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Thermodynamic analysis and experimental study of hydrogen production from oxidative reforming of n-butanol

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HIGHLIGHTS

- A Gibbs free energy minimization method was applied for thermodynamic analysis.
- Experiments were carried out using Ni– and Rh–Al_2O_3 catalysts.
- Thermoneutral conditions obtained at OBR of 2.70–2.80 at 700 °C and 2.65–2.75 at 800 °C.
- The thermodynamic predictions were in good agreement with experimental results.

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ABSTRACT

A Gibbs free energy minimization method was applied to analyze the thermodynamics of hydrogen production via oxidative reforming of n-butanol. The conditions studied were a temperature range of 300–1100 °C under atmospheric pressure with steam to n-butanol molar feed ratios (SBR) ranging from 0 to 12 and oxygen to n-butanol molar feed ratios (OBR) of 0–6. The thermoneutral conditions can be obtained at OBR of 2.70–2.80 at 700 °C and 2.65–2.75 at 800 °C, respectively. The maximum hydrogen yield of 5.56 $mol/mol_{Butanol}$ can be achieved at 700 °C with SBR of 12, conditions under which carbon formation and methane generation are predicted to be relatively low. The thermodynamic predictions were in good agreement with experimental results using Ni/Al_2O_3 and Rh/Al_2O_3 catalysts, from which the reaction was studied at different SBR, OBR, and temperatures. Under atmospheric pressure at 700 °C with OBR of 2.70 and SBR of 9, the product yields from the reaction in the presence of Rh/Al_2O_3 were close to the thermodynamic values.

1. Introduction

In response to the energy crisis and environmental concerns, new energy supply technologies are being researched to utilize renewable energy sources in an efficient and environmentally-friendly manner [1]. Hydrogen is considered to be an attractive replacement for fuels among these alternative energy technologies. Hydrogen can be utilized in fuel cells for example to produce electricity at high efficiencies (40–60% depending on fuel cell type) with clean exhaust [2]. Hydrogen can be produced by coal gasification, steam and dry reforming, partial oxidation, electrolysis and thermal decomposition of water as well as fermentation processes.

Conventionally, steam reforming is applied commercially to produce hydrogen from hydrocarbons (e.g. reactions of natural gas (methane) with steam under high temperatures) for diverse applications such as ammonia and methanol production. Steam reforming is a strongly endothermic reaction ($\Delta H^\circ_{298.15} = 206.2$ and 558.3 kJ mol^{-1} for natural gas and n-butanol steam reforming respectively [3,4]), thus, in conventional steam reforming of, some of the natural gas is used to supply heat for reaction. This affects both the costs of hydrogen production and time spent during start up [5]. Oxidative reforming, in which steam reforming and exothermic partial oxidation simultaneously occur, was developed as a possible solution for reducing these costs [6]. In this process, the heat released during the partial oxidation can reduce the endothermic energy requirement for steam reforming reaction to proceed.

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While natural gas is conventionally used for commercial hydrogen production, catalytic developments over the last few decades have enabled use of increasingly heavier hydrocarbon feedstocks up to naphtha, biomass derived compounds such as bio-methanol [7–9], ethanol [10–12], glycerol [13–15], methane [16], bio-oil [17,18] and dimethyl ether [19,20] are also viewed as potential sources for hydrogen production. n-Butanol can be another choice of renewable fuel. Bio-butanol, is sometimes called biogasoline, can be derived from biomass feedstocks. Recent studies have shown that n-butanol can also be used to produce hydrogen [21–26]. However, due to complex multiple reactions in the oxidative reforming of n-butanol, the purity of the hydrogen product is affected by numerous undesirable side reactions e.g. reverse water gas shift, methanation and the Boudouard reaction (disproportionation of carbon monoxide to carbon dioxide and carbon). In order to achieve industrially acceptable production efficiencies and product purities, it is necessary to know the effect of temperatures, steam to n-butanol molar feed ratios (SBR) and oxygen to n-butanol feed ratios (OBR); on the product composition. A thermodynamics analysis of the process can be pursued to understand if the process is feasible and industrially significant.

Catalytic performance of other catalysts towards the butanol steam reforming had been experimentally studied previously by other researchers. Medrano [27] studied steam reforming of butanol using Ni/Al. It was found that Ni/Al with 28.5 wt.% gave 75% conversion, roughly, when using 14.7 ratio of SBR at 650 °C. Cai [28] studied catalytic performance of monometallic and bimetallic catalysts towards steam reforming of bio-butanol for hydrogen production at 500 °C, SBR = 3 and OBR = 1.5. The results showed that conversion of bio-butanol over bimetallic catalysts; CoPd/ZnO (97%), CoRh/ZnO (95%), CoRu/ZnO (90%), and CoIr/ZnO (84%); were higher than that of monometallic catalyst, Co/ZnO (78%). Harju [29] investigated steam reforming of n-butanol over ZrO_2 and Rh–ZrO_2 catalyst at temperature range from 500 to 700 °C. ZrO_2 gave lower conversion of butanol, compared to Rh–ZrO_2 at all temperatures. Conversion of butanol over ZrO_2 at 500, 600 and 700 °C were 50%, 82%, and 84%, respectively, while Rh–ZrO_2 gave 80% conversion of butanol at 500 °C and showed complete conversion at 600 and 700 °C.

In the present work, the thermodynamics analysis of n-butanol oxidative reforming process under various operating conditions was carried out with the aim of maximizing the hydrogen yield. The total Gibbs free energy minimization method was adopted to estimate the equilibrium composition over a range of temperatures, SBRs and OBRs at atmospheric pressure while maximizing the hydrogen yield and minimizing carbon formation. Product distribution and heat consumptions were examined under thermoneutral conditions. Experimental n-butanol oxidative reforming was also performed to check the robustness of the predictions. The experimental operating conditions of reaction temperature, SBR and OBR were selected based on the thermodynamic analyses using Ni/Al_2O_3 and Rh/Al_2O_3 (5% Ni and Rh, respectively) as catalysts.

2. Methods

2.1. Computational thermodynamic analysis

Calculation of equilibrium chemical compositions can be performed by either calculating the equilibrium constant or minimization of the total Gibbs free energy. Calculation of equilibrium chemical compositions for reactions with solid components is difficult to perform by calculation of the equilibrium constant since information of the associated chemical reactions is also required. However, by minimization of the total Gibbs free energy (which can be applied to the reacting system including condensed components and non-reacting components) it may be easily achieved. Therefore, the Gibbs free energy minimization method was chosen for this study. The total Gibbs free energy of a system is given by the sum of the partial molar Gibbs free energy of a species *i* multiplied by the number of moles of a species *i* according to Eq. (1) [11,21,30,31]:

$$G_T = \sum_{i=1}^{m} n_i G_i = \sum_{i=1}^{m} n_{ii} = \sum_{i=1}^{m} n_i G_i^\circ + RT \sum n_i \ln \frac{f_i}{f_i^\circ} \tag{1}$$

where G_T is the total Gibbs free energy. G_i is the partial molar Gibbs free energy of species *i*. G_i° is the standard Gibbs free energy of species *i*. n_i is the mole of species *i*. μ_i is the chemical potential of species *i*. f_i is the fugacity of species *i*. f_i° is the standard-state fugacity of species *i*. *R* is the molar gas constant and *T* is the temperature of system.

The assumptions for the reaction equilibrium in gas phase used were:

$$f_i = y_{ii} P \tag{2}$$

$$f_i^\circ = P^\circ \tag{3}$$

$$G_i^\circ = \Delta G_{fi}^\circ \tag{4}$$

Using Lagrange's undetermined multiplier method, the minimum Gibbs free energy of each gaseous species and that of the total system can be expressed according to Eqs. (5) and (6), respectively:

$$\Delta G_{fi}^\circ + RT \ln \frac{y_{ii} P}{P^\circ} + \sum_k \lambda_k a_{ik} = 0 \tag{5}$$

$$\sum_{i=1}^{N} n_i \left(\Delta G_{fi}^\circ + RT \ln \frac{y_{ii} P}{P^\circ} + \sum_k \lambda_k a_{ik} \right) = 0 \tag{6}$$

The constraints of elemental balance as Eq. (7):

$$\sum_{i=1}^{N} n_i a_{ik} = A_k \tag{7}$$

where G_{fi}° is the standard Gibbs function of formation of species *i*. P° is the standard-state pressure of 101.3 kPa. y_i is the gas phase mole fraction. *i* is the fugacity coefficient of species *i*. λ_k is the Lagrange multiplier. a_{ik} is the number of atoms of the element *k* present in each molecule of species *i* and A_k is the total mass of element *k* in the feed (where *i* and *k* represent compound and element in the compound, respectively). Eq. (8) illustrates the Gibbs energy of carbon when the solid carbon occurs in the system utilizing the vapor–solid equilibrium:

$$G_{C(g)} = G_{C(s)} \cong G_{fC(s)}^\circ = 0 \tag{8}$$

Substituting Eq. (1) with Eq. (5) for gaseous species and with Eq. (8) for solid species gives the minimization function of Gibbs-energy for the following Eq. (9) which is the equation of this vapor–solid system:

$$\sum_{i=1}^{N-1} n_i \left(\Delta G_{fi}^\circ + RT \ln \frac{y_{ii} P}{P^\circ} + \sum_k \lambda_k a_{ik} \right) + (n_C \Delta G_{fC(s)}^\circ) = 0 \tag{9}$$

where $G_{C(g)}$ is the partial molar Gibbs free energy of gaseous carbon. $G_{C(s)}$ is the molar Gibbs free energy of solid carbon. $G_{fC(s)}^\circ$ is the standard Gibbs function of formation of solid carbon and n_C is the number of moles of carbon.