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Article

The catalytic effect of H₂ in the dehydrogenation coupling production of ethylene glycol from methanol using a dielectric barrier discharge

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ARTICLE INFO

Article history:

Received 17 August 2014

Accepted 12 October 2014

Published 20 March 2015

Keywords:

Dielectric barrier discharge plasma

Hydrogen catalysis

Ethylene glycol synthesis

Hydrogen atom

Carbon-hydrogen bond activation

ABSTRACT

The catalytic effect of H₂ in the one-step synthesis of ethylene glycol (EG) from methanol dehydrogenation coupling reaction using dielectric barrier discharge (DBD) was studied by in-situ optical emission spectroscopy and online chromatographic analysis. The influence of discharge frequency, methanol and H₂ flow rates as well as reaction pressure was investigated systematically. Results show that, in the non-equilibrium plasma produced by DBD, H₂ dramatically improved not only the conversion of methanol but also the selectivity for EG. Using the reaction conditions of 300 °C, 0.1 MPa, input power 11 W, discharge frequency 12.0 kHz, methanol gas flow rate 11.0 mL/min, and H₂ flow rate 80–180 mL/min, the reaction of the CH₃OH/H₂ DBD plasma gave a methanol conversion close to 30% and a selectivity for EG of more than 75%. The change of the EG yield correlated with the intensity of the H_α spectral line. H atoms appear to be the catalytically active species in the reaction. In the DBD plasma, the stable ground state H₂ molecule undergoes cumulative collision excitation with electrons before transitioning from higher energy excited states to the first excited state. The spontaneous dissociation of the first excited state H₂ molecules generates the catalytically active H atom. The discharge reaction condition affects the catalytic performance of H₂ by influencing the dissociation of H₂ molecules into H atoms. The catalytic effect of H₂ exhibited in the non-equilibrium plasma may be a new opportunity for the synthesis of chemicals.

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1. Introduction

Ethylene glycol (EG), the simplest diol, is used extensively all over the world [1] and is currently produced by the hydration of ethylene oxide. However, with the depletion of petroleum resources, the synthesis of EG from coal is more appealing [2,3]. The coal-based EG production process involves dimethyl oxalate as an intermediate and requires the oxidative dehydrogenation of syngas, oxidative esterification, coupling of CO and hydrogenation of dimethyl oxalate to produce EG. Although

many researchers have investigated this method, problems due to the multistep process, high capital input and complex technology remain as impediments [4,5].

We recently reported a one-step synthesis of EG from methanol by dielectric barrier discharge (DBD) in the presence of H₂. The 71.5% EG selectivity and 15.8% methanol conversion have been reached at atmospheric pressure [6]. The reaction pathway for the one-step synthesis of EG from methanol is characterized by the breaking of the C–H bond of methanol in the non-equilibrium plasma of the DBD. The dissociation of one

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DOI: 10.1016/S1872-2067(14)60239-4 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 36, No. 3, March 2015

methanol molecule gives one hydroxymethyl radical and one H atom; the coupling of two hydroxymethyl radicals gives the desired EG molecule. The simultaneous coupling of two H atoms leads to a H_2 molecule. Theoretically, this reaction has an atom economy of 100%, as the EG and hydrogen are both value-added products. Obviously, the one-step synthesis of EG is much more attractive for commercial application. What is more, as the selective activation of the C–H bond of methanol molecule is made difficult by conventional catalytic methods due to the bond energy of C–H falling between that of the O–H bond and the C–O bond [7], the function of the non-equilibrium plasma in the selective dissociation of the C–H bond of methanol might help research into the selective activation of other chemical bonds.

In the previous work [6], we observed hydrogen acting as a catalyst during the one-step synthesis of EG from methanol in a DBD. In this paper, with in-situ optical emission spectroscopy (OES) and online chromatographic analysis, we have studied the relationship between hydrogen dissociation activation and methanol dehydrogenation coupling to form EG under different discharge conditions. On this basis, the catalytic mechanism of H_2 in the one-step EG synthesis from methanol is discussed.

2. Experimental

The schematic of the experimental setup and the reactor structure is shown in Fig. 1. H_2 (99.99%, Dalian gas company, Ltd) was introduced into a vaporizing mixer and reactor under the control of a D07-19B mass flow controller (Beijing Sevenstar Electronics Co. Ltd., Beijing, China). When all the air in the reaction system had been fully replaced by H_2 , liquid methanol (AR, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was introduced by a pump. It was vaporized and mixed with H_2 in the vaporizing mixer, and this mixture was introduced into the plasma reactor through a thermally insulated pipeline. Then, the high-voltage (HV) power supply (CTP-2000 K cold plasma power supply, Nanjing Suman Electronics Co. Ltd) was turned on and the voltage output was regulated to generate a DBD. The voltage, current and power of the discharge were measured on an oscilloscope (DPO3012 digital oscilloscope, American Tektronix Company, Beaverton, United States). The H_2 dissociation in the plasma zone was observed with an in-situ OES (SP2758, Princeton Instruments, United States; grating 300 G/mm, exposure time 1.0 s). The effluent of the reactor

was introduced through a second insulated pipeline into a double detector online GC for compositional analysis (GC SP-6890, Rainbow Chemical Instrument Co. Ltd. Shandong Lunan. FID for the detection of CH_3OH , $HOCH_2CH_2OH$, C_2H_5OH , C_3H_7OH and CH_4 , etc., TCD for the detection of CH_4 , CO , H_2O , etc.). The CH_3OH conversion (X) and product selectivity (S) were calculated according to the following equations:

$$X(CH_3OH) = (n_0(CH_3OH) - n(CH_3OH)) / n_0(CH_3OH)$$

$$S_i = n_i(CH_3OH) / (n_0(CH_3OH) - n(CH_3OH))$$

where, $n_0(CH_3OH)$ and $n(CH_3OH)$ were the moles of CH_3OH before and after the reaction, respectively, and $n_i(CH_3OH)$ was the moles of CH_3OH converted to product i .

3. Results and discussion

3.1. The promoting effect of H_2 in the synthesis of EG from methanol under DBD

The conversion of methanol using different discharge methods has been extensively studied, but the purpose of those studies was to produce hydrogen and/or syngas [8–17]. It is worth mentioning that Liu's group [18,19] once observed trace amounts of EG in the product of their methanol to hydrogen reaction using a corona discharge. In our previous work, we found two factors played key roles in the direct synthesis EG from methanol discharge: one was the discharge intensity of DBD, and the other was that methanol had to be fed into the DBD reactor together with the H_2 . A moderate discharge intensity was favorable for the production of EG. In this paper, the effect of the H_2 flow rate on EG synthesis was investigated in a DBD reactor of moderate discharge intensity at a fixed methanol flow rate. As shown in Table 1, in the absence of H_2 , the conversion of methanol was only 9.6%. The major products were CO and CH_4 , making EG the minor product. The selectivity towards these products were 55.2%, 16.6% and 8.0%, respectively. At a H_2 flow rate of 80 mL/min, however, the conversion of methanol reached 30.5%, 2.2 times greater than without H_2 . The selectivity for EG reached 75.4%, which is 8.4 times greater than without H_2 . These results showed that the presence of H_2 improved not only the conversion of methanol but also the selectivity for EG. This is extraordinary because if H_2 served merely as carrier or dilution gas, as is expected, the conversion of methanol should have decreased with increasing H_2 flow rate due to the decrease in the residence time of the reactant

Fig. 1. Schematic of the experimental setup (a) and the reactor structure (b).

Table 1Effect of the H₂ flow rate on methanol conversion under DBD.

H ₂ flow rate (mL/min)	X(CH ₃ OH)/ %	S(Product)/%					
		EG	C ₂ H ₅ OH	n-C ₃ H ₇ OH	CH ₄	CO	Others
0	9.6	8.0	8.5	1.4	16.6	55.2	10.3
20	19.3	45.7	4.5	1.1	10.1	32.6	6.0
40	21.6	68.5	2.7	0.6	6.7	17.4	4.1
60	24.8	71.1	2.7	0.4	5.4	17.2	3.2
80	30.5	75.4	2.2	0.3	5.2	14.3	2.6
100	29.3	76.3	2.4	0.4	5.5	12.7	2.7
120	28.8	77.1	2.0	0.2	4.8	13.9	2.0
140	27.3	76.1	2.2	0.2	5.3	14.1	2.1
160	29.3	74.2	2.4	0.3	6.0	14.7	2.4
180	28.6	75.5	2.4	0.2	5.6	14.1	2.2

Reaction conditions: CH₃OH gas flow rate = 11.1 mL/min, pressure = 0.1 MPa, input power = 11 W, discharge frequency = 12.0 kHz, discharge voltage = 16.8 kV, temperature = 300 °C.

molecule in the discharge zone. The fact that H₂ enhanced both methanol conversion and EG selectivity suggested that H₂ behaves as a catalyst. It accelerates the methanol reaction selectively for EG. The conversion of methanol and selectivity for EG did not increase further at H₂ flow rates beyond 80 mL/min. This is most probably due to the dilution effect of H₂ at higher flow rates exceeding the catalytic enhancement. Dilution decreases the opportunities for the coupling reaction for hydroxymethyl radicals but increases the recombination reaction between H atoms and hydroxymethyl radicals. This recombination reaction is the reverse of the C–H bond dissociation of methanol.

3.2. The dissociation of H₂ in DBD reactor and the relationship between EG yield and hydrogen atom concentration

The in-situ OES analysis was used to study the DBD plasma of the CH₃OH/H₂ mixture at different flow rates of H₂ (0–100 mL/min) to investigate the catalytic mechanism of H₂ in the direct synthesis of EG from methanol in a DBD reactor. As shown in Fig. 2(a), all the active species detected in the DBD plasma involved hydrogen. They were the excited H₂ molecule (corresponding to the continuous spectrum bands in 380–550 and 580–650 nm, respectively), and the excited H atom (cor-

responding to line in 656.3 nm). Specifically, the continuous spectrum in 380–550 nm belongs to the radiative dissociation continuum band of H₂ molecule (H₂ a³Σ_g⁺ → H₂ b³Σ_u⁺), the continuous spectrum band in 580–650 nm belongs to the Fulcher transition band of the H₂ molecule (H₂ d³Π_u⁺ → H₂ a³Σ_g⁺) [20], while the spectral line in 656.3 nm belongs to the H_α line (H 3d²D → H 2p²P⁰) [21]. Generally, the signals of the excited state H₂ molecule and H atom were intense in the presence of H₂, and this increased as the H₂ flow rate increased. In the absence of H₂ the signals of the excited state H₂ molecule and H atom were too weak to see the bands of the Fulcher transition and radiative dissociation continuum of H₂. This means that methanol alone does not produce significant amounts of hydrogen via the dissociation of the C–H bond in the DBD plasma.

The intensity of the H_α spectral line is related to the concentration of the ground state H atom [22]. Although the electron temperature of the plasma, or the electron energy, has an influence on the intensity of the H_α spectral line, it also influences the concentration of the ground state H atom. Based on the relationship of the intensity of the H_α spectral line with the concentration of the ground state H atom, we believed that a large number of H₂ molecules dissociate into ground state H atoms during the discharge of CH₃OH/H₂, and that the concentration of ground state H atom increases with the flow rate of H₂ at least within the range investigated.

The OES observations revealed two pathways by which the dissociation of H₂ molecule into a ground state H atom proceeds in a DBD plasma [23]. (1) The ground state H₂ molecule is excited to the a³Σ_g⁺ state via a non-elastic collision with an electron, the excited H₂ molecule, in an a³Σ_g⁺ state, transitions to the first excited state (b³Σ_u⁺). This is accompanied by the dissociation continuous spectrum band of 380–550 nm and is followed by the spontaneous dissociation of the b³Σ_u⁺ state (repulsive state) into two ground state H atoms. This pathway can be expressed as H₂ (a³Σ_g⁺) → H₂ (b³Σ_u⁺) → H (1s) + H (1s). (2) The ground state H₂ molecule collides with an electron as above but is excited to the d³Π_u⁺ state. The d³Π_u⁺ state H₂ molecule transitions to the a³Σ_g⁺ state, which is followed by a transition of the a³Σ_g⁺ state, which gives rise to the continuous Fulcher transition band of 580–650 nm, and finally transitions

Fig. 2. OES of the CH₃OH/H₂ non-equilibrium plasma (a), and the correlation between the intensity of the H_α line and EG yield (b) at different flow rates of H₂. Reaction conditions: CH₃OH gas flow rate = 11.1 mL/min, pressure = 0.1 MPa, discharge frequency = 12.0 kHz, input power = 11 W, discharge voltage = 16.8 kV, temperature = 300 °C.

to the $b^3\Sigma_u^+$ state, with the associated dissociation continuous spectrum band of 380–550 nm as above. This pathway can be expressed as $H_2 (d^3\Pi_u^+) \rightarrow H_2 (a^3\Sigma_g^+) \rightarrow H_2 (b^3\Sigma_u^+) \rightarrow H (1s) + H (1s)$.

Among the active hydrogen species, the lifetime of the excited state species of H_2 molecule ($d^3\Pi_u^+$, $a^3\Sigma_g^+$ and $b^3\Sigma_u^+$) and H atom (H_α) is too short for them to participate in any chemical reactions. However, the ground state H atom has a longer lifetime and is active enough to participate in chemical reactions. As shown by Fig. 2(b), the intensity of the H_α spectral line (corresponding to the concentration of H atom) and EG yield increased with increasing H_2 flow rate. This suggests that the H atom was closely related to the selective dissociation of the methanol C–H bond. In another word, this suggests that the H atom is the catalytic active species in the direct synthesis of EG from methanol by DBD.

3.3. The influence of the discharge reaction conditions on the catalytic performance of H_2

In addition to the flow rate of H_2 , the discharge conditions were further investigated in terms of discharge frequency, methanol flow rate, and reaction pressure. In-situ OES was used at different reaction conditions to observe the CH_3OH/H_2

plasma, and the intensity of the H_α spectral line was also correlated with the yield of EG.

As shown in Figs. 3, 4 and 5, when the discharge frequency increased from 7 to 19 kHz, the intensity of the H_α spectral line first increased and then decreased, with a maximum at about 12.0 kHz. However, when methanol flow rate was increased from 11.1 to 55.4 mL/min and reaction pressure increased from 0.07 to 0.275 MPa, the intensity of H_α spectral line simply decreased. These results showed that discharge frequency, methanol flow rate, and reaction pressure all influence the CH_3OH/H_2 DBD plasma. In each case, however, the yield of EG was seen to correlate with the intensity of H_α spectral line. This phenomenon strongly supports our judgment that H atoms are the catalytic active species for the direct synthesis of EG with CH_3OH/H_2 in a DBD plasma. Additionally, it also shows that the discharge frequency, methanol flow rate, and reaction pressure have an influence on the catalytic effect of H_2 . Apparently, these effects act through the dissociation of the H_2 molecule into H atoms.

The influence of discharge frequency on the dissociation of H_2 could be attributed to either the shortening of the electron acceleration distance with the increase in the discharge frequency or the increase of electron density as discharge frequency increases at a fixed input power. Shortening the elec-

Fig. 3. OES of the CH_3OH/H_2 non-equilibrium plasma (a) and the correlation between the intensity of the H_α line and EG yield (b) at different discharge frequencies. Reaction conditions: CH_3OH gas flow rate = 11.1 mL/min, H_2 flow rate = 60 mL/min, pressure = 0.1 MPa, input power = 17 W, discharge voltage = 16.8 kV, temperature = 300 °C.

Fig. 4. OES of the CH_3OH/H_2 non-equilibrium plasma (a) and the correlation between the intensity of the H_α line and EG yield (b) at different CH_3OH gas flow rates. Reaction conditions: H_2 flow rate = 80 mL/min, pressure = 0.1 MPa, discharge frequency = 12.0 kHz, input power = 17 W, discharge voltage = 16.8 kV, temperature = 300 °C.

Fig. 5. OES of the $\text{CH}_3\text{OH}/\text{H}_2$ non-equilibrium plasma (a) and the correlation between the intensity of the H_α line and EG yield (b) at different pressures. Reaction conditions: CH_3OH gas flow rate = 11.1 mL/min, H_2 flow rate = 80 mL/min, discharge frequency = 12.0 kHz, input power = 17 W, discharge voltage = 16.8 kV, temperature = 300 °C.

tron acceleration tends to decrease the electron temperature or electron kinetic energy. This decrease of electron energy decreases the dissociation of H_2 , whereas the increase of electron density increases the dissociation of H_2 . Thus when the discharge frequency was lower than the optimum frequency of 12.0 kHz, the dissociation of H_2 was most probably limited by the electron density, and when the discharge frequency was higher than 12.0 kHz, the dissociation of H_2 was limited by the energy of electrons. The methanol flow rate and reaction pressure simply decreased the dissociation of H_2 molecule over the range examined here. Both of these observations are explainable as an increase in the methanol flow rate. An increase in the methanol flow rate will decrease the chance of collision between an electron and H_2 molecule, and an increase of reaction pressure will decrease electron kinetic energy.

3.4. The catalytic cycle of H_2 in the $\text{CH}_3\text{OH}/\text{H}_2$ DBD plasma

According to the experimental results, the catalytic mechanism of H_2 in the direct synthesis of EG from a $\text{CH}_3\text{OH}/\text{H}_2$ DBD plasma can be described by the following steps. First, the H_2 molecule acquires energy via a non-elastic collision with an electron, and is excited to either the $\text{d}^3\Pi_u^+$ or $\text{a}^3\Sigma_g^+$ state. These states are not stable. They transition to lower energy states (as indicated by the observation of the Fulcher transition band and dissociation continuous spectrum band), and spontaneously dissociate into ground state H atoms from the $\text{b}^3\Sigma_u^+$ repulsive state. H atoms then selectively dissociated the C–H bond of methanol by collision. Previous reports support the selective dissociation of the C–H bond of methanol by H atoms [24–26]. These reports discuss the collision of H atoms with methanol molecules, and that methyl H atoms are preferentially abstracted as opposed to alcoholic H atoms of methanol. By colliding with a H atom, the activation energy of the C–H bond dissociation reaction of methanol molecule ($\text{H} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} + \text{H}_2$) is reduced to 11.78 kcal/mol, far lower than for the direct dissociation of C–H, or dissociation of the C–O and O–H bonds, which are 94.57, 81.51 and 100.78 kcal/mol, respectively. These data seem to show that there is no fundamental difference between the catalytic effect of H_2 and that of

Fig. 6. Schematic of H_2 catalytic cycle in the EG synthesis with $\text{CH}_3\text{OH}/\text{H}_2$ plasma.

the well-known conventional catalysts. The reduction of the activation energy was observed for the H_2 catalyst in the C–H bond dissociation of methanol. Therefore, the H_2 catalyzed methanol to EG reaction can be described as follows. The C–H bond of the methanol molecule is catalytically dissociated by hydrogen with hydrogen atoms acting as the catalytic active species, and the hydroxymethyl radicals so produced react to form EG via a homocoupling reaction. Meanwhile, the H atoms dissociated from methanol react to form H_2 via a coupling reaction as well. Overall, the methanol to EG reaction is a H_2 producing reaction rather than a H_2 consuming one. It means that more H_2 molecules will leave the DBD reactor than are introduced. Based on the above discussion, we have proposed a catalytic cycle for H_2 , as shown in Fig. 6. It should be pointed out that the catalytic effect of H_2 will only be present in the high-voltage electric field or, in other words, in its plasma state. H_2 will return to its stable molecular state as soon as it leaves the discharge zone. This is perhaps an obvious trait of the H_2 catalyst. Knowing that the dissociation of H_2 molecule is a high energy process (103.55 kcal/mol), one may wonder why H_2 is so efficient in accelerating this reaction. The answer might lie in hydrogen's ability to undergo cumulative collision excitation by low energy electrons [27].

4. Conclusions

H_2 exhibited catalytic enhancement of the dehydrogenation coupling of methanol to produce EG in a DBD reactor. Based on

Graphical Abstract

Chin. J. Catal., 2015, 36: 274–282 doi: 10.1016/S1872-2067(14)60239-4

The catalytic effect of H₂ in the dehydrogenation coupling production of ethylene glycol from methanol using a dielectric barrier dischargeJing Zhang, Teng Li, Dongjiang Wang, Jialiang Zhang, Hongchen Guo*
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In the non-equilibrium plasma generated by a dielectric barrier discharge, H₂ exhibited a catalytic effect on the dehydrogenation coupling reaction of methanol, which permitted the direct synthesis of ethylene glycol with high selectivity.

the close relationship between EG yield and the H_α spectral line intensity of the excited H atoms, we speculate that ground state H atom is the catalytically active hydrogen species. In the DBD plasma, the stable ground state H₂ molecule underwent cumulative collision excitation with electrons and transitions from higher energy excited states to the first excited state. The spontaneous dissociation of the first excited state H₂ molecule generates the catalytically active H atom. The discharge reaction conditions affect the catalytic performance of H₂ by influencing the dissociation of the H₂ molecule into H atoms. The catalytic performance of H₂ observed here in the non-equilibrium plasma may be a new opportunity for the synthesis of chemicals.

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介质阻挡放电甲醇脱氢偶联一步合成乙二醇反应中氢气的催化作用

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摘要: 利用原位发射光谱表征和在线色谱分析, 研究了甲醇介质阻挡放电脱氢偶联一步合成乙二醇反应中氢气的催化作用, 考察了放电频率、甲醇和氢气进料量以及反应压力的影响。结果表明, 在介质阻挡放电产生的非平衡等离子体中, H₂不但能显著提高甲醇转化率, 而且能显著提高乙二醇的选择性。在300 °C, 0.1 MPa, 反应器注入功率为11 W, 放电频率为12.0 kHz, 甲醇气体进料量为11.1 mL/min, 氢气进料量为80–180 mL/min的条件下, 甲醇转化率接近30%, 乙二醇选择性大于75%。乙二醇收率与激发态氢

原子的 H_{α} 谱线强度之间存在同增同减关系。由此推测,氢原子是起催化作用的活性氢物种。活性氢物种的生成途径是:基态氢分子通过与电子碰撞变成激发态,激发态氢分子通过第一激发态氢自动解离为基态氢原子。放电反应条件通过影响氢分子解离来影响氢气的催化作用。氢气在非平衡等离子体中显示的催化作用有可能为开辟新的化学合成途径提供重要机遇。

关键词: 介质阻挡放电等离子体; 氢气催化作用; 乙二醇合成; 氢原子; 碳-氢键活化

收稿日期: 2014-08-17. 接受日期: 2014-10-12. 出版日期: 2015-03-20.

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本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

1. 前言

乙二醇(EG)是最简单的二元醇,用途十分广泛^[1];目前,普遍采用环氧乙烷直接水合法生产。然而,随着石油资源的日益枯竭,近年来煤制乙二醇技术广受关注^[2,3]。煤制乙二醇须由合成气制草酸二酯中间体,其工艺过程包括合成气氧化脱氢、氧化酯化、CO偶联和草酸二酯加氢等单元。目前,虽然不少研究机构都在开发该工艺,但存在流程长、投资大和工艺技术复杂等问题^[4,5]。

最近,我们报道了在 H_2 存在下,采用甲醇介质阻挡放电一步合成乙二醇的研究工作。在常压条件下,甲醇转化率和乙二醇选择性分别达15.8%和71.5%^[6]。该方法的基本原理是:甲醇分子在介质阻挡放电产生的非平衡等离子体的作用下解离一个C-H键,生成羟甲基自由基(CH_2OH)和氢原子;两个羟甲基自由基(CH_2OH)偶联生成乙二醇,同时两个氢原子复合生成 H_2 。由于 H_2 也是高附加值产物,所以上述甲醇脱氢偶联合成乙二醇反应在理论上原子经济性可达100%,因而在应用上更具吸引力。不仅如此,由于常规催化法在选择性活化甲醇分子的C-H键方面难度很大(键能顺序: $O-H > C-H > C-O$)^[7],因此非平衡等离子体所表现出的选择性解离甲醇C-H键现象,对于化学键的定向活化研究会有启发作用。

我们已经发现, H_2 在甲醇介质阻挡放电一步合成乙二醇的反应过程中起到了催化剂的作用。本文借助于发射光谱原位表征和在线色谱分析手段,重点研究了 H_2 在不同放电反应条件下的解离活化及其与甲醇脱氢偶联反应的关系。在此基础上讨论了 H_2 对甲醇一步合成乙二醇反应的分子催化作用机制。

2. 实验部分

装置流程和反应器如图1所示。实验时,先将 H_2 (纯度为99.99%,大连气体有限公司)通过质量流量计(D07-19B,北京七星华创电子股份有限公司)精确控制流量后进入汽化混合器,然后进入反应器。待反应系统被 H_2 充分置换后,将 CH_3OH 液体(分析纯,国药集团化学试剂有限公司)经高压恒流泵(P230,大连依利特分析仪器

有限公司)精确控制流量后进入汽化混合器。汽化后的 CH_3OH 在汽化混合器中与 H_2 充分混合后,经保温管线进入等离子体反应器。打开高压电源(CTP-2000K低温等离子电源,南京苏曼公司),调节电源电压产生介质阻挡放电。放电电压、电流及功率等参数通过示波器(DPO3012数字示波器,美国Tektronix公司)进行测量。 H_2 在等离子体区的解离情况通过原位发射光谱仪(SP2758型,美国Princeton仪器公司,300 G/mm光栅,1.0 s曝光时间)进行监测。从反应器出口流出的反应产物经保温管线进入双检测器在线色谱进行组成分析(SP-6890型气相色谱仪,山东鲁南瑞虹化工仪器有限公司,其FID用于测定 CH_3OH , $HOCH_2CH_2OH$, C_2H_5OH , C_3H_7OH 和 CH_4 等, TCD用于测定 CH_4 , CO , H_2O 等)。 CH_3OH 转化率及各种产物的选择性由下述公式计算:

$$X(CH_3OH) = (n_0(CH_3OH) - n(CH_3OH)) / n_0(CH_3OH)$$

$$S_i = n_i(CH_3OH) / (n_0(CH_3OH) - n(CH_3OH))$$

其中, $n_0(CH_3OH)$ 和 $n(CH_3OH)$ 分别为反应前及反应后 CH_3OH 的摩尔数, $n_i(CH_3OH)$ 为生成产物 i 消耗的 CH_3OH 摩尔数。

3. 结果与讨论

3.1. 在介质阻挡放电条件下 H_2 对甲醇合成乙二醇反应的促进作用

用等离子体方法转化甲醇已有许多研究报道,但目的产物主要是 H_2 或合成气^[8-17]。刘昌俊课题组^[18,19]曾在甲醇电晕放电制氢的研究中发现有微量乙二醇生成。我们也发现,用甲醇的等离子体直接合成乙二醇需要具备两个关键性的前提条件:一是等离子体的放电强度要适中;二是要用 H_2 和甲醇共进料^[6]。本文用一种放电强度适中的介质阻挡放电反应器,在甲醇进料量不变的情况下,考察了不同 H_2 进料流量对介质阻挡放电转化甲醇的影响。如表1所示,当不加入 H_2 时,甲醇转化率仅为9.6%,放电主产物是 CO 和 CH_4 ,其选择性分别为55.2%和16.6%。此时乙二醇选择性仅为8.0%左右。当 H_2 流量为80 mL/min时,甲醇转化率可达30.5%,乙二醇选择性高达75.4%,比没有 H_2 时分别增加了近2.2和8.4倍。由此可见,

在介质阻挡放电转化甲醇时,加入 H_2 不但能提高甲醇转化率,而且能选择性促进甲醇C–H键的解离,从而提高乙二醇选择性.该现象非同寻常.这是因为,如果 H_2 仅仅起载气和稀释气作用的话,那么,当乙二醇的选择性随着 H_2 流量增加而提高时,甲醇转化率很可能会因为反应物分子在放电区的停留时间缩短而下降. H_2 能够同时提高甲醇转化率及乙二醇选择性的现象意味着 H_2 不但加快了甲醇反应的速率,而且使反应按照生成乙二醇产物的特定途径进行,即 H_2 表现出了对甲醇直接生成乙二醇反应的催化作用.需要说明的是,继续增加 H_2 流量,则甲醇转化率和乙二醇选择性不再增加.这可能是由于大量 H_2 的稀释作用抑制了羟甲基自由基的偶联反应,而促进了氢原子和羟甲基自由基之间的偶合反应,即甲醇C–H键解离反应的逆过程.

3.2. H_2 在介质阻挡放电中的解离及氢原子浓度与乙二醇产率的关系

为了研究 H_2 在甲醇介质阻挡放电直接合成乙二醇反应过程中的催化作用机制,我们用发射光谱对不同 H_2 流量(0–100 mL/min)下的 CH_3OH/H_2 介质阻挡放电等离子体进行了原位表征.如图2(a)所示,在 CH_3OH/H_2 介质阻挡放电等离子体中,能检测到的活性物种都是氢的活性物种,包括激发态的氢分子(子(380–550 nm和580–650 nm两处连续谱带)和激发态的氢原子(子(656.3 nm处谱线).其中,380–550 nm处的连续谱带归属为氢分子的辐射解离带(带(H_2 $a^3\Sigma_g^+ \rightarrow H_2$ $b^3\Sigma_u^+$); 580–650 nm处的连续谱带归属为氢分子的Fulcher跃迁带(带(H_2 $d^3\Pi_u^+ \rightarrow H_2$ $a^3\Sigma_g^+$)^[20]; 656.3 nm谱线归属为 H_α 谱线(线(H $3d^2D \rightarrow H$ $2p^2P^0$)^[21].一般来说,激发态氢分子和原子的OES信号在加入 H_2 的情况下比较强,而且随着 H_2 流量的增加而增强.当不加入 H_2 时,甲醇等离子体发射光谱的 H_α 谱线非常弱,且几乎看不到氢分子Fulcher跃迁带和辐射解离带.这反映出单纯的甲醇等离子体不能通过C–H键解离反应产生大量 H_2 .

从物理学上讲, H_α 谱线的强度与等离子体中基态氢原子浓度有关^[22].尽管等离子体中的电子温度,或者说电子能量,对 H_α 谱线的强度有影响,但它同时对基态氢原子的浓度也有影响.基于 H_α 谱线强度与等离子体中基态氢原子浓度的关系,本文认为,在 CH_3OH/H_2 介质阻挡放电等离子体中氢分子被大量解离为氢原子,在实验范围内等离子体中氢原子浓度随着 H_2 流量增加而增加.

OES诊断揭示出以下两种氢分子解离为氢原子的途径^[23].一是基态氢分子通过与电子碰撞获得能量变成

$a^3\Sigma_g^+$ 态,接着 $a^3\Sigma_g^+$ 态氢分子跃迁到第一激发态($b^3\Sigma_u^+$),同时在380–550 nm范围产生连续的辐射解离带,然后再由 $b^3\Sigma_u^+$ 态氢分子(排斥态)自发解离为基态氢原子.这条途径可以表示为: $H_2(a^3\Sigma_g^+) \rightarrow H_2(b^3\Sigma_u^+) \rightarrow H(1s) + H(1s)$.二是基态氢分子通过与电子碰撞获得能量变成能量更高的 $d^3\Pi_u^+$ 激发态,接着 $d^3\Pi_u^+$ 态氢分子先跃迁到 $a^3\Sigma_g^+$ 态,同时在580–650 nm范围内产生连续的Fulcher跃迁带,然后 $a^3\Sigma_g^+$ 态氢分子跃迁到 $b^3\Sigma_u^+$ 态,伴随产生辐射解离带,最后由 $b^3\Sigma_u^+$ 态氢分子自发解离为基态氢原子.这条路径可以表示为: $H_2(d^3\Pi_u^+) \rightarrow H_2(a^3\Sigma_g^+) \rightarrow H_2(b^3\Sigma_u^+) \rightarrow H(1s) + H(1s)$].

在各种活泼氢物种中,激发态氢分子($d^3\Pi_u^+$, $a^3\Sigma_g^+$ 及 $b^3\Sigma_u^+$)和激发态氢原子(H_α)寿命都很短,在发生化学反应之前就退激发了.然而,基态氢原子寿命较长,且具有较高的化学反应活性,能够参与化学反应.从图2(b)可以看出,在 CH_3OH/H_2 介质阻挡放电等离子体中, H_α 谱线强度(对应于氢原子的浓度)与乙二醇的收率都随着 H_2 流量的增加而增大,且变化趋势非常相似.这说明等离子体中的氢原子与甲醇选择性解离C–H键,进而偶联生成乙二醇的反应关系密切.因此本文认为, H 原子应该是甲醇介质阻挡放电直接合成乙二醇反应的催化活性物种.

3.3. 放电反应条件对 H_2 催化性能的影响

除了 H_2 流量之外,本文还考察了放电频率、甲醇进料流量和反应压力的影响,原位监测了不同条件下 CH_3OH/H_2 等离子体的发射光谱,并将得到的 H_α 谱线强度(对应于氢原子浓度)与乙二醇收率进行了关联.

如图3–5所示,随着放电频率的提高,激发态氢原子的 H_α 谱线强度先增加后减小,在放电频率为12.0 kHz附近达到最大值;另一方面,随着甲醇进料流量从11.1增至55.4 mL/min,以及反应压力从0.07增至0.275 MPa, H_α 谱线强度都呈单调降低变化.由此可见,放电频率、甲醇进料量和反应压力都对 CH_3OH/H_2 等离子体有显著影响.然而,在上述条件变化过程中,乙二醇收率的变化始终与激发态氢原子的 H_α 谱线强度变化趋势保持一致.这有力支持了前面的判断,即氢原子是甲醇介质阻挡放电直接合成乙二醇反应的催化活性物种.很显然,放电频率、甲醇进料流量和反应压力对甲醇介质阻挡放电过程中 H_2 分子催化作用的影响是通过影响 H_2 分子解离来实现的.

放电频率对 H_2 解离的影响可归结于两个方面:一方面,增加放电频率缩短了等离子体中的电子加速距离,从而导致电子温度,或者说电子动能的降低;另一方面,随着放电频率的增加,等离子体中的电子密度将增加,这是

在放电功率一定的情况下等离子体中电子能量降低导致的必然结果. 电子动能降低不利于 H_2 解离, 但电子密度增加有利于 H_2 解离. 因此不难理解, 当放电频率低于最佳值12.0 kHz时, 等离子体中电子密度低可能是制约 H_2 解离的主要因素, 而当放电频率高于最佳值12.0 kHz时, 等离子体中电子能量低可能是制约 H_2 解离的主要因素. 与放电频率的影响不同, 在实验范围内甲醇进料流量和反应压力对 H_2 分子解离的影响都是单调变化的. 这是因为增大甲醇进料流量会降低电子与 H_2 分子的碰撞机会, 而增加反应压力会降低电子动能.

3.4. 在介质阻挡放电条件下甲醇合成乙二醇中 H_2 的催化循环

根据上述实验结果, 我们对 H_2 的催化作用机制归纳如下. 首先, H_2 分子通过与电子碰撞获得能量, 变成激发态 H_2 分子($d^3[{}^1u^+$, $a^3\Sigma_g^+$). 激发态的氢分子不稳定, 向低激发态跃迁(产生Fulcher跃迁带和辐射解离带), 并通过 $b^3\Sigma_u^+$ 排斥态自发解离为基态氢原子. 然后, 氢原子与甲醇分子发生碰撞反应导致C–H键选择性解离. 据报道, 当H原子与甲醇分子碰撞反应时, 优先夺取醇甲基上的H原子而不是醇羟基上的H原子^[24–26]. 由氢原子与甲醇分子发生碰撞而导致的甲醇分子C–H键解离反应($H + CH_3OH \rightarrow CH_2OH + H_2$)活化能很低, 只有11.78 kcal/mol, 远低于甲醇分子直接解离C–H键的活化能(94.57 kcal/mol), 也远低于甲醇分子直接解离C–O键(81.51 kcal/mol)和O–H键(100.78 kcal/mol)等反应的活化能. 由此可见, 氢分子催化作用的本质与常规催化剂相同, 都是降低目标反应的活化能. 乙二醇由两个羟甲基自由基偶

联得到. 上述反应的净结果是: 甲醇在 H_2 的催化作用下(氢原子是催化活性物种)发生C–H解离反应, 生成的羟甲基自由基偶联成为乙二醇, 生成的氢原子则复合成为 H_2 . 作为催化剂引入反应器的 H_2 在等离子体区参与了化学反应, 但最后仍然以 H_2 的形式离开等离子体区. 由于甲醇脱氢偶联是一个产氢过程, 因此 H_2 作为催化剂在反应过程中不会被消耗. 本文为此设计了 H_2 的催化循环, 如图6所示. 应该指出的是, 本文所说的 H_2 催化作用只存在于高压电场或者说 H_2 的等离子体中. 一旦离开放电区, H_2 就会回复到我们所熟悉的稳定状态. 这可能是 H_2 分子催化作用的特别之处. 另外, 由于 H_2 分子的解离并不容易(键能为103.55 kcal/mol), 那么在 CH_3OH/H_2 等离子体中为什么氢分子会如此高效率地加速甲醇生成乙二醇反应呢? 这可能与氢分子的特性有关: 氢分子可以被能量较低电子经多次碰撞导致累积激发^[27].

4. 结论

在甲醇介质阻挡放电脱氢偶联一步合成乙二醇过程中, H_2 表现出明显的催化作用. 根据乙二醇收率与激发态氢原子的 H_α 谱线强度的密切关系推测, 氢原子应该是起催化作用的活性氢物种. 在介质阻挡放电等离子体中, 基态氢分子通过与电子碰撞获得能量变成激发态, 激发态氢分子通过退激发跃迁到第一激发态后, 自动解离为具有催化作用的基态氢原子. 放电反应条件通过影响氢分子解离即活性氢物种的生成影响 H_2 的催化作用. H_2 在非平衡等离子体中显露出来的催化作用有可能为开辟新的化学合成途径提供重要机遇.