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Evaluation of the thermodynamic equilibrium of the autothermal reforming of dimethyl ether

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ABSTRACT

In the present study, a thermodynamic analysis of the autothermal reforming of dimethyl ether (DME) for the production of hydrogen was carried out. The results clearly indicated that the carbon formation behavior, the boundary conditions between coke-free and coking regions, and the equilibrium composition of the reformat were dependent on the steam/DME ratio, O₂/DME ratio, temperature, and pressure of the system. For instance, carbon formation was effectively suppressed as the steam/DME ratio increased from 0 to 5, the O₂/DME ratio increased from 0 to 3, or the temperature rose from 100 to 1000 °C. In contrast, carbon formation was enhanced as the pressure was increased from 0.5 to 10 atm. The boundary temperature of coke-free operation decreased with an increase in the steam/DME and O₂/DME ratios. More specifically, at a steam/DME ratio of 3–5 and an O₂/DME ratio of 0–3, the boundary temperature ranged from 50 to 280 °C (when CH₄ formation was promoted) and 380 to 670 °C (when CH₄ formation was suppressed), respectively. Furthermore, at elevated temperatures, H₂ and CO formations were enhanced, and CH₄ formation was inhibited. The addition of steam enhanced H₂ production while reducing CO formation. On the contrary, an increase in the O₂/DME ratio reduced H₂ production while enhancing CO formation. Interestingly, the desired temperature for thermo-neutral condition, in which energy consumption was zero, can be achieved by correctly controlling the O₂/DME and steam/DME ratios.

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1. Introduction

Global warming is an important issue due to its effects on the environment and human life [1,2]. Carbon dioxide (CO₂) is the principal greenhouse gas, and CO₂ emissions are derived primarily from the burning of fossil fuels for transportation (vehicles) and the generation of electricity (power plants). Due to global warming threat and the limited supply and rising demand for fossil fuels, alternative energy sources are

currently being actively developed. A sustainable solution to the energy crisis must include the generation of energy from renewable resources and a reduction in both pollution emissions and gross consumption of raw materials.

Hydrogen (H₂) is a promising energy carrier because it can be produced via environmentally benign methods. For instance, biomass, especially agriculture wastes [3,4], and water can react to produce hydrogen gas. Hydrogen is an important reactant used in the oil refinery industry and the

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manufacturing of various chemicals. Mixed with natural gas, hydrogen can be used to run combustion engines [5]. As an energy carrier, hydrogen can efficiently and cleanly be used to produce electricity by electrochemical reactions in fuel cells [6–8]. Several types of fuel cells have been developed, including proton-exchange-membrane fuel cells (PEMFC), solid-oxide fuel cells (SOFC), and molten carbonate fuel cells (MCFC) [6,7], either for mobile or stationary applications. The reforming of hydrocarbons is a well-known technology for hydrogen production. Typical hydrocarbon reforming techniques are steam reforming (SR), partial oxidation (PO), and autothermal reforming (ATR) [9,10]; in fact, ATR is considered to be the most energetically efficient and cost-effective reforming method.

As a renewable energy source, biomass and biomass-derived fuels such as bioethanol [11], biogas [12–14], methanol [15] and dimethyl ether (DME) [10,16] have attracted considerable attention as eco-friendly fuels because they are CO₂-neutral. Due to its high hydrogen to carbon ratio and high energy density, DME is a promising candidate as a source of hydrogen via the reforming process. DME is preferable to methanol (MeOH) because it is non-toxic and non-corrosive. In addition, DME (>180 °C) [10,16] can be catalytically reformed at a lower temperature than ethanol (>300 °C) [16] and methane (>700 °C) [16–18]. DME has remarkable potential for use in automotive fuels, generation of electric power, and domestic applications such as heating and cooking. Like LPG, DME is a gas at normal temperature and pressure, and can readily be transformed into a liquid when it is subjected to modest pressure or cooling. As a result, DME can be easily stored and transported. Moreover, the infrastructure used for LPG distribution can be readily adapted to DME due to their similar physical properties. Lastly, thanks to its high oxygen content, ultra clean combustion, and lack of noxious compounds such as sulfur, DME is a promising versatile alternative to other clean, renewable, low-carbon fuels.

Numerous studies on the catalytic production of hydrogen from DME SR, PO, and ATR have been conducted. Novel DME-reforming catalysts have been developed to improve the activity, stability, and selectivity of the reaction for practical applications. In general, solid acids coupled to Cu [19–21], Ni [22–24], or Pd-based [25] are used in DME catalytic reforming processes. Indeed, Cu-based catalyst has recently attracted wide interest because of its cost effectiveness [26–28]. The durability of a catalyst is an important factor affecting commercialization, and carbon (coke) formation and metal sintering have a significant effect on catalyst deactivation. Of course, if the reforming process is carried out under appropriate conditions, deactivation can effectively be suppressed [29]. In several studies, the thermodynamic equilibrium of various reforming processes such as MeOH SR [30–32], ethanol SR [32], methane SR, dry reforming [33], propane SR [34,35] and glycerol SR [36,37] has been evaluated and used to avoid coke formation and optimize the quality of the reformat. Recently, we reported the thermodynamic yield of H₂ and carbon content of DME SR [38]. However, further investigation into the carbon formation behavior and the boundary conditions between coke-free and coking regions in the cases of DME SR, PO, and ATR must be conducted to obtain useful information for the design of catalysts and the optimization of reforming conditions.

In the present study, the thermodynamic equilibrium of DME ATR, SR, and PO was examined. The effect of the steam to DME ratio (steam/DME = 0–5), oxygen to DME ratio (O₂/DME = 0–3), reforming temperature (100–1000 °C), and operating pressure (0.5–10 atm) on the boundary conditions, carbon formation, DME conversion, and gaseous chemical composition will be evaluated by applying a Gibbs free energy minimization technique.

2. Methodology

2.1. Minimization of Gibbs free energy

Gibbs free energy is the most commonly used thermodynamic function for the identification of equilibrium conditions. The minimization of the total Gibbs free energy of a system is an appropriate method for calculating the equilibrium composition of reactive systems [39]. The total Gibbs free energy is equal to the sum of the free energy of the *i*th species:

$$G^t = \sum_{i=1}^N n_i \bar{G}_i = \sum_{i=1}^N n_i \mu_i = \sum_{i=1}^N n_i G_i^0 + R(T + 273.15) \sum_{i=1}^N n_i \ln \frac{\hat{f}_i}{f_i^0}$$

where G^t is the total Gibbs free energy, \bar{G}_i is the partial molar Gibbs free energy of species *i*, G_i^0 is the standard Gibbs free energy, μ_i is the chemical potential, R is the molar gas constant, T is the temperature of the system, \hat{f}_i is the fugacity of species *i*, f_i^0 is the standard-state fugacity of species *i*, and n_i is the number of moles of the *i*th species. For gas phase equilibria, $\hat{f}_i = y_i \phi_i P$, $f_i^0 = P^0$, and $G_i^0 = \Delta G_{f_i}^0$. Using the Lagrange multiplier method, the minimization function of the Gibbs free energy of each gaseous species and that of the Gibbs free energy of the entire system can, respectively, be expressed as follows:

$$\Delta G_{f_i}^0 + R(T + 273.15) \ln \frac{y_i \phi_i P}{P^0} + \sum_k \lambda_k a_{ik} = 0,$$

$$\sum_{i=1}^N n_i \left(\Delta G_{f_i}^0 + R(T + 273.15) \ln \frac{y_i \phi_i P}{P^0} + \sum_k \lambda_k a_{ik} \right) = 0.$$

The minimum Gibbs free energy is subjected to the following equality constraint:

$$\sum_i n_i a_{ik} = A_k,$$

where $\Delta G_{f_i}^0$ is the standard Gibbs free energy of the formation of species *i*, P^0 is the pressure of the standard state (101.3 kPa), P is the pressure of the system, y_i is the mole fraction of gas species *i*, ϕ_i is the fugacity coefficient of the *i*th species, λ_k is the Lagrange multiplier, a_{ik} is the number of atoms of the *k*th element in species *i*, and A_k is the total mass of the *k*th element in the feed. When solid carbon (graphite) is included in the system, the vapor–solid phase equilibrium can be applied to the Gibbs free energy of carbon: $\bar{G}_{C(g)} = \bar{G}_{C(s)} = G_{C(s)} \cong \Delta G_{f_{C(s)}}^0 = 0$; where $\bar{G}_{C(g)}$, $\bar{G}_{C(s)}$, $G_{C(s)}$, and $\Delta G_{f_{C(s)}}^0$ are, respectively, the partial molar Gibbs free energy of gaseous carbon, of solid carbon, the molar Gibbs free energy of solid carbon, and the standard Gibbs free energy of the formation of solid carbon.

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