

# Production of high-purity hydrogen by sorption-enhanced steam reforming process of methanol

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## Abstract

The sorption-enhanced steam reforming process of methanol (SESRP-MeOH) to produce high-purity H<sub>2</sub> was thermodynamically and experimentally studied. Thermodynamic calculations showed that at a CO<sub>2</sub> adsorption ratio of 95%, product gas contains 98.36% H<sub>2</sub>, 32.8 ppm CO under temperature of 130 °C and steam-to-methanol (S/M) molar ratio of 2. However, without adsorption-enhanced, the product gas contains nearly 74.99% H<sub>2</sub> with 24.96% CO<sub>2</sub> and 525 ppm CO. To verify the thermodynamic calculation results, experiments were performed in a fixed-bed reactor loaded with commercial CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol reforming catalyst and 22% K<sub>2</sub>CO<sub>3</sub>-promoted hydrotalcite as CO<sub>2</sub> adsorbent. Experimental results showed that 99.61% H<sub>2</sub> could be obtained by SESRP-MeOH at reaction temperature of 230 °C and S/M of 2. Under the same CH<sub>3</sub>OH conversion, the reaction temperature decreased by almost 50 °C and H<sub>2</sub> concentration increased of more than 20% using SESRP-MeOH compared with solely steam reforming of methanol. The characterization of the adsorbent and catalyst showed that the adsorbent showed good stability while the catalyst was seriously sintered under the high regeneration temperature of the adsorbent.

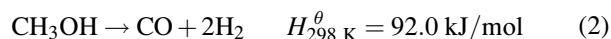
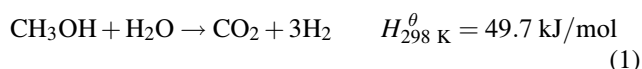
## Key words

hydrogen; methanol; sorption-enhanced reforming; carbon dioxide; hydrotalcite

## 1. Introduction

With the increasing global traditional energy consumption, many researchers have investigated H<sub>2</sub> as a clean energy source for environment-friendly internal engines and proton-exchange membrane fuel cells (PEMFCs) [1–4]. H<sub>2</sub> can be obtained by steam methane reforming (SMR) at 800–900 °C [5], or by water electrolysis which is electrically intensive [6], or by biomass reforming which is energy intensive and lowly efficient [7]. H<sub>2</sub> produced from steam methanol reforming is a process with a low reaction temperature of approximately 240–260 °C [8,9] and with high hydrogen-to-carbon ratio, making it a high-potential approach to H<sub>2</sub> production [10].

It is reported that the steam methanol reforming on the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst can be expressed as Equations (1) to (3) [11,12]. The main reaction is methanol reforming (Equation 1), and the two side reactions are methanol decomposition (Equation 2) and reverse water gas shift (r-WGS, Equation 3).



The product gas comprises nearly 25% CO<sub>2</sub> and 1% CO. Given that CO is a poisonous gas to the Pt electrode of PEMFCs, no more than 10 ppm CO should be contained in H<sub>2</sub> before it is provided to PEMFCs [13]. Thus, an additional purification method such as methanation [14], pressure swing adsorption [15], or membrane separation [16] must be used to significantly reduce CO to less than 10 ppm [13].

Sorption-enhanced steam reforming process (SESRP) uses hydrotalcite as CO<sub>2</sub> adsorbent to adsorb CO<sub>2</sub> produced from methane steam reforming to obtain high-purity H<sub>2</sub> with a low CO<sub>2</sub> and CO content [17]. Similar studies have also been applied on ethanol steam reforming [18] but till now none have been applied on methanol steam reforming to produce high-purity H<sub>2</sub>. Moreover, it has been found that Mg-Al hydrotalcite-like compounds (HTLcs) as CO<sub>2</sub> adsorbent have a wide range of adsorption temperature (from 20 °C to 400 °C) and moderate CO<sub>2</sub> adsorption capacity (0.3–0.8 mol/kg), with good mechanical strength and stability [19–23]. In order to further increase its CO<sub>2</sub> adsorption capacity, K<sub>2</sub>CO<sub>3</sub> has

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been added into the HTlcs as promoter [24–26]. All research results reported recently have confirmed that  $K_2CO_3$ -promoted HTlcs is a good  $CO_2$  adsorbent which is suitable to be applied in the SESRP-MeOH.

The effectiveness of  $CO_2$  adsorption enhanced steam reforming of methanol has been thermodynamically studied [27–29]. However, there is no experimental study on the SESRP-MeOH. In this work, a thermodynamic model and experiments by using  $K_2CO_3$ -promoted HTlcs as  $CO_2$  adsorbent was designed and conducted to investigate the effects of  $CO_2$  adsorption on steam reforming of methanol for the first time. And the results obtained from thermodynamic analysis and experimental studies were discussed in detail.

## 2. Thermodynamic approach

The effect of different  $CO_2$  adsorption ratios on product-gas composition was studied from thermodynamic point of view. According to above mentioned Equations (1), (2) and (3), the entire system can be described as two independent reactions, i.e., Equation (1) and Equation (2). Assuming adsorption-enhanced reaction occurred in a batch reactor packed with catalyst and adsorbent, with the feed containing a vaporized mixture of  $H_2O$  and  $CH_3OH$ . The following equations describe the equilibrium molar ratio of each component in the reactor.

$$[CH_3OH] = \frac{1 - X_1 - X_2}{1 + \beta + 2X_1 + 2X_2 - \zeta \cdot X_1} \quad (4)$$

$$[H_2O] = \frac{\beta - X_1}{1 + \beta + 2X_1 + 2X_2 - \zeta \cdot X_1} \quad (5)$$

$$[CO_2] = \frac{(1 - \zeta) \cdot X_1}{1 + \beta + 2X_1 + 2X_2 - \zeta \cdot X_1} \quad (6)$$

$$[H_2] = \frac{3X_1 + 2X_2}{1 + \beta + 2X_1 + 2X_2 - \zeta \cdot X_1} \quad (7)$$

$$[CO] = \frac{X_2}{1 + \beta + 2X_1 + 2X_2 - \zeta \cdot X_1} \quad (8)$$

where,  $\beta$  is the S/M ratio,  $\zeta$  is the fraction of  $CO_2$  adsorbed from gaseous phase by  $CO_2$  adsorbent.  $X_1$  and  $X_2$  are the conversion of  $CH_3OH$  reacted in reforming path (Equation 1) and decomposition path (Equation 2), respectively.

The corresponding equilibrium constants of Equation (1) and Equation (2) can be expressed as follows:

$$K_1 = P^2 \frac{[CO_2] \cdot [H_2]^3}{[H_2O] \cdot [CH_3OH]} \quad (9)$$

$$K_2 = P^2 \frac{[CO] \cdot [H_2]^2}{[CH_3OH]} \quad (10)$$

where,  $P$  is the system pressure, and equals to 101.325 kPa in this simulation;  $K_1$  and  $K_2$  are functions of temperature  $T$ .

By combining Equation (4) to Equation (10) and solving the equations using Matlab, the relationship between  $\zeta$  and gas-product composition could be obtained.

## 3. Experimental

### 3.1. Materials and characterizations

Commercial HTlcs powder with a chemical composition of 33.85 wt% MgO and 23.25 wt%  $Al_2O_3$ , purchased from Tiangtang Auxiliaries Chemical Ltd., was used as adsorbent precursor. Industrial  $CuO/ZnO/Al_2O_3$  catalyst with a chemical composition of 60.2 wt% CuO, 9.2 wt% ZnO, purchased from Sichuan Tianyi Chemical Co., Ltd., was used as reforming catalyst.  $K_2CO_3$ , purchased from Sino-Chemical Reagent Corp., was used as an additive to enhance the adsorption capacity of HTlcs.

22 wt%  $K_2CO_3$  promoted hydrotalcite denoted as K-HTlcs was prepared according to the procedure reported by Halabi et al. [30] and Nataraj et al. [31]. The prepared K-HTlcs was ground to particle sizes of 0.8–1.3 mm. Meanwhile,  $CuO/ZnO/Al_2O_3$  catalyst was also ground to particle sizes of 0.8–1.3 mm and labeled as O-CAT.

X-ray diffraction (XRD) was performed on a D/MAX-RA X-ray diffractometer (Rigaku, Japan) with copper anode at a voltage of 40 kV and current of 40 mA.

The specific area and pore volume of the material used in this work were calculated by BET and BJH methods from  $N_2$  adsorption-desorption isotherms at 77 K determined with Micromeritics BELSORP-mini II (BEL Japan, Inc.).

Temperature-programmed reduction (TPR) was carried out on TP-5000III (Tianjin Xianquan Industry and Trade Development Co., Ltd.).

SEM images of the pristine and reacted catalysts were taken on SU-8010 (Hitachi, Tokyo, Japan).

### 3.2. $CO_2$ adsorption capacity and SESRP-MeOH evaluation

$CO_2$  adsorption capacity of the adsorbent was calculated according to Equation (11):

$$C = \frac{n_{ad-CO_2}(\text{mol})}{m_{ad}(\text{kg})} \quad (11)$$

where,  $C$  is the adsorption capacity of the adsorbent,  $n_{ad-CO_2}$  is the molar of  $CO_2$  adsorbed and  $m_{ad}$  is the mass weight of the adsorbent.

An apparatus consists of a stainless tubular single-column reactor with a length of 60 cm and inner diameter of 2.5 cm was set up as shown in Figure 1. A programmable heat controller was installed to keep the reaction temperature constant. A water pump was used to introduce the liquid feedstock, and a heating belt was installed to vaporize the liquid feedstock. A condenser was used to condense the unreacted  $CH_3OH$  or  $H_2O$ . A gas chromatograph and  $H_2$ ,  $CO_2$  gas detectors were installed to detect the  $H_2$ ,  $CO_2$ , and CO contents. A regeneration temperature of 400 °C was applied to the reactor to regenerate the adsorbent after reaction.

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