



## Review

Catalytic carbon dioxide hydrogenation to methane: A review of recent studies<sup>☆</sup>Xiong Su<sup>a,1</sup>, Jinghua Xu<sup>a,b,1</sup>, Binglian Liang<sup>a</sup>, Hongmin Duan<sup>a</sup>, Baolin Hou<sup>a</sup>, Yanqiang Huang<sup>a,\*</sup><sup>a</sup> State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China<sup>b</sup> Dalian Institute of Standardization, Dalian 116023, Liaoning, China

## ARTICLE INFO

## Article history:

Received 29 January 2016

Revised 23 February 2016

Accepted 26 February 2016

Available online 10 March 2016

## Keywords:

Methanation

Carbon dioxide

Hydrogenation

Ni catalyst

Ru catalyst

## ABSTRACT

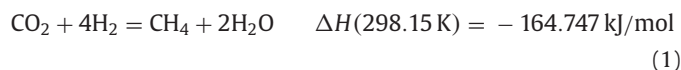
Recently, various efforts have been put forward on the development of technologies for the synthesis of methane from CO<sub>2</sub> and H<sub>2</sub>, since it can offer a solution for renewable H<sub>2</sub> storage and transportation. In parallel, this reaction is considered to be a critical step in reclaiming oxygen within a closed cycle. Over the years, extensive fundamental research works on CO<sub>2</sub> methanation have been investigated and reported in the literatures. In this updated review, we present a comprehensive overview of recent publications during the last 3 years. Various aspects on this reaction system are described in detail, such as thermodynamic considerations, catalyst innovations, the influence of reaction conditions, overall catalytic performance, and reaction mechanism. Finally, the future development of CO<sub>2</sub> methanation is discussed.

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## 1. Introduction

Power-to-gas processes are considered as a possible and interesting solution to integrate renewable resources, such as wind and solar energy, into the current energy mix efficiently. This strategy aims at using power to convert water into hydrogen via electrolysis [1], and storing the obtained fuel until the implementation in a high power consumption period that would reconvert it into electricity [2]. Thanks to the Sabatier reaction [3], a more practical route that provides energy in a more convenient and safer way, i.e., toward the conversion of electrochemically generated hydrogen into methane, is achievable. Methane, the dominant component of synthetic natural gas (SNG), has several advantages over hydrogen, e.g., higher volumetric energy content and safety insurance. Meanwhile, there is no limit for SNG admittance into the gas grid [4]. In addition, researches on the application of Sabatier reaction are also conducted for the use of reclaiming oxygen in International Space Station, where the oxygen resource in the exhalant CO<sub>2</sub> from breathing can be transformed into precious water for as-

tronaut life-support system [5].



As represented by Eq. (1), CO<sub>2</sub> methanation is a highly exothermic reaction. However, it is difficult to achieve because of the high kinetic barriers of the eight-electron reduction process. In recent years, considerable works have been done with the aim to develop thermally stable catalysts with high activities at low temperatures, as demonstrated by the burgeoning number of academic publications (Fig. 1). Among them, Ni-based catalysts have been widely investigated for industrial purposes due to their low cost and ease of availability. However, Ni catalyst may be deactivated even at low temperature due to the sintering of Ni particles, formation of mobile nickel sub-carbonyls, or formation of carbon deposits [6,7]. Various strategies have been attempted to enhance the stability and catalytic activity of the Ni-based catalysts, such as appending additives to the catalyst systems, altering the type of supports and preparation methods. Ru-based catalysts, by contrast, have been reported to be the most stable one when operated over a wide range of conditions [8,9]. Meanwhile, other active metals, such as Rh, Co, Fe, and so forth on various supports have been also reported to be effective methanation catalysts. Therefore, the present review attempts to provide current understanding of the updated catalytic performance and further insight into the reaction mechanism over heterogeneous catalysts between 2013 and 2015, as well as the future prospects of CO<sub>2</sub> methanation.

<sup>☆</sup> This work was supported by the National Natural Science Foundation of China (Nos. 21103173, 21476226 and 21506204), the Key Research Programme of the CAS (KGZD-EW-T05), the Youth Innovation Promotion Association of the CAS and DICP Fundamental Research Program for Clean Energy (DICPM201307).

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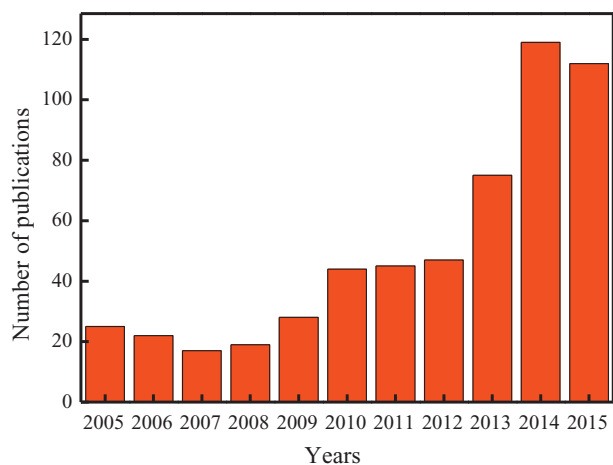


Fig. 1. Number of publications, dealing with CO<sub>2</sub> methanation versus years (2005–2015), extracted from ISI Web of Science (Thomson Reuters) database retrieved using the keywords “CO<sub>2</sub> methanation”.

## 2. Thermodynamic analysis

Thermodynamics is useful in the assessment of processes occurring in the methanation system and predicting the optimal reaction condition [10–13]. The effects of reaction temperature, pressure, H<sub>2</sub>/CO<sub>x</sub> ratio, and the addition of other reactants (H<sub>2</sub>O, CH<sub>4</sub>, O<sub>2</sub>, et al.) are the most commonly discussed conditions on the influence of the CO<sub>x</sub> conversion, CH<sub>4</sub> selectivity, and carbon deposition. Recently, some thermodynamic analysis on the methanation process has been done. Greyson et al. [14] have evaluated the thermodynamic equilibrium compositions of the CO methanation system based on the following three independent reactions: (1) CO + 3H<sub>2</sub> = CH<sub>4</sub> + H<sub>2</sub>O; (2) CO + H<sub>2</sub>O = CO<sub>2</sub> + H<sub>2</sub>; (3) 2CO = C + CO<sub>2</sub>. In the work of Beuls et al. [15], the authors implemented a thermodynamic calculation of CO<sub>2</sub> methanation over the designed Rh/γ-Al<sub>2</sub>O<sub>3</sub> catalyst under given reaction conditions. Gao and co-workers [16] have systematically conducted a thermodynamic analysis of CO<sub>x</sub> methanation by applying the total Gibbs free energy minimization method. They have also compared the thermodynamic calculations of the methanation processes with the experimental results obtained over two commercialized methanation catalysts.

From the already reported works, it seems that the methanation process is favored at low reaction temperature, high pressure and high H<sub>2</sub>/CO<sub>x</sub> ratio. In the present work, we systematically discussed the thermodynamics of the CO<sub>2</sub> methanation process to gain a better cognition on the Sabatier reaction. The thermodynamic analysis of CO<sub>2</sub> hydrogenation was performed using the Gibbs reactor model available from the HSC (enthalpy, entropy and heat capacity) Chemistry. A comprehensive description on the hydrogenation process is conducted starting from CO<sub>2</sub> and H<sub>2</sub> raw materials with six kinds of possible products of CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O and C deposit. There are three independent reactions for the methanation process, as listed in Eq. (1) and the following two equations.



Based on these reactions, the equilibrium composition of different components was obtained in the product under a constant pressure of 1 bar with respect to different H<sub>2</sub>/CO<sub>2</sub> ratios and temperatures. As shown in Fig. 2, all the results are presented in terms of the mole equilibrium fraction of each component. Only the major components are taken into consideration in the present study and the species presented in a trace amount might be neglected. From these data, we can draw a conclusion that, as the reaction

temperature increases to a degree higher than 600 °C, CO derived from the reverse water gas shift reaction (Eq. 3) dominates the product in the CO<sub>2</sub> hydrogenation process, while CH<sub>4</sub> is disfavored. Meanwhile, the formation of carbon deposits can be prohibited to a great extent. Increasing the H<sub>2</sub>/CO<sub>2</sub> ratio has a positive effect on the production of CH<sub>4</sub>. All these trends and calculations with the reaction condition variations consistent well with the results reported by Swapnesh et al. [10] and Miguel et al. [11].

From the perspective of thermodynamic equilibrium, in order to gain a better CH<sub>4</sub> yield from CO<sub>2</sub> and H<sub>2</sub>, the reaction pathways of Eqs. 2 and 3 should be avoided, i.e., the reaction conditions of H<sub>2</sub>/CO<sub>2</sub> ratios and temperatures are better to be controlled as far away from the optimal range of the formation of CO and carbon deposit. The most effective way toward the production of methane is to explore effective catalysts which can efficiently accelerate the reaction rate of CO<sub>2</sub> methanation process and prohibit the unnecessary reactions of Eqs. 2 and 3 simultaneously. Such a strategy may keep the whole reaction system away from the region of thermodynamic equilibrium, realize the maximization of methane yield, and determine the optimal operating temperature range for the methanation reaction preliminarily.

As mentioned above, the thermodynamic analysis of the CO<sub>2</sub> hydrogenation can be confined in a single process of CO<sub>2</sub> methanation as revealed by Eq. 1. Fig. 3 shows the equilibrium conversion of H<sub>2</sub> in the CO<sub>2</sub> methanation reactions when operated in the temperature range of 100–700 °C. In the case of controlling the consumption of H<sub>2</sub> to a degree of up to 98% of its conversion, the reaction system should be restricted to the lower temperature region. For instance, with the CO<sub>2</sub> hydrogenation process conducted at a fitted H<sub>2</sub>/CO<sub>2</sub> ratio of 4, which corresponds to a desired stoichiometry ratio for the methanation reaction, the optimized operation temperature should be not higher than 230 °C. Similarly, for the case of reaction condition with the H<sub>2</sub>/CO<sub>2</sub> ratio of 3, the optimized operation temperature should be not higher than 270 °C.

CO<sub>2</sub> methanation is a reversible reaction and the reverse reaction is called steam reforming of methane. If this reaction was conducted under adiabatic condition, there exists a maximum theoretical temperature when the reaction arrives at its thermodynamic equilibrium. The adiabatic temperature rise of the CO<sub>2</sub> methanation reaction systems under various temperatures and a constant pressure of 1 bar was calculated and shown in Fig. 4. It is observed that the adiabatic temperature rise of the practical methanation reaction system declines with increasing the real reaction temperature. More specifically, in the case of a H<sub>2</sub>/CO<sub>2</sub> stoichiometry ratio of 4, when the reaction temperature is fixed at 595 °C, the adiabatic temperature rise of the reaction system is 0 °C. This implies that the highest temperature of the reaction system can reach up to 595 °C without providing external heating. In similar situations, the highest temperature of the reaction systems with varied H<sub>2</sub>/CO<sub>2</sub> ratios of 3.5, 3.0, 2.0 and 1.0 are calculated to be 570 °C, 550 °C, 470 °C, and 300 °C, respectively. If we want to keep the methanation reaction system without external heat input, the real working conditions of the reaction systems should be lower than the temperatures of these highest values as mentioned above.

## 3. Discussion on catalytic features

In the past decades, extensive research works for CO<sub>2</sub> hydrogenation to methane have been reported, aiming at the designing of active catalysts, such as supported Ni, Ru, Rh, Pd Co, Fe, Cu. Herein, the investigations of these catalysts since 2013 have been described in detail. A number of works, focusing on the development of promising catalysts, are highlighted.

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