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Carbon dioxide utilization for methane production: A thermodynamic analysis

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ABSTRACT

Thermodynamic equilibrium analysis of carbon dioxide hydrogenation to methane and side reactions was performed using constrained Gibbs free energy minimization. The applicability for upgrading of CO_2-rich natural gas in particular was investigated as a case study. The thermodynamics simulation to obtain equilibrium CO_2 conversions and product compositions was performed in the range $T=200–550\ °C$, $P=1–30$ bar and $H_2/CO_2=1–8$ mol/mol. Over the range of practical interest, the carbon dioxide conversion is very high, while the competitive reverse water gas shift is relatively insignificant. Consequently, the equilibrium selectivity to methane is also very high. Below 300 °C, in most cases, complete conversion of CO_2 to methane with very high selectivity is thermodynamically feasible. The approach to equilibrium analysis of experimental data suggested that over Ni-based catalysts CO_2 methanation could occur via reverse water-gas-shift reaction.

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1. Introduction

The global warming due to the increase of the atmospheric concentration of greenhouse gases (GHG) such as carbon dioxide is considered to be one of the greatest environmental threats of our times (Wang and Gong, 2011). Anthropogenic carbon dioxide emissions come from combustion of carbon containing fuels and some chemical processing. The reduction of emission and/or the capture and utilization of CO_2 from the emission sources have many benefits from environmental and economical viewpoints.

Carbon dioxide is an attractive C_1 building block in organic syntheses as it is a highly functional, abundant, renewable carbon source and an environmentally friendly chemical reagent (Arakawa et al., 2001; Aresta and Dibenedetto, 2007; Jessop et al., 2004; Omae, 2006; Sakakura et al., 2007; Sakakura and Kohno, 2009). Currently, the utilization of CO_2 as chemical feedstock is limited to a few processes such as the synthesis of urea (for nitrogen fertilizers and plastics), salicylic acid (a pharmaceutical ingredient), and polycarbonates (for plastics) (Centi and Perathoner, 2009). The potential of chemical fixation of carbon dioxide in CO_2 emission reduction, however, is realized when used in production of bulk chemicals and fuels through heterogeneous catalytic reactions provided the green (e.g. renewable) hydrogen and energy sources are available (Tahriri Zangeneh et al., 2011).

Catalytic hydrogenation of carbon dioxide to methane, also called the Sabatier reaction, has been known since the beginning of the 20th century and is an important process of fundamental academic interest with potential commercial application (Takht Ravanchi and Sahebdelfar, 2014; Wang and Gong, 2011).

$$CO_2 + 4H_2 \Leftrightarrow CH_4 + 2H_2O \quad \Delta H_{298}^0 = -165\ \text{kJ/mol} \tag{1}$$
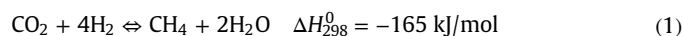
The water constituent in the resulting synthetic natural gas (SNG) can be easily separated by condensation and a complementary conventional drying process. The reaction is highly exothermic and is accompanied by volume reduction. The heat of reaction could be used for pre-heating of the feed when CO_2 concentration is sufficiently high.

Other competitive hydrogenation reactions can occur according to the catalyst employed and operating conditions including reverse water-gas shift (RWGS) reaction.

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \quad \Delta H_{298}^0 = +41\ \text{kJ/mol} \tag{2}$$
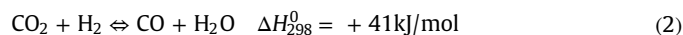
and the formation of higher hydrocarbons, methanol and higher alcohols and formic acid.

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Nomenclature

a_{ik}	number of atoms of the kth element in each molecular species
A_k	total mass of the kth element in the feed
$\hat{f}_i$	fugacity of the species i
G^t	total Gibbs free energy (J)
$\bar{G}_i$	partial molar Gibbs free energy of the species i (J mol^{-1})
G_i^0	standard free energy of the species i (J)
G^0_{fi}	standard Gibbs free energy of formation of the species i (J)
$\bar{G}_{C(g)}$	partial molar Gibbs free energy of gaseous carbon (J mol^{-1})
$\bar{G}_{C(S)}$	partial molar Gibbs free energy of solid carbon (J mol^{-1})
$G_{C(S)}$	molar Gibbs free energy of solid carbon (J mol^{-1})
$G^0_{fC(S)}$	standard Gibbs function of formation of solid carbon
K_{e1}	equilibrium constant of reaction (1) at reaction

	temperature (bar^{-2})
K_{e2}	equilibrium constant of reaction (2) at reaction temperature (dimensionless)
N	number of components
n_i	moles of species i (mol)
P	system pressure (bar)
P^0	pressure of the standard state (1 bar) (bar)
R	universal gas constant (J mol^{-1} K^{-1})
T	system temperature (K)
y_i	mole fraction of species i

Greek symbols

μ_i	chemical potential of species i (J mol^{-1})
$\hat{\varphi}_i$	fugacity coefficient of the species i
λ_k	Lagrange multiplier
η	approach to equilibrium (dimensionless)

Coke formation is possible though methane decomposition.

$$CH_4 \Leftrightarrow C + 2H_2 \quad \Delta H^0_{298} = +75 \text{ kJ/mol} \tag{3}$$
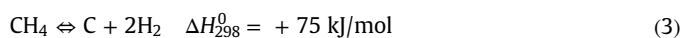
and carbon monoxide disproportionation (Boudouard reaction).

$$2CO \Leftrightarrow C + CO_2 \quad \Delta H^0_{298} = -172 \text{ kJ/mol} \tag{4}$$
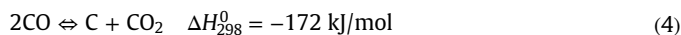
among others. Thermodynamically, reactions (2) and (3) are favored at higher temperatures while reactions (2) and (4) are favored at lower temperatures.

The conversion of carbon dioxide to methane is not economically feasible due to the higher price of hydrogen compared to carbon dioxide. However, when integrated in gas processing, its economy could be improved. The methanation of carbon dioxide has some potential applications including upgrading of low quality natural gases containing large amounts of CO_2 (Table 1) and in temporary energy storage in high energy methane molecules.

The low-quality syngas produced by gasification (partial oxidation) of biomass or in combination of waste plastics, comprising a mixture of carbon dioxide, carbon monoxide, hydrogen, water and some methane (Arena, 2012), could be used to produce renewable SNG as substitute for fossil fuels in heating (Heidenreich and Foscolo, 2015). Mass conversions, energetic and exergetic efficiencies showed that SNG production is one of the most efficient routes in biomass to biofuels via gasification (Sues et al., 2010).

Unlike most carbon dioxide reactions, CO_2 methanation is thermodynamically favorable ($\Delta G^0_{298} = -130.8$ kJ/mol); however, selectively bypassing less reduced products (e.g. CO and CH_3OH) via an eight-electron process makes this catalysis difficult and the state of art is less advanced than that for hydrogenation of CO_2 to CO and methanol (Heyn, 2003).

Compared to methanation of carbon monoxide being operated at 300 °C and 25 bar in commercial practice, methanation of carbon dioxide may need more severe operating conditions, although the reactions could be linked by water-gas shift reaction (Vesselli et al., 2011). In general, the same catalysts are active for methanation of both CO and CO_2, although CO_2 gives a higher selectivity for CH_4 (Peebles et al., 1983). Many studies have been focused on using Group VIII B noble metals such as, Ru, Pt, Pd and Rh supported on various metal oxides such as SiO_2, Al_2O_3, ZrO_2, TiO_2, CeO_2 as base catalyst for CO_2 methanation (Abu Bakar et al., 2010; Nurunnabi et al., 2008; Panagiotopoulou et al., 2008; Safariamin et al., 2009; Zamani et al., 2014). The high price of noble metals limits their application in commercial practice. Nevertheless, researchers still need to explore the use of various inexpensive transition metals such as Mn (Abu Bakar et al., 2010), Ni (Abu Bakar et al., 2009a; Daniela et al., 2012; Shohei et al., 2012; Wang and Lu, 1998; Zhihong et al., 2012), Cu (Peng et al., 2010; Qi et al.,

Table 1
Composition of natural gas reservoirs in some parts of the world in volume percent basis.

Component	Reservoir					
	Lacq[a] (France)	Uch[a] (Pakistan)	Uthmaniyah[a] (Saudi Arabia)	Ardjuna[a] (Indonesia)	Eurofisk[b] (Norway)	Coal Gas[b,c]
CH_4	69.0	27.3	55.5	65.7	85.2	19.1
C_2H_6	3.0	0.7	18.0	8.5	8.6	1.7
C_3H_8	0.9	0.3	9.8	14.5	2.9	–
C_4H_{10}	0.5	0.3	4.5	5.1	0.9	–
C_{5+}	0.5	–	1.6	0.8	–	–
N_2	1.5	25.2	0.2	1.3	0.5	6.0
H_2S	15.3	–	1.5	–	–	–
CO_2	9.3	46.2	8.9	4.1	1.7	3.6
H_2	–	–	–	–	–	51.0
CO	–	–	–	–	–	14.6

[a] Data obtained from Shimekit and Mukhtar (2012).
[b] Data obtained from Crabtree (1995).
[c] For comparison.