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Thermodynamic analysis of methane dry reforming: Effect of the catalyst particle size on carbon formation

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ABSTRACT

The effect of catalyst particle size on thermodynamic equilibrium of methane dry reforming and carbon formation has been studied through the Gibbs free energy minimization method taking into account the deviation of carbon formed from graphite Gibbs energy and its dependence on catalyst particle size. Methane and CO_2 conversions are maximized at low pressure and high temperature, and a molar H_2/CO ratio of 1 is obtained at 1100–1200 K and 5–10 bar. Carbon formation was found to increase with particle diameter, and carbon presence was noticed at conditions of high pressure/low temperature and high temperature/low pressure. Optimal operating conditions were found to be close to carbon limits, highlighting the need for active metal particle size to be less than 5–6 nm to minimize coking. CO was identified as the precursor for carbon at low temperature, while CH_4 was found to be the main precursor at high temperature.
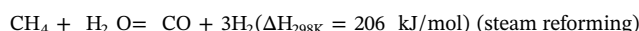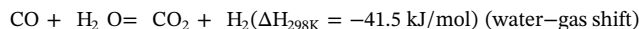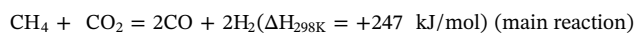
1. Introduction

The ongoing depletion of fossil fuels is driving the world to search for alternative, sustainable and renewable sources of energy [1] to meet its ever increasing energy demand [2]. Furthermore, global warming and environmental consequences from the continuously growing economies, in addition to environmental regulations, require new energy sources to produce less pollutants such as SO_x, NO_x and greenhouse gases. In parallel, the population growth has caused waste to be generated at a higher rate [3] and frequently mismanaged [4,5]. Landfill is a widely used method of municipal solid waste disposal, especially in developing countries such as Lebanon [5], and large amounts of greenhouse gases, especially carbon dioxide and methane, are produced in landfills.
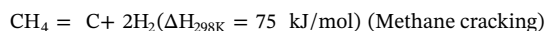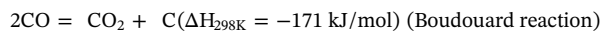
Hydrogen is a promising alternative fuel due to its high efficiency and clean combustion [6]. It is also attractive as a renewable energy source since it can be produced from biomass, water and solar energy [7]. Steam reforming has been the most common process to produce hydrogen from hydrocarbon feedstock, especially methane from natural gas, through further processing of the syngas product, essentially composed of hydrogen, carbon monoxide, CO_2 and water. Traditionally, ammonia synthesis has been the primary consumer of syngas [8]. However, more recent developments in the field of hydrocarbon reforming allowed for a better control of syngas composition, making it a very desirable feedstock for gas to liquid applications. Recently, it has

been of interest to use biogas from landfills or anaerobic digestors as a feedstock for syngas production through the dry reforming process, both due to the expected syngas H_2/CO ratio being close to unity, which is suitable for gas-to-liquid applications and Fischer-Tropsch synthesis [9,10], and due to the possibility of recycling two greenhouse gases, methane and CO_2, into useful products.

The main reactions governing the process are as follows:

$CH_4 + CO_2 = 2CO + 2H_2 (\Delta H_{298K} = +247 \text{ kJ/mol})$ (main reaction)

$CO + H_2O = CO_2 + H_2 (\Delta H_{298K} = -41.5 \text{ kJ/mol})$ (water−gas shift)

$CH_4 + H_2O = CO + 3H_2 (\Delta H_{298K} = 206 \text{ kJ/mol})$ (steam reforming)

In addition to the carbon formation reactions

$2CO = CO_2 + C (\Delta H_{298K} = -171 \text{ kJ/mol})$ (Boudouard reaction)

$CH_4 = C + 2H_2 (\Delta H_{298K} = 75 \text{ kJ/mol})$ (Methane cracking)

For more comprehensive set of possible reaction see the work of Nikoo and Amin [11].

The industrial application of the dry reforming process, however, has been heavily hindered by the performance of catalysts [12–16]. Traditional, nickel-based catalysts used in reforming technologies are cheap and active, but are prone to deactivation by sintering and carbon deposition [17]. This problem is more severe in the case of dry reforming, where the endothermic nature of the reaction requires high

operating temperatures. The increased presence of carbon in the feed gas as compared to steam reforming or dry reforming, in addition to the elevated temperatures, causes a significant amount of carbon to form on the catalyst, leading to quick deactivation [18]. Sintering of the nickel particles during operation leads to a loss of dispersion, ultimately leading to catalyst deactivation and increased carbon formation [19]: Carbon layers that grow from nuclei on step sites on the nickel particle are stable above 80 atoms in diameter (approximately 6 nm), meaning that larger particles are more likely to yield carbon. Noble metals, such as ruthenium or rhodium, are less prone to coking and have a high dispersion [20,21], but are very expensive and hence their use is limited.

It is imperative to model the reactions and carbon formation in order to decide on the optimal operating conditions for the reforming process. The first indication to the feasibility of the process is a thermodynamic evaluation of the equilibrium conditions to estimate the expected conversion and carbon formation. This can be done through the computation of the equilibrium constants based on standard ΔH and ΔG values [22,23], entropy maximization calculations [24] or Gibbs energy minimization routines [6,11,25–30].The Gibbs minimization method has been widely used due to its simplicity and its ability to compute equilibrium compositions even for systems where the reaction pathways are not known. Challiwala et al. [28] noted that many studies assumed the gas phase behaved as an ideal gas, while the group's work, amongst others cited above, use non-ideal equations of state to model the non-ideal gas-phase such as the Peng-Robinson and Soave-Redlich-Kwong equations of state.

The majority of thermodynamic studies in reforming have accounted for carbon formation tendencies with the assumption that the carbon species formed is graphite, which has a zero standard Gibbs energy of formation and negligible dependence of fugacity on operating conditions, [11,28,31], with the exception of Atashi et al.[29] and Ayodele et al. [32] who have ignored carbon formation within the dry reforming process in their simulations, and Nematollahi et al. [33] who incorporated the activity of graphite into their model. However, practical experience has shown that three general types of carbonaceous species can be distinguished on a used reforming catalyst based on temperature programmed hydrogenation (TPH) studies [34]: C_α refers to surface carbide that can be hydrogenated below 323 K, C_β (or amorphous carbon) can be hydrogenated between 373 and 573 K, while C_γ (graphitic carbon) is only hydrogenated above 673 K. Electron microscopy imaging shows that filamentous carbon 'whiskers' often grow from nickel and non-noble active metal particles, and many studies have noted that carbon filaments, and carbon deposits on reforming catalysts in general, deviate from graphite thermodynamics. Whisker carbon is the most dangerous form of carbon growing on a catalyst due to its high strength. Whisker growth can cause pore damage and detachment of active metal particles from the support, leading to dusting and increased pressure drop, hot bands and eventually plant shutdown [35]. It has been observed that the Boudouard reaction and methane cracking reactions have lower equilibrium constants than graphite formation [8,36,37].

Alstrup [38] studied the formation of carbon filaments on Ni, Ni-Cu and Ni-Fe catalysts and found deviations from graphite deposition thermodynamics that are dependent on particle size, irrespective of the (non-noble) active metal. In the same study, the author combined his finding to those of Rostrup-Nielsen [39] and proposed an expression for the deviation from the Gibbs free energy of graphite in function of the size of the largest particle catalyzing filament growth: ΔG_c^{dev} (kJ/mol) $= 2.6 + 93/d$ (nm).

To the knowledge of the authors, such a deviation has not been considered in a thermodynamic analysis of a reforming process prior to this work. The practical implications of this deviation are twofold: On one hand, there is some uncertainty around the present carbon limits calculated in thermodynamic studies. On the other hand, the carbon limits in a reformer are a function of the catalyst particle size: in other terms, the age of the bed, and consequently the severity of sintering in the catalyst batch, affects the carbon limits and it is then possible to define dynamic carbon limits from a semi-empirical approach. By incorporating the deviation parameter, this study shows the impact of non-graphite behavior and bed aging on the main parameters of the dry reforming process. The intricate reaction mechanism on the catalyst surface, in addition to the added complexity of modeling carbon whisker formation on a catalyst particle makes it very difficult to use a set of chemical reactions as a basis for thermodynamic equilibrium [40]. The Gibbs energy minimization method was chosen to model the chemical equilibrium of the process while incorporating the deviation Gibbs energy into the model while avoiding the difficulties of working with multiphase chemical reactions where the thermodynamic and kinetic constants are not well-defined.

2. Modeling

The Gibbs energy minimization problem is treated as an optimization problem, with the objective being to minimize the total Gibbs energy of a system that can contain CH_4, CO_2, CO, H_2, H_2O and solid carbon, subject to atomic species conservation constraints. The pressure and temperature are fixed, as it is assumed that the reaction takes place in a heated reactor.

2.1. Objective function

In a given multicomponent system, the total Gibbs energy is given by:

$$G^T = \sum_{i=1}^{N} n_i \left(\Delta G_{f_i}^0 + RT \ln \frac{\overline{f_i}}{f_i^0} \right) \tag{1}$$

With the chemical potential, μ_i, defined as:

$$\mu_i = \Delta G_{f_i}^0 + RT \ln \frac{\overline{f_i}}{f_i^0} \tag{2}$$

$$G^T = \sum_{i=1}^{N} n_i \mu_i \tag{3}$$

The partial fugacity and standard state fugacities for every component is given respectively by:

$$\overline{f_i} = y_i \phi_i P \tag{4}$$