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Direct synthesis of ethylene glycol from methanol by dielectric barrier discharge†

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Ethylene glycol (EG) has been obtained with 71.53% selectivity and 15.77% methanol conversion under optimized conditions using a double dielectric barrier discharge (DDBD) reactor. The importance of the discharge intensity and the obvious catalytic effect of the hydrogen co-feed were observed.

Ethylene glycol (EG) is an important chemical which is widely used as an antifreeze, lubricant, plasticizer, surfactant, and a precursor for manufacturing polyester fibers and resins.[1] At present, ethylene oxidation is a universal industrial approach to produce EG. However, as crude oil resources shrink, the synthesis of EG using other alternative approaches such as the conversion of syngas to EG through dimethyl oxalate (DMO) attracts more and more interest.[1a,b,2] Dielectric barrier discharge (DBD) as well as other electrical discharge techniques have been used for methanol conversion, mainly aimed at obtaining hydrogen and syngas.[3–7] A trace amount of EG has been occasionally found in the product effluent,[3b,c] however, the direct synthesis of EG from methanol by an electric discharge method has not been formally reported so far.

An EG molecule can be formed by the coupling of two hydroxymethyl ($^{\bullet}CH_2OH$) groups, and the C–H bond dissociation of methanol can produce such groups. Therefore, if the C–H bond of methanol can be selectively dissociated by electric discharge, EG may be obtained as the main product by the direct coupling of $^{\bullet}CH_2OH$ groups. It would be very attractive. Unfortunately, the energy of C–H bonds is much higher than that of C–O bonds although it is smaller than that of O–H bonds in a methanol molecule, which means the selective activation of the C–H bond of methanol will be challengeable.

Recently, we have carried out a systematic study exploring the direct synthesis of EG from the plasma of methanol vapor, and encouraging results were obtained by using hydrogen as a carrier gas and a double dielectric barrier discharge (DDBD) reactor.

The DDBD reactor (reactor A) consists of a quartz cylinder and two metal electrodes. The high-voltage electrode was a stainless steel wire, which was covered with a quartz tube and placed along the axis of the cylinder. A soft metal wire or foil wound on the outer surface of the cylinder served as the ground electrode. Both the cylinder and the tube cover of the high-voltage electrode served as dielectric barriers for the discharge. The reactor was connected to an AC power supply which generated 16.8 kV sinusoid waveform output voltage at a frequency of 12.0 kHz. The power regulation was achieved by changing current at basically fixed voltage. Methanol was fed with hydrogen into the reactor, it was first pumped at a rate of 1.2 mL liquid per h into an evaporator, and then the vapor of methanol was brought forward by hydrogen at the exit of the evaporator. The flow rate of hydrogen co-feed was controlled using a mass flow meter. The molar ratio of hydrogen and methanol was about 7 unless otherwise stated. The discharge reaction was *in situ* diagnosed by optical emission spectroscopy (OES). The effluent of the reactor was sampled by a ten-way valve and analyzed online using a gas chromatograph equipped with a flame ionization detector (FID) for the detection of organics and a thermal conductivity detector (TCD) for the detection of CO and CO_2. To guarantee the sampling reality, the line pipe and the valve between the reactor and the chromatograph was kept at 503 K.

In order to investigate the effect of reactor structure on the synthesis of EG, reference reactors B and C (see Fig. 3) were used. Reactor B was a single dielectric barrier discharge reactor (SDBD) using a naked stainless steel wire as its HV electrode. Reactor C was also a DDBD reactor but its ground electrode was tap-water recycled in a water jacket to keep the temperature at 80 °C; the detailed configuration of reactors B and C has been described in our previous reports.[8]

As shown in Fig. 1, the discharge reactor A was excellent for the direct synthesis of EG from methanol. During a 100 hour continuous discharge operation, the methanol conversion and ethylene glycol selectivity were fairly stable. The average values of methanol conversion and EG selectivity were 15.77% and 71.53%, respectively. The other main co-products obtained were C_2H_5OH, n-C_3H_7OH, CH_4 and CO, and their selectivities were 4.02, 0.63, 6.57 and 14.14, respectively. Hydrogen was certainly produced, its selectivity can

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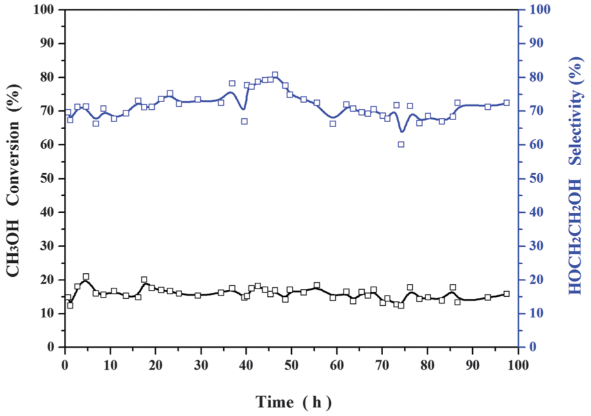

Fig. 1 Methanol conversion and ethylene glycol selectivity *versus* time in discharge reactor A.

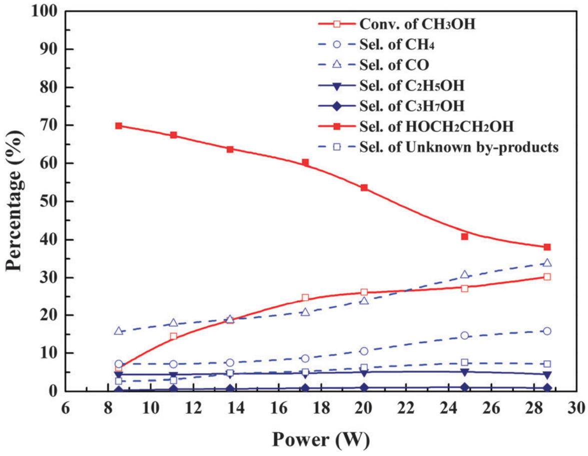

Fig. 2 Effect of input power on the conversion of CH_3OH in discharge reactor A.

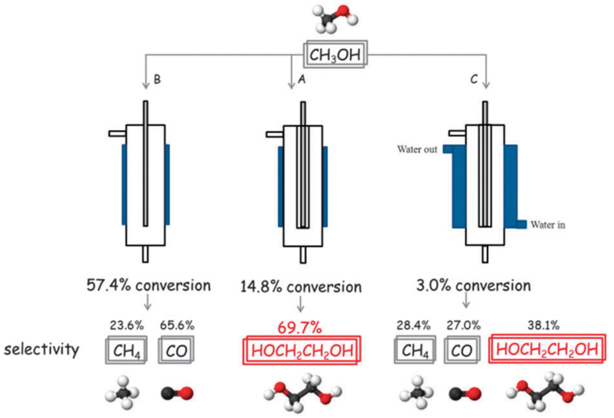

Fig. 3 Configuration schematic of different discharge reactors and main products obtained with them during the conversion of methanol (A) DDBD-metal ground electrode; (B) SDBD-metal ground electrode; (C) DDBD-water ground electrode.

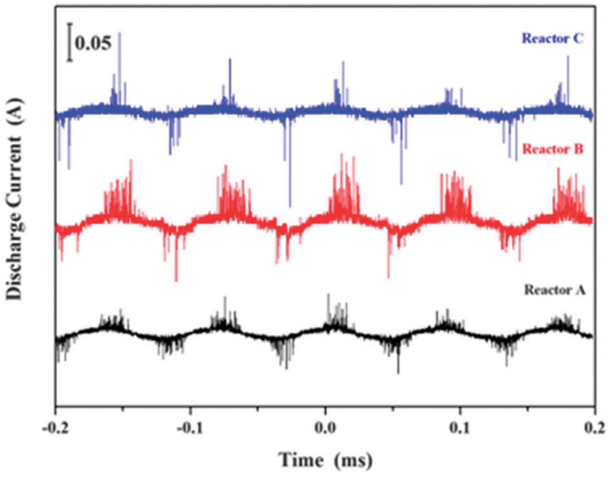

Fig. 4 Current waveforms of the different discharge reactors during methanol conversion under the same conditions.

be worked out according to the hydrogen balance (not measured because hydrogen was a co-feed in the discharge reaction). The average total electric power input into the reactor was approximately 11.3 W. Therefore, the ethylene glycol formation efficiency was estimated to be 42.55 g kW h^{-1}.

Fig. 2 shows that the discharge power had a significant effect on the EG selectivity. For example, the plasma reaction gave 6.1% of methanol conversion and 69.8% of EG selectivity when the input power was 8.5 W. As the input power increased from 8.5 W to 28.6 W, the conversion of methanol increased from 6.1% to 30.2%, while the EG selectivity decreased from 69.8% to 38.0%. The elevation of input power mainly resulted in the increase in CO and CH_4 by-products.

Fig. 3 indicates that the configuration of the discharge reactor also had very strong influence on the conversion of CH_3OH. Under the same conditions, the highest EG selectivity (69.7%) was obtained with reactor A which also gave moderate methanol conversion (14.8%). Reactor B gave the highest CH_3OH conversion (57.4%), but the lowest EG selectivity (6.0%), CO and CH_4 were the main products, their selectivities were 65.6% and 23.6%, respectively. While reactor C showed the lowest methanol conversion (3.0%) and moderate EG selectivity (38.1%). From Fig. 4 it can be seen that the number and intensity of current pulses of the different reactors vary in the following sequence: reactor B > reactor A > reactor C. This means that the discharge intensity decreased in the sequence, because the number and intensity of current pulses are proportional to the electron density.

Therefore, we believe that the discharge intensity of a reactor is an important factor which affects the product distribution. It is clear that the discharge intensity is decided by the structure of a reactor, and it could be regulated to some extent by changing the input power for a given reactor. According to the literature,[9] the conversion of methanol can proceed *via* the following seven radical paths:

Reaction		Calculated energy/ kcal mol^{-1} (298.15 K)
$CH_3OH \rightarrow CH_3 + OH$	(1)	81.51
$CH_3OH \rightarrow CH_2OH + H$	(2)	94.57
$CH_3OH \rightarrow CH_3O + H$	(3)	100.78
$CH_3OH \rightarrow CH_2O + H_2$	(4)	88.62
$CH_3OH \rightarrow$ *cis*-HCHO + H_2	(5)	85.02
$CH_3OH \rightarrow$ *trans*-HCHO + H_2	(6)	84.45
$CH_3OH \rightarrow {}^1CH_2 + H_2O$	(7)	83.60

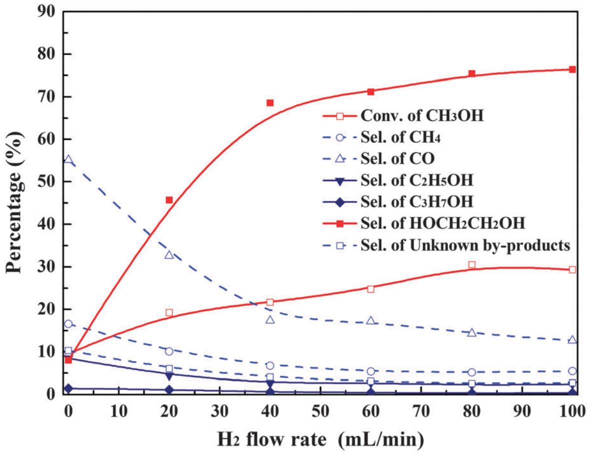

Fig. 5 Effect of the H_2 flow rate on the conversion of CH_3OH with reactor A.

Among them, eqn (2) is a C–H bond dissociation process which generates a CH_2OH intermediate, the recombination of the CH_2OH intermediate produces EG. The other paths will lead to CH_4 and CO by-products. The energy barrier for these reactions is approximately 80–100 kcal mol^{-1}. Generally, the electron energy of non-equilibrium plasma ranged from 23.06 to 230.61 kcal mol^{-1}. This means that any of these reaction paths of methanol is possible in the present electric barrier discharge. As mentioned above (Fig. 3 and 4), reactor A that had moderate discharge intensity showed the best EG selectivity. This is in line with the results of theoretical calculation, which shows that eqn (2) has a medium level of energy barrier.

In addition, the significant effect of the hydrogen co-feed on the DBD discharge of methanol was observed. As indicated by Fig. 5, in the absence of hydrogen the discharge of methanol vapor in reactor A mainly produced CO and CH_4, their selectivities were 55.2% and 16.6%, respectively. While the selectivity of EG was only about 8.0%. As the flow rate of hydrogen increased from 0 to 40 mL min^{-1}, the CO selectivity rapidly decreased from 55.2% to 17.4%; the selectivities of CH_4 and other by-products also obviously decreased. Consequently, the EG selectivity quickly increased from 8.0% to 68.5%. A continuous improvement in the EG selectivity can be seen when the hydrogen flow rate is further increased. It is interesting that the conversion of methanol also increased with the hydrogen flow rate up to 80 mL min^{-1}. This means that the introduction of hydrogen can selectively accelerate the C–H bond dissociation of methanol. The *in situ* OES diagnoses (shown in Fig. S1–S3, ESI†) indicated that the introduction of the hydrogen co-feed not only enhanced the discharge of methanol, but also increased the $H^{\bullet}$ radical concentration in the plasma. The $H^{\bullet}$ radical can abstract hydrogen from the methyl group to generate the $^{\bullet}CH_2OH$ intermediate: $CH_3OH + H^{\bullet} \rightarrow {}^{\bullet}CH_2OH + H_2$. According to the literature,[10] the methyl hydrogen atoms are preferentially abstracted rather than alcoholic hydrogen when the $H^{\bullet}$ radical reacts with methanol; the reaction has an activation energy of 11.78 kcal mol^{-1},[9b] which is very low compared with those of the other possible reactions of methanol plasma mentioned above. It is worth mentioning that the role of the hydrogen co-feed in the methanol plasma reactions seems to be very similar to that of a molecular catalyst. It provides $H^{\bullet}$ radicals as active sites under discharge conditions, and the active sites selectively activate the C–H bonds of the methyl group resulting in the abstraction of hydrogen atoms from the group. The coupling of the $^{\bullet}CH_2OH$ formed gives an EG product. The hydrogen molecules take part in the reaction, but are recovered without consumption after reaction.

In summary, EG can be selectively synthesized through the one-step plasma reaction of methanol using a DDBD reactor. It was found that the moderate discharge intensity benefited the high selectivity of EG. The discharge intensity can be optimized by the configuration of the reactor and the discharge conditions. Furthermore, the hydrogen co-feed can significantly improve the methanol conversion and EG selectivity. In the reaction, hydrogen molecules play an obvious catalytic role by releasing a $H^{\bullet}$ radical which selectively accelerated the formation of the $^{\bullet}CH_2OH$ intermediate *via* the abstraction of methyl hydrogen of methanol.

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