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Hydrogen Production from Methanol Using Corona Discharges

Xi Zhen LIU[1,2], Chang Jun LIU[2]*, Baldur ELIASSON[3]

[1]School of Management, Tianjin University, Tianjin 300072
[2]ABB Plasma Greenhouse Gas Chemistry Laboratory, State Key Laboratory of C1 Chemistry and Technology, Tianjin University, Tianjin 300072
[3]ABB Switzerland Ltd., CH5405, Baden, Switzerland

Abstract: Hydrogen production at room temperature from liquid methanol has been conducted using corona discharge. The content of water in methanol solution has a significant effect on this production. When water concentration increases from 1.0 % to 16.7 %, the methanol conversion rate changes from 0.196 to 0.284 mol/h. An important finding in this investigation is the formation of ethylene glycol as a major by-product. The yield of ethylene glycol is ranged from 0.0045 to 0.0075 mol/h based on the water content.

Keywords: Hydrogen, methanol, plasma, corona discharge.

Hydrogen production from methanol is an interesting and promising option for the energy supply of fuel cells and other applications. Compared to the developed hydrogen storage technologies, the use of methanol as an effective storage of hydrogen is much safer and cheaper. The developed hydrogen production technologies from methanol include steam reforming[1,2], partial oxidation[3], oxidative steam reforming[4] and decomposition[5,6]. The decomposition of methanol provides a better alternative for the hydrogen production.

The catalytic hydrogen production from methanol has disadvantages as follows: 1. The methanol reformers mostly are the packed bed reactors which may cause the occurrence of hot and cold spots; 2. There are some problems during the cold start-up and transients; 3. The catalytic activity and stability still need to be improved.

The methanol decomposition can be carried out more effectively under the conditions of cold plasmas. A higher one-pass conversion rate can be achieved. Especially, the plasma methanol decomposition can be operated at ambient conditions. Tanaba *et al*[7] recently reported a dielectric-barrier discharge (DBD) decomposition of methanol into hydrogen. Such DBD plasma methanol conversion is easier to be operated than the catalytic process, with an input power ranged from 0.27 to 6.40 Wh/(Ncm^{3}H$_2$). The maximum conversion of CH_3OH to H_2 is 80%, which can be achieved in the absence or presence of water with the major by-products CO, CO_2,

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*E-mail: changliu@public.tpt.tj.cn

respectively[7]. In this regard, a corona discharge would be much better than DBD since corona discharge would also lead to a high conversion with much lower input power (less than 0.04 Wh/Ncm^3H_2 in this work).

The gas/liquid corona discharge reactor applied in this work is similar to that reported previously[8,9]. **Table 1** shows the effect of water contents in methanol solution on methanol decomposition with an input power of 30 W. The presence of water in methanol solution has a significant effect on room temperature hydrogen production. As shown in **Table 1**, when water concentration increases from 1.0 % to 16.7 %, the methanol conversion changes from 0.196 to 0.284 mol/h (methanol conversion increases from 15.8 % to 27.3%) and the hydrogen production rate increases from 0.375 to 0.549 mol/h. The experimental result also showed that the methanol decomposition to CO and hydrogen could be achieved at room temperature. An important finding in this investigation is that ethylene glycol (EGL) is a major by-product. The formation rate of EGL ranged from 0.0045 to 0.0075 mol/h based on the water content, as shown in **Table 1**. In addition to EGL, trace ethanol, propanol and allyl alcohol have also been detected.

Table 1 Effect of water content on the hydrogen production from methanol

water content (wt%)	methanol conversion rate (mol/h)	hydrogen production rate (mol/h)	EGL production rate (mol/h)	energy consumption (Wh/Ncm^3H_2)
16.7	0.284	0.549	0.0075	0.0025
10.1	0.264	0.515	0.0045	0.0026
4.7	0.240	0.466	0.0049	0.0029
1.0	0.196	0.375	0.0062	0.0036

The molecule of EGL contains two radicals of $\cdot CH_2OH$ that could be produced from the dissociation of methanol:

$$CH_3OH + e \rightarrow \cdot CH_2OH + \cdot H + e' \tag{1}$$

The combination of two radicals of $\cdot CH_2OH$ generated EGL. However, both methanol decomposition and the direct production of EGL from methanol are thermodynamically unfavored:

$$CH_3OH\ (liquid) \rightarrow 2H_2 + CO \qquad \Delta G_{298K} = 29.29\ kJ/mol \tag{2}$$

$$2CH_3OH\ (liquid) \rightarrow (CH_2OH)_2 + H_2 \quad \Delta G_{298K} = 13.14\ kJ/mol \tag{3}$$

The use of corona discharge, one of non-equilibrium plasma phenomena, can lead to an effective conversion of methanol into hydrogen and EGL (as a major by-product). A DFT study confirms that the presence of water will promote the formation of the radicals of $\cdot CH_2OH$ *via* the dissociation of water (the dissociation energy of O-H bond of water is 116.8643 kcal/mol, while the calculated dissociation energy of C-O bond, C-H bond and O-H bond of the methanol molecule is 91.4068, 95.4810 and 101.7749 kcal/mol, respectively):

$$H_2O \rightarrow \cdot H + \cdot OH \quad (4)$$

The generation of •OH will induce an oxidative dissociation of methanol to generate some extra radicals of $\cdot CH_2OH$:

$$\cdot OH + CH_3OH \rightarrow H_2O + \cdot CH_2OH \quad (5)$$

If EGL can be produced from methanol in this way, it would be very promising. This process is very simple and just methanol is used as the feedstock. The source of methanol is very rich. It can be produced from coal, natural gas, refinery gas and, especially, renewable resources such as wood, municipal solid wastes and sewage.

The present investigation confirmed that hydrogen production from methanol is available using corona discharges at room temperature. A new formation pathway of EGL directly from methanol is also demonstrated. Further investigation is being conducted to understand these reactions.

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