for the formation of considerable amount of CO. The conversions of feedstocks rise above 50 % at temperature of 800 °C as shown in Figure 4.

The effect of pressure on the product distribution is presented in Figure 5.

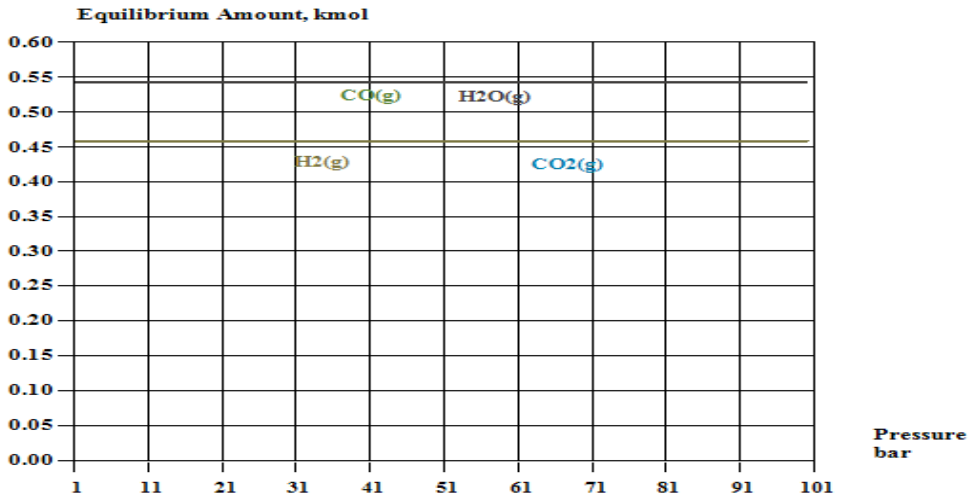

Figure 5. Equilibrium composition as a function of pressure in reverse water gas shift reaction (feed: CO_2/H2 = 1, T = 925 °C)

As Figure 5 shows pressure has no effect on the product distribution, thus the reaction is independent of the pressure level.

The effect of feed ratio on the product distribution is presented in Figure 6.

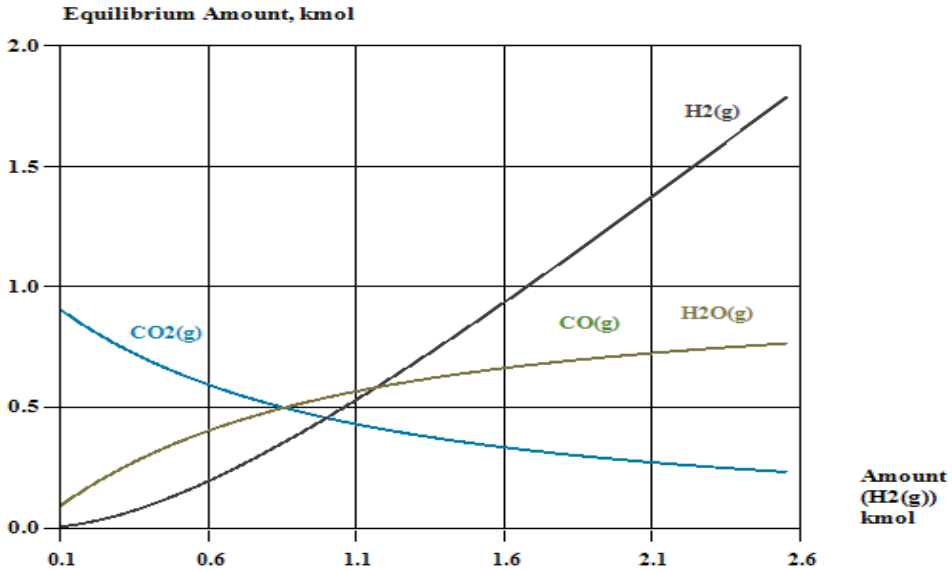

Figure 6. Equilibrium composition as a function of feedstock in reverse water shift gas reaction (feed: T= 925 °C, P = 1 bar)

It is possible to increase conversion of CO_2 by feeding surplus of H_2 as shown in Figure 6. However, at the same time amount of unreacted H_2 rises substantially. Thus, using near stoichiometric feed ratio ($H_2 : CO_2 = 1$) gives a good compromise between conversions of feedtocks and yield of CO.

3.2 Catalysts

As RWGS is a reversible reaction, catalysts active in the water gas shift (WGS) reaction are often active in the reverse reaction (Centi and Perathoner 2009). Many efforts in recent years have attempted to find the best heterogeneous catalysts to carry out the WGS reaction. At the moment, there are two main classes of materials being used in industry as CO-shift catalysts: Iron-based and Copper based catalysts (Kochloefl 1997). Since their first industrial application, numerous developments have taken place in catalyst compositions and manufacturing procedures, attempting to improve their activity, stability, and selectivity.

The iron-based catalysts are some of the earliest heterogeneous catalysts used industrially in the WGS reaction and are commonly called high temperature (HT) shift catalysts, operating in the temperature range of around 350–450 ◦C, because of improved catalytic performance and selectivity. There is still a need to develop catalysts which are active at higher temperatures because

at this temperature the equilibrium constant is low and there is a significant problem in driving the RWGS reaction to completion. Most industrial HT shift catalysts contain Cr oxide (Cr_2O_3) as well as Fe oxide, and it is being generally believed that Cr_2O_3 is a structural promoter, retarding sintering and loss of surface area of the Fe oxide, thus enhancing the activity and stability of Fe catalysts. (Kochloefl 1997)

The industrial WGS process was significantly improved by the use of Cu-based catalysts because the enhancement obtained in the process allows higher CO conversions and yields in the production of H_2. Since their first usage, several Cu formulations have been employed in the LT-WGS stage. However, copper-based catalyst is not suitable at high temperature because of its poor thermal stability (e.g., sintering of copper nanoparticles) unless modified by adding a thermal stabilizer (e.g. Iron) (Wang et al. 2011).

Cerium-based catalysts are also active in both WGS and RWGS reactions (Trovalli 1996). However, deactivation of ceria supported catalysts is a crucial issue one needs to consider. In addition, supported noble metal catalysts (e.g., Pt, Ru, and Rh) typically have high ability toward H_2 dissociation, and thus they have been used as efficient catalysts for CO_2 hydrogenation (Wang et al. 2011).

4. METHANOL SYNTHESIS

Much effort is now being put on CO_2 conversion to methanol (CH_3OH, (Eq. 3)) even though it is a great challenge due to the high activation of CO_2 and the demand of substantial energy input.

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H_{25°C} = -49.3 \text{ kJ/mol}, \quad \Delta G_{25°C} = 3.5 \text{ kJ/mol} \qquad (3)$$

Methanol is commonly used as solvent and feedstock for the production of chemicals and fuel additives. Methanol is a liquid energy-carrier suitable for transportation applications. It is an excellent alternative fuel, and it can also be blended with gasoline and it be used in fuel cells, too. (Olah et al. 2009)

In view of reaction, selection of catalysts, generation of water and consumption of hydrogen should be concerned. The generation of water in the reaction decreases methanol production because water acts as an inhibitor to active sites of catalysts. Furthermore, other by-products are formed during the hydrogenation of CO_2, such as CO, hydrocarbons, and higher alcohols (Liaw and Chen, 2001). Therefore, a highly selective catalyst is in need to avoid the formation of undesired by-products for methanol synthesis.

4.1 Thermodynamics

From the thermodynamic point of view, a decrease in reaction temperature or an increase in reaction pressure could favor the synthesis of methanol. Indeed, enhanced reaction temperature (e.g., higher than 240 °C) facilitates CO_2 activation and subsequent methanol formation.

The effect of temperature on the product distribution is illustrated in Figure 7.

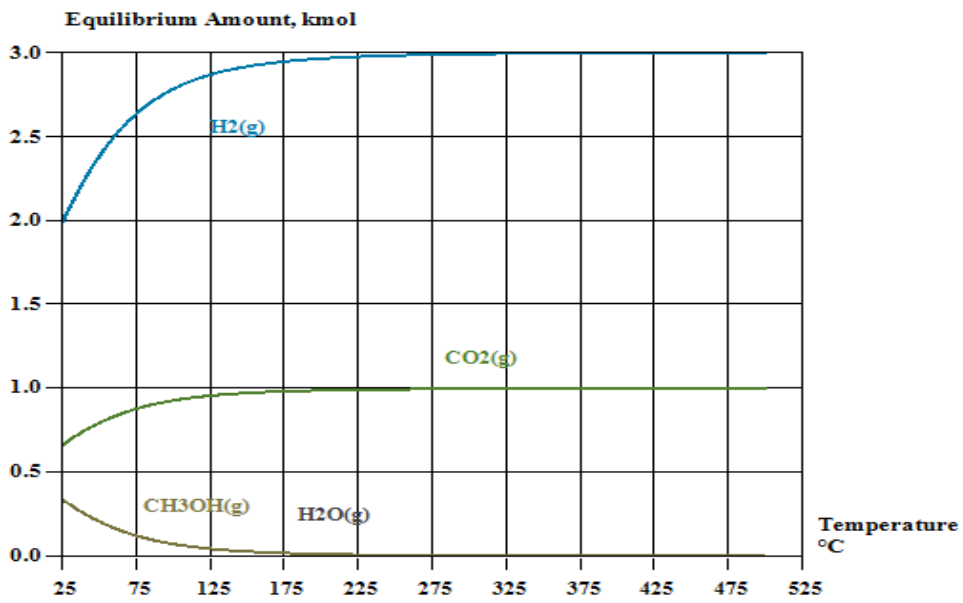

Figure 7. Equilibrium composition as a function of temperature in methanol synthesis (feed: H_2/CO_2 = 3, P = 1 bar).

Low temperature favors the formation of methanol but at temperatures needed for catalyst activation (~ 250 °C) the formation of methanol is practically negligible at pressure of 1 bar.

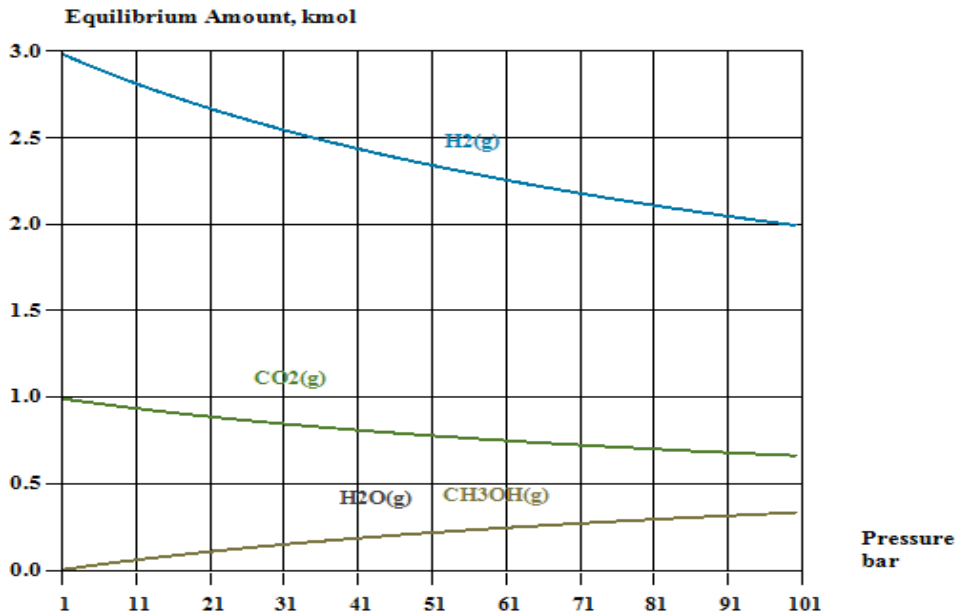

Figure 8. Equilibrium composition as a function of pressure in methanol synthesis (feed: H_2/CO_2 = 3, T = 250 °C)

Pressure increase enhances the formation of methanol but the formation is quite modest even at 100 bar. The generation of undesired water hinders the yield of methanol.

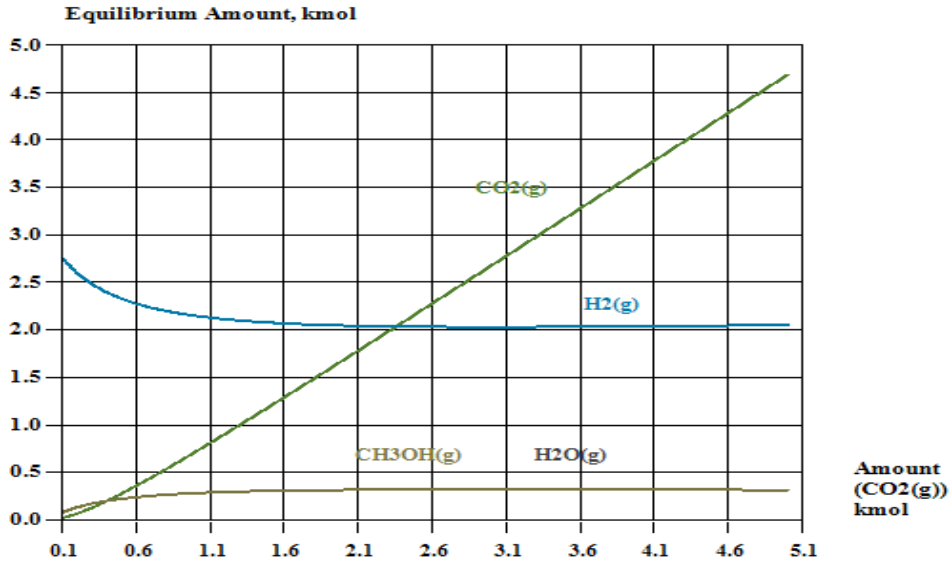

Figure 9. Equilibrium composition as a function of feed ratio in methanol synthesis (feed:, T = 250 °C, P= 75 bar)

There is no reason to increase amount of input CO_2 much above stoichiometric ratio as shown in Figure 9. There is a slight increase in yield but it is practically insignificant.

4.2 Catalysts

As shown in the previous Chapter, hydrogenation of CO_2 to methanol has quite favorable thermodynamics, but high activation energy barriers should be overcome by appropriate catalysts. Typically, catalysts used in CO_2 hydrogenation are those for methanol synthesis from CO hydrogenation (Wang et al. 2011) A number of investigations have addressed the effects of active components, supports, promoters, preparation methods, and surface morphology on reactivity. Although many kinds of metal-based catalysts have been examined for the synthesis of methanol, Cu remains the main active catalyst component, together with different modifiers (Zn, Zr, Ce, Al, Si, V, Ti, Ga, B, Cr, etc.) (Liaw and Chen 2001, Arena et al. 2007, Saito and Murata 2004). Cu/ZnO catalyst is well known for its high activity and selectivity for the methanol synthesis reaction (Jadhav et al. 2014).

An appropriate support affects the formation and stabilization of the active phase of the catalyst and is capable of tuning the interactions between the major component and promoter. In addition, basicity and/or acidity characteristics of the catalyst are also determined by the selected support (Liu et al. 2003). Zinc oxide improves the dispersion and stabilization of copper (Ovesen et al. 1997, Yoshihara and Campbell 1996). Zirconia has been considered as an excellent promoter because of the high stability under reducing or oxidizing atmospheres (Liu et al. 2001, An et al. 2007). Cerium has found to have an excellent oxygen storage capacity. Addition of many components (e.g. Ga, B,

and Al) may decrease the adsorption rate of water, which inhibits the formation of methanol (152,157, Sloczynski et al. 2006, 77).

5. METHANATION

The reaction of CO_2 methanation, which is the hydrogenation of CO_2 to methane (CH_4, (Eq. 4)), has been known for over a century as the Sabatier reaction but has received renewed interest recently for the development of new CO_2 fixation technologies. Methane formation from CO_2 is a simple reaction which can generate methane under atmospheric pressure.

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta H_{25°C} = -165 \text{ kJ/mol}, \quad \Delta G_{25°C} = -113 \text{ kJ/mol} \qquad (4)$$

The CO_2 hydrogenation to methane presents a promising approach because produced methane can be injected directly into already existing natural gas pipelines, and it can be used as a fuel or raw material for the production of chemicals. Another reason for the increasing importance of the methanation process is the need for storing excess electrical energy from renewable sources. (Schaaf et al. 2014)

The methanation of carbon dioxide is thermodynamically favorable at low temperatures ($\Delta G_{25\,°C}$ = -113 kJ/mol). Thus, the methanation process generally operates at around 400 °C (Gao *et al.*, 2009). The methanation reaction is highly exothermic ($\Delta H_{25\,°C}$ = -165 kJ/mol). However, an eight-electron transfer process is needed to reduce the most oxidized form of carbon to methane and due to the kinetic limitations an effective catalyst is needed to achieve acceptable reaction rate and selectivity (Park and McFarland, 2009).

5.1 Thermodynamics

The effect of temperature on the product distribution is illustrated in Figure 10.

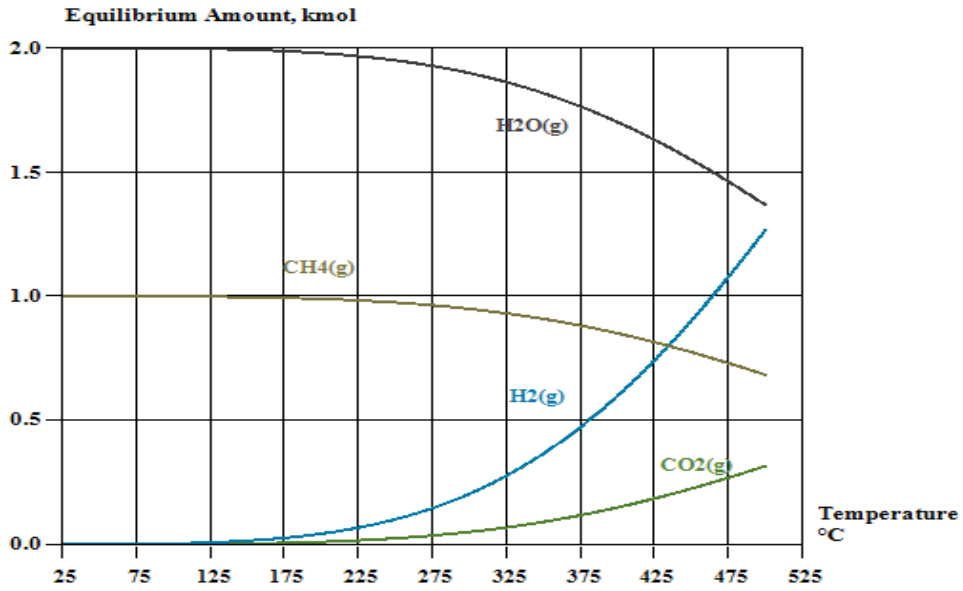

Figure 10. Equilibrium composition as a function of temperature (feed: P = 1 bar).

The methanation of carbon dioxide is thermodynamically strongly exothermic reaction and thus favorable at low temperatures. The equilibrium is completely on the side of products at low temperatures (up to 100 °C). However, the reaction is kinetically restricted at low temperatures and thus the reactions happens at around 400 °C.

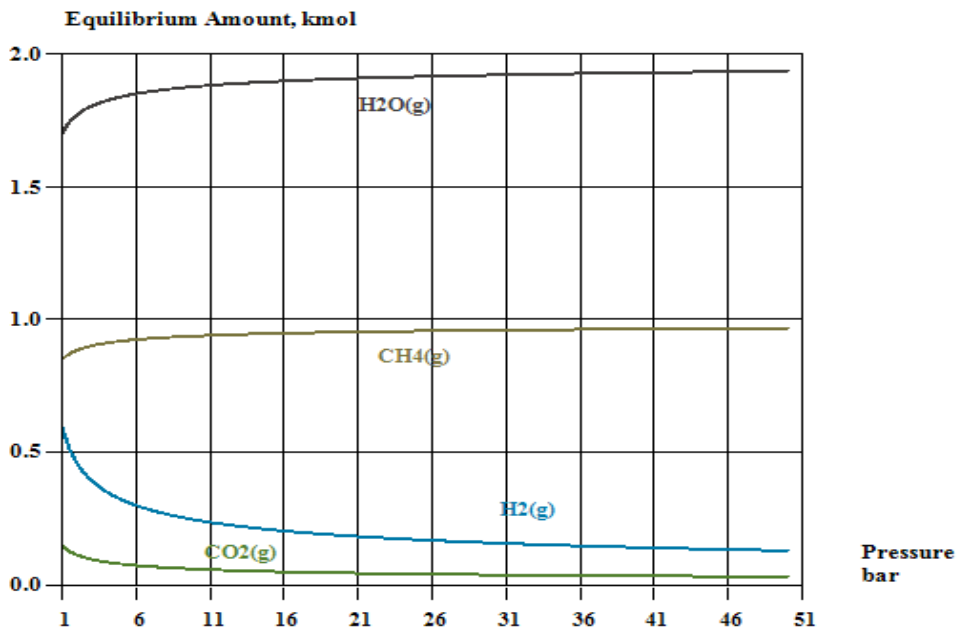

Figure 11. Equilibrium composition as a function of pressure ratio in the CO_2 methanation reaction (feed: T = 400 °C).

Figure 11 shows that that the yield of methane increases with increasing pressure. By increasing the pressure to 20 bar and keeping the temperature at 400°C, the methane yield reaches approximately 95 % of theoretical limit. A further increase of the operating pressure does not significantly increase the methane yield.

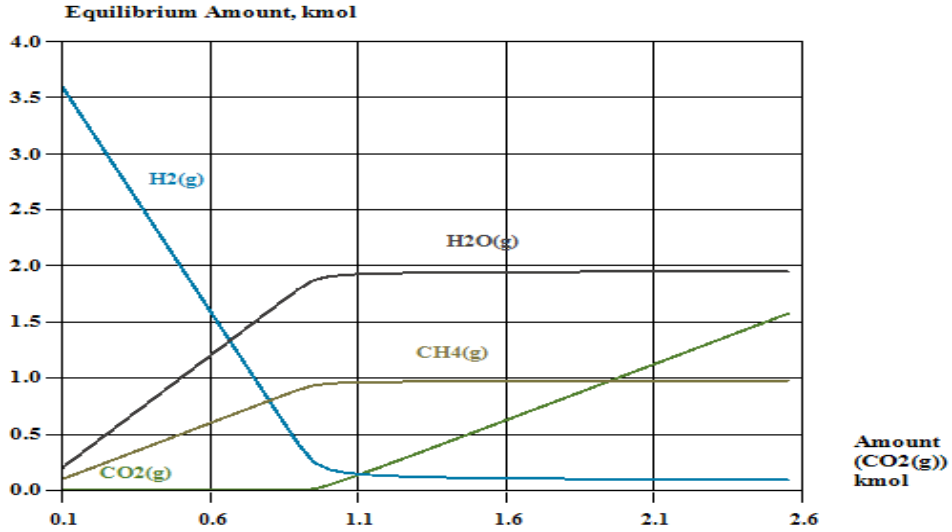

Figure 12. Equilibrium composition as a function of feed ratio in CO_2 methanation reaction (feed:, T = 400 °C, P= 20 bar)

Figure 12 illustrates the effect of input CO_2 on the equilibrium product composition. The yield of methane attains maximum with stoichiometric value of CO_2 (=1). Surplus CO_2 has no positive effect on the yield of CH_4.

5.2 Catalysts

Apart from these purely thermodynamic considerations, the choice of catalysts has a significant influence on the methanation reaction. Most of the methanation studies have been focused on metal-based catalytic systems. Both homogeneous and heterogeneous catalysts have been applied to CO_2 hydrogenation. Hydrogenation of CO_2 toward methane has been investigated using alternative suitable catalytic systems based on supported group VIII metals (e.g. Ni, Ru, Rh) on various oxide supports (TiO_2, SiO_2, Al_2O_3, CeO_2, ZrO_2) (Wang et al. 2011). Supported nickel catalysts remain the most widely studied materials (Abello *et al.* 2013). High surface area supports, usually oxides, have been used extensively for the preparation of metal catalysts. The nature of support plays a crucial role in the interaction between the nickel and the support, and thus determines catalytic performances toward activity and selectivity for the methanation of CO_2 (Chang et al. 2003) The catalysts used in the methanation reaction have many similarities to those for CO_2 reforming (dry reforming).

Operating temperatures below 200°C are not allowed in the presence of a nickel-based catalyst because of the potential formation of highly toxic nickel carbonyl from carbon monoxide. The operating temperature should, on the other hand, never exceed 550°C to avoid deactivation of the catalyst by sintering or carbon formation. (Pedersen et al. 1980)

6. FORMIC ACID SYNTHESIS

Formic acid (HCOOH) is an important chemical feedstock in the organic chemical industry. It has been used e.g. as a mordant in the dyeing industry, as a neutralizer in tanning, and as a disinfectant and preservative agent in cleaning applications. As a feedstock in the chemical industry, it has promoted the production of formate esters, which have been used to produce a variety of organic derivatives such as aldehydes, ketones, carboxylic acids and amides. (Hao et al. 2011, Ullmann's 2012)

Currently, HCOOH synthesis is mainly conducted through a two-step process (Ullmann's 2012): [1] the carbonylation of methanol to methyl formate ($HCOOCH_3$) using high-pressure CO as the feedstock, which is toxic, and [2] the hydrolysis of $HCOOCH_3$ to HCOOH and CH_3OH. Producing formic acid by direct hydrogenation of CO_2 (Eq. 5) could be a promising alternate route from economic, environmental, and safety perspectives.

$$CO_2 + H_2 \leftrightarrow HCOOH \qquad \Delta H_{25°C} = 32.7 \text{ kJ/mol}, \ \Delta G_{25°C} = 32.7 \text{ kJ/mol} \qquad (5)$$

However, as free Gibbs energy (positive ΔG value) shows the reaction is unfavourable and thermodynamic limits must be circumvented somehow in order to make this reaction route feasible. To shift the reaction equilibrium, it is necessary to add a base (inorganic or organic) to the reaction system. With the addition of an inorganic base, formate is generated which subsequently needs strong acid to convert to formic acid (Zhang et al. 2009).

6.1 Thermodynamics

The effect of temperature and pressure on the product distribution are illustrated in Figure 13.

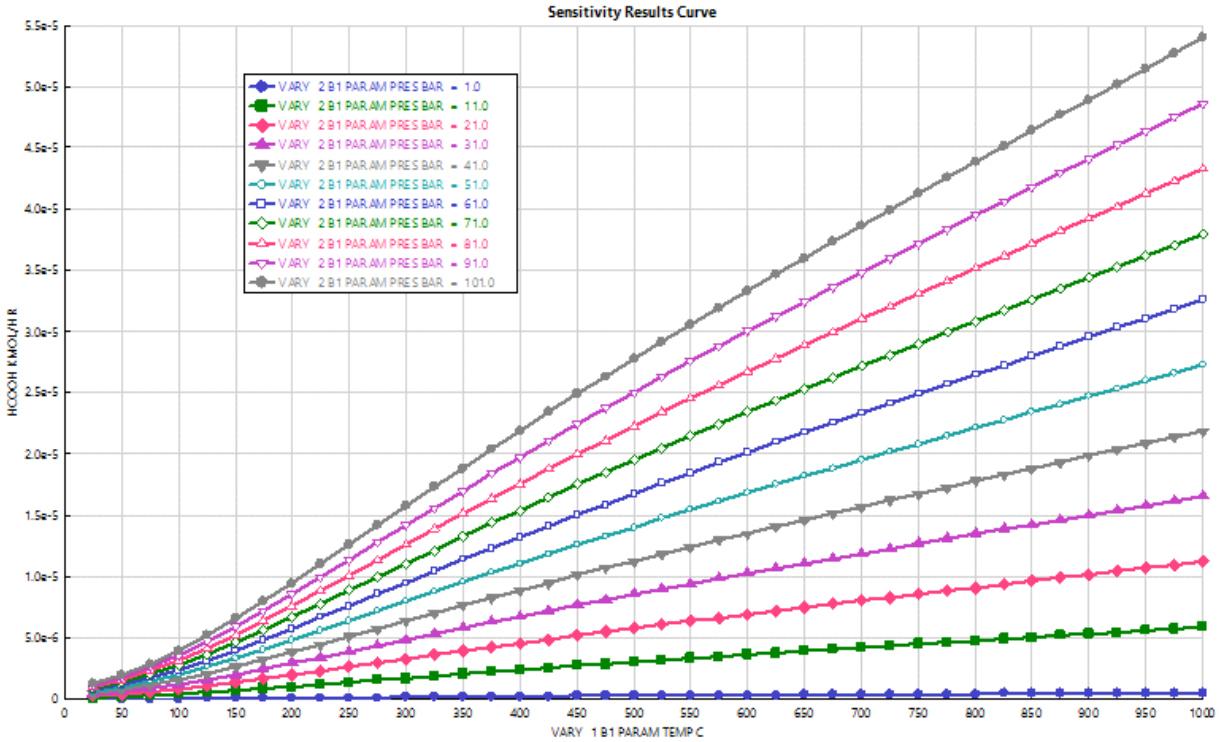

Figure 13. Equilibrium composition as a function of temperature and pressure in formic acid synthesis (feed: H2:CO2 = 1).

The calculations showed that the hydrogenation of CO_2 to formic acid is thermodynamically unfavorable reaction. Even at the severest conditions, the formation of formic acid is practically negligible. To have an efficient conversion of CO_2 to formic acid thermodynamic limitations must be circumvented somehow. The increase in the reaction pressure and temperature improve the evolving of formic acid. The amount of formic acid formed increases linearly as a function of pressure. In the studied conditions the amount of formic acid reaches its maximum (2.5×10^{-4} mol %) at 100 bar and at 1000 °C.

6.2 Catalysts

Hydrogenation of CO_2 has been widely studied by using mainly homogeneous catalysts. Ru complexes generally offer favourable activity and selectivity for formic acid, and have become focus of studies (Gao et al. 2000). In addition, various transition metal complexes based on Rh, Ir, Pd, Ni, Fe and Mo have been studied (Gassner and Leitner 1993, Jessop et al. 2004, Behr et al. 2004, Behr and Nowakowski 2014, Tanaka et al. 2009.) A limited literature is available on direct hydrogenation of CO_2 to form formic acid with heterogeneous catalysts. Although homogeneous catalysts have been proved to be efficient for CO_2 hydrogenation to formic acid, they have some drawbacks such as separation of products and recycling the catalyst (Zhang et al. 2004). Immobilization of a complex onto a supporting material would improve the reusability and stability of the catalyst. For example,

ruthenium complexes immobilized over amine-functionalized-silica have been developed with an in situ synthetic approach for CO_2 hydrogenation to formic acid (Zhang et al. 2004).

Ionic liquids have some unique properties, such as excellent thermal stability, wide liquid regions, and favourable solvation properties for various substances. Upon the reaction, formic acid could be collected by heating due to the non-volatility and moderate basicity of ionic liquid (Wang et al. 2011). Hydrogenation of $scCO_2$ has gained a growing interest since CO_2 can play a dual role as both reactant and solvent.

7. DIMETHYL CARBONATE SYNTHESIS

The synthesis of dimethyl carbonate (DMC) based on the utilization of carbon dioxide (Eq. 6) is attracting much attention because of its potential industrial applications and ecological benefits. DMC exhibits versatile chemical reactivity and unique physical properties such as low toxicity and excellent biodegradability and thus is an environmentally benign building block for chemicals (Yanji et al. 1998). It also finds applications in the synthesis of higher carbonates, carbamates, polyurethane, and a promising octane booster in gasoline. Furthermore, it can be used as a solvent, an alkylation agent, and a substitute for toxic carbonylating and methylating agents (Pachero and Marshall 1997).

$$2CH_3OH + CO_2 \leftrightarrow (CH_3O)_2CO + H2O \qquad \Delta H = -27.9 \text{ kJ mol}^{-1}, \Delta G=26.2 \text{ kJ mol}^{-1} \qquad (6)$$

7.1 Thermodynamics

The major difficulty associated with the synthesis of DMC in high yields from the direct reaction of carbon dioxide and methanol is the thermodynamic limitations of the reaction. The effect of temperature and pressure on the product distribution are illustrated in Figure 14.

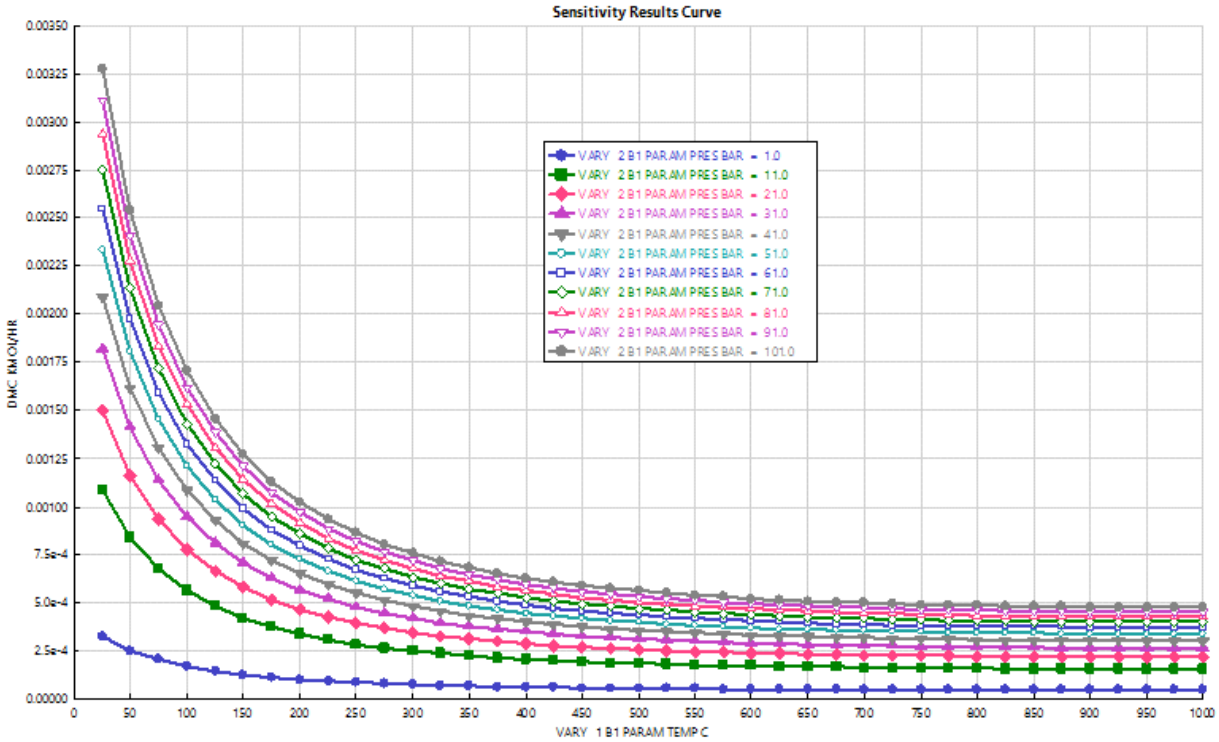

Figure 14 Equilibrium composition as a function of temperature and pressure DMC synthesis (feed: = 1).

Low temperature and high pressure promote the DMC synthesis reaction as shown in Fig. 14. Thermodynamics plays a decisive and critical role in the synthesis of DMC from CO_2 and methanol, limiting the DMC yield lower than 0.5% even at favorable high-pressure (100 bar) and at low-temperature (25 °C) conditions.

7.2 Catalysts

Efforts toward improving the yield of DMC from the direct route have mainly been focused on catalyst development and optimization of reaction conditions without addressing the limitations imposed by thermodynamics. Several types of catalysts have been reported for the direct synthesis of organic carbonates, especially DMC: homogenous metal complexes, complexes anchored to supports, and metal oxide catalysts. Organometallic complexes such as $Me_2Sn(OMe)_2$ have been the widely studied catalysts in the homogenous systems for DMC synthesis (Dibenedetto et. al 2013). However, these catalysts suffer from low activity and are easily decomposed or deactivated by coproduced water (Ma et al. 2009). Among metal oxides, CeO_2 and ZrO_2 were found to be consistently active in this reaction (Tomishige et al. 1999).

Although the selectivity of DMC over these catalysts was high (> 90%) under the reaction conditions reported, the yields of DMC obtained were nevertheless lower than 0.5 mol % relative to methanol even in the presence of additives like $CaCl_2$ (Eta et al. 2010). Without a dehydration system the yields are very low (1-2%) over any catalysts (Sakakura and Kohno 2009). In particular, dehydration systems are essential for high yield synthesis of organic carbonates. A chemical dehydrating agent

can enhance the yield of DMC by disrupting the thermodynamic limitation, thereby shifting the equilibrium toward higher DMC yields. Among several strategies reported, simple dehydration of methanol before the reaction (Sakakura et al. 1998), the use of organic molecules as a dehydrating agent (Sakakura et al. 2000), incorporation of a dehydration unit filled with inorganic (zeolite) materials (Choi et al. 2002), and the use of a membrane reactor for selective water removal (Li and Zhong 2003). have been attempted. Using a membrane reactor to shift the equilibrium by removing water in situ, 10% methanol conversion and 96% DMC selectivity have been achieved (Li and Zhong 2003). Dehydrating additives like trimethyl orthoacetate, and a dehydrating tube packed with molecular sieves have proven that the equilibrium yield can indeed be shifted thereby improving the yield of DMC (Tomishige and Kunimori 2002).

8. SUMMARY

Carbon dioxide is well known to be a stable molecule. It lays in an energy well, and is, together with water, the end product in any combustion process, either chemical or biological. Thus, utilization of CO_2 for the production of fine chemicals is severely limited by the reaction equilibrium in most cases. Nevertheless, use of CO_2 as a reactant is thermodynamically possible in several reactions involving its reduction or its incorporation into other compounds. Reactions in which carbon dioxide is involved can be categorized into two types, namely low energy reactions (when CO_2 is incorporated as the entire molecule into an organic or inorganic substrate) and high energy reactions (when there is a reduction of the carbon atom oxidation state from 4 down to minimum −4). As carbon in CO_2 is in the oxidised form, many of the resulting reactions are reductions, either through the addition of hydrogen or electrons. The exceptions are CO_2 insertion reactions where there is no overall change in oxidation state.

While CO_2 has low chemical activity, it is possible to activate it towards reaction by using catalysts and proper process conditions (temperature and pressure). CO_2 conversion into useful chemicals and fuels can be driven by homogeneous, heterogeneous and enzymatic catalytic systems. Both homogeneous and heterogeneous catalysts possess advantages and disadvantages. Homogenous catalysts typically show higher catalytic activity and selectivity than heterogeneous catalysts under mild conditions. Heterogeneous catalysts, however, have superior stability and durability and provide simplicity in separation, handling and reactor design, and thus are preferred in CO_2 conversion. The reusability of heterogeneous catalysts can reduce the production cost especially for large-scale industrial processes. Combining the unique properties and benefits of homogeneous and heterogeneous catalysts are of great significance. This presents an interesting challenge and opportunities to explore and develop new concepts and technologies for chemical industries and research.

Although CO_2 conversion by heterogeneous catalytic routes is still limited, efforts have been made to synthesize e.g. dimethyl carbonate, formic acid, and synthesis gas (CO, H_2), synthetic natural gas as well as methanol via CO_2 hydrogenation. Hydrogen and methane are two high-energy materials, which can be used for the large-scale transformation of carbon dioxide. Since CO_2 is just a carbon

source without hydrogen, clean, sustainable and cheap sources of hydrogen should be developed for viable CO_2 utilization to chemicals or energy products.

Much research has been conducted in the field of chemical CO_2 utilization but a number of barriers (mainly technical and economic) still exist and slow down the advancement of CO_2 utilization processes. Therefore, more research is necessary towards effective chemical CO_2 utilization breakthroughs.

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