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Article

The catalytic effect of H_2 in the dehydrogenation coupling production of ethylene glycol from methanol using a dielectric barrier discharge

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ABSTRACT

The catalytic effect of H_2 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 H_2 flow rates as well as reaction pressure was investigated systematically. Results show that, in the non-equilibrium plasma produced by DBD, H_2 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 H_2 flow rate 80–180 mL/min, the reaction of the CH_3OH/H_2 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 H_2 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 H_2 molecules generates the catalytically active H atom. The discharge reaction condition affects the catalytic performance of H_2 by influencing the dissociation of H_2 molecules into H atoms. The catalytic effect of H_2 exhibited in the non-equilibrium plasma may be a new opportunity for the synthesis of chemicals.

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 H_2. 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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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 though 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:

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

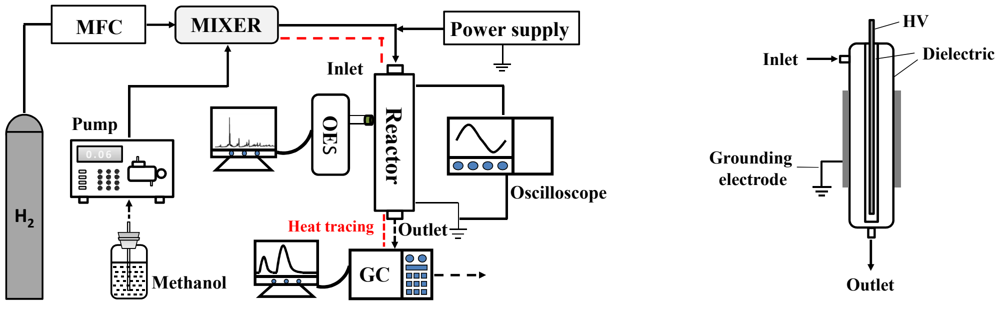
$$S_i = n_i(CH_3OH)/(n_0(CH_3OH)-n(CH_3OH))$$

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



(a) (b)

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

Table 1
Effect of the H_2 flow rate on methanol conversion under DBD.

H_2 flow rate (mL/min)	$X(CH_3OH)$/ %	S(Product)/%					
		EG	C_2H_5OH	n-C_3H_7OH	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: CH_3OH 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 H_2 enhanced both methanol conversion and EG selectivity suggested that H_2 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 H_2 flow rates beyond 80 mL/min. This is most probably due to the dilution effect of H_2 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 recombinational reaction is the reverse of the C–H bond dissociation of methanol.

3.2. The dissociation of H_2 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 CH_3OH/H_2 mixture at different flow rates of H_2 (0–100 mL/min) to investigate the catalytic mechanism of H_2 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 H_2 molecule (corresponding to the continuous spectrum bands in 380–550 and 580–650 nm, respectively), and the excited H atom (corresponding to line in 656.3 nm). Specifically, the continuous spectrum in 380–550 nm belongs to the radiative dissociation continuum band of H_2 molecule ($H_2\ a^3\Sigma_g^+ \rightarrow H_2\ b^3\Sigma_u^+$), the continuous spectrum band in 580–650 nm belongs to the Fulcher transition band of the H_2 molecule ($H_2\ d^3\Pi_u^+ \rightarrow H_2\ a^3\Sigma_g^+$) [20], while the spectral line in 656.3 nm belongs to the H_α line ($H\ 3d^2D \rightarrow H\ 2p^2P^0$) [21]. Generally, the signals of the excited state H_2 molecule and H atom were intense in the presence of H_2, and this increased as the H_2 flow rate increased. In the absence of H_2 the signals of the excited state H_2 molecule and H atom were too weak to see the bands of the Fulcher transition and radiative dissociation continuum of H_2. 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 H_2 molecules dissociate into ground state H atoms during the discharge of CH_3OH/H_2, and that the concentration of ground state H atom increases with the flow rate of H_2 at least within the range investigated.

The OES observations revealed two pathways by which the dissociation of H_2 molecule into a ground state H atom proceeds in a DBD plasma [23]. (1) The ground state H_2 molecule is excited to the $a^3\Sigma_g^+$ state via a non-elastic collision with an electron, the excited H_2 molecule, in an $a^3\Sigma_g^+$ state, transitions to the first excited state ($b^3\Sigma_u^+$). This is accompanied by the dissociation continuous spectrum band of 380–550 nm and is followed by the spontaneous dissociation of the $b^3\Sigma_u^+$ state (repulsive state) into two ground state H atoms. This pathway can be expressed as $H_2\ (a^3\Sigma_g^+) \rightarrow H_2\ (b^3\Sigma_u^+) \rightarrow H\ (1s) + H\ (1s)$. (2) The ground state H_2 molecule collides with an electron as above but is excited to the $d^3\Pi_u^+$ state. The $d^3\Pi_u^+$ state H_2 molecule transitions to the $a^3\Sigma_g^+$ state, which is followed by a transition of the $a^3\Sigma_g^+$ state, which gives rise to the continuous Fulcher transition band of 580–650 nm, and finally transitions

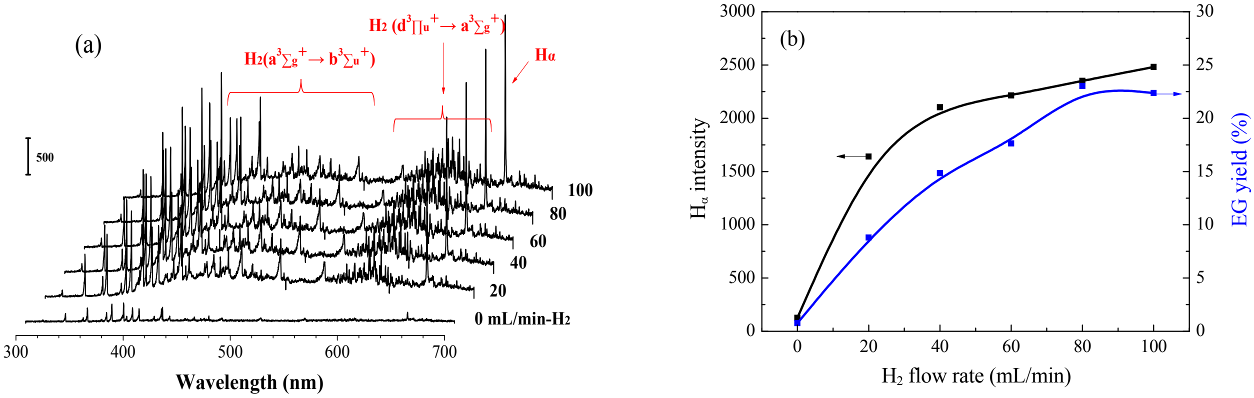


Fig. 2. OES of the CH_3OH/H_2 non-equilibrium plasma (a), and the correlation between the intensity of the H_α line and EG yield (b) at different flow rates of H_2. Reaction conditions: CH_3OH gas flow rate = 11.1 mL/min, pressure = 0.1 MPa, discharge frequency = 12.0 kHz, input power = 11 W, discharge 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 ($d^3\Pi_u^+$) → H_2 ($a^3\Sigma_g^+$) → H_2 ($b^3\Sigma_u^+$) → 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-

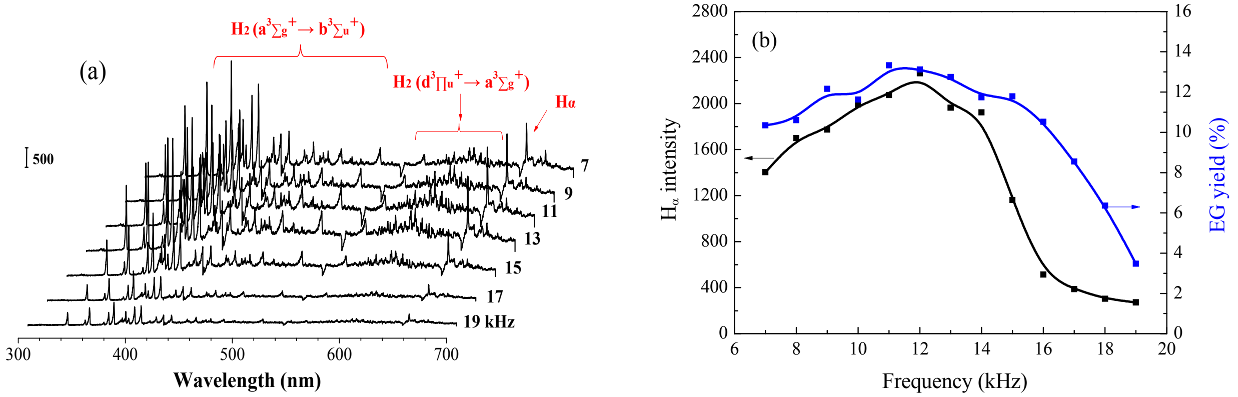


Fig. 3. OES of the CH_3OH/H_2 non-equilibrium plasma (a) and the correlation between the intensity of the H_α line and EG yield (b) at different discharge frequencies. Reaction conditions: CH_3OH gas flow rate = 11.1 mL/min, H_2 flow rate = 60 mL/min, pressure = 0.1 MPa, input power = 17 W, discharge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

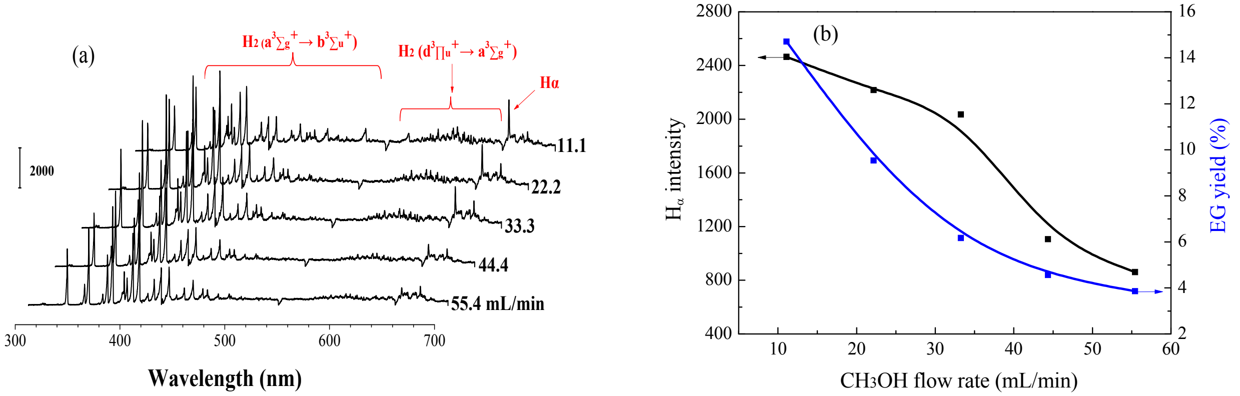


Fig. 4. OES of the CH_3OH/H_2 non-equilibrium plasma (a) and the correlation between the intensity of the H_α line and EG yield (b) at different CH_3OH gas flow rates. Reaction conditions: H_2 flow rate = 80 mL/min, pressure = 0.1 MPa, discharge frequency = 12.0 kHz, input power = 17 W, discharge voltage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

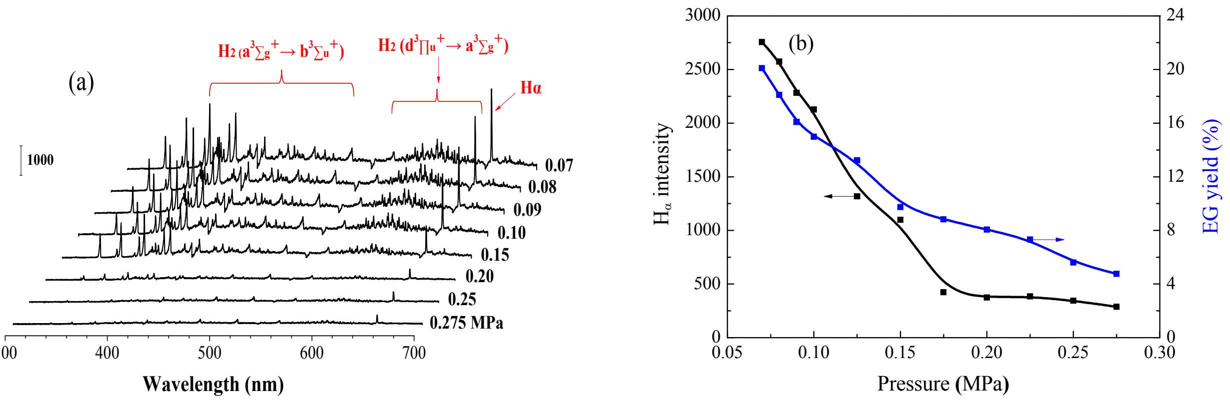


Fig. 5. OES of the CH_3OH/H_2 non-equilibrium plasma (a) and the correlation between the intensity of the Hα line and EG yield (b) at different pressures. Reaction conditions: CH_3OH gas flow rate = 11.1 mL/min, H_2 flow rate = 80 mL/min, discharge frequency = 12.0 kHz, input power = 17 W, discharge 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 CH_3OH/H_2 DBD plasma

According to the experimental results, the catalytic mechanism of H_2 in the direct synthesis of EG from a CH_3OH/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 $d^3\Pi_u^+$ or $a^3\Sigma_g^+$ 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 $b^3\Sigma_u^+$ 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 ($H + CH_3OH \rightarrow CH_2OH + H_2$) 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 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].

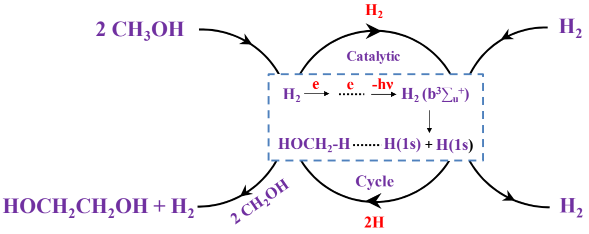


Fig. 6. Schematic of H_2 catalytic cycle in the EG synthesis with CH_3OH/H_2 plasma.

4. Conclusions

H_2 exhibited catalytic enhancement of the dehydrogenation coupling of methanol to produce EG in a DBD reactor. Based on the close relationship between EG yield and the Hα spectral line

Graphical Abstract

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The catalytic effect of H_2 in the dehydrogenation coupling production of ethylene glycol from methanol using a dielectric barrier discharge

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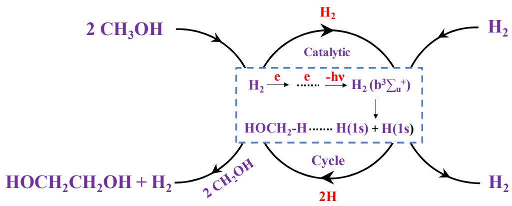
Dalian University of Technology

In the non-equilibrium plasma generated by a dielectric barrier discharge, H_2 exhibited a catalytic effect on the dehydrogenation coupling reaction of methanol, which permitted the direct synthesis of ethylene glycol with high selectivity.



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 H_2 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 H_2 molecule generates the catalytically active H atom. The discharge reaction conditions affect the catalytic performance of H_2 by influencing the dissociation of the H_2 molecule into H atoms. The catalytic performance of H_2 observed here in the non-equilibrium plasma may be a new opportunity for the synthesis of chemicals.

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