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Plasma catalytic collaborative decomposition of methanol to hydrogen production



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ABSTRACT

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Keywords: Hydrogen production Methanol Dielectric barrier discharge Non-equilibrium plasma A novel plasma-assisted methanol decomposition kinetic model is developed through experimental investigations which can reasonably predict the species concentration at different voltages. The methanol decomposition does not occur at 600 K without plasma, whereas it initiates at 450 K under plasma conditions. This is attributed to the new reactions between the high-energy electrons and Ar^{*} with the methanol under the electric field. However, under plasma alone, H₂ selectivity is low as the formation of CH₃, which decreases the fluxes of H-abstraction reactions, such as CH₂OH + H=CH₂O + H₂. With plasma-catalyst, 15 % increase in H₂ selectivity and 12 % increase in CH₃OH conversion are achieved at 493 K and methanol tends to be converted more to CH₃O than to CH₂OH or CH₃ compared with plasma alone, which increases the CH₃O adsorbed on the surface of catalyst, facilitating the chain reaction (CH₃O→CH₂O→CO + H₂) and inhibits the conversion of CH₃O/CH₂OH to CH₃ and CH₂ by plasma, and as a result, the CH₃OH conversion rate and H₂ yield rate increase.

1. Introduction

Global industrialization and economic growth have significantly increased energy demand [1,2]. However, the high fuel consumption and emissions from fossil fuels necessitate an urgent transition to low-carbon and zero-carbon energy sources [3].

Hydrogen is recognized as a promising energy carrier due to its high energy density and zero carbon emissions. However, conventional hydrogen production methods heavily rely on fossil fuels, while the safety concerns and high costs associated with liquid hydrogen transportation hinder its widespread adoption. Utilizing liquid fuels, such as methanol, as hydrogen sources offers an effective solution to these challenges. Methanol is an ideal candidate for hydrogen storage owing to its ease of transportation, high carbon-to-hydrogen ratio, abundant availability, and low cost. Additionally, methanol can be readily converted into hydrocarbons and related products [4-6]. However, there are still some challenges in the current application of methanol. Although methanol decomposition decreases direct CO₂ emissions, the CO production is highly susceptible to fuel cell poisoning; while the use of methanol steam reforming can control CO emissions but the heat demand and power consumption increases the whole life cycle carbon emissions. Zhang et al. [7] proposed an innovative carbon cycle system integrating CO₂ hydrogenation to methanol with methanol reforming to hydrogen, and the results showed that the life cycle carbon emissions of the system were $6.3 \text{ kgCO}_2/\text{kg H}_2$, classifying the produced hydrogen as low-carbon hydrogen rather than green hydrogen, and larger CO₂ emissions was caused by electrical and thermal equipment. Regarding energy consumption, the exergy loss of its system is as high as 204.24 GJ/h, which is attributed to the large amount of electrical energy required to overcome the strong chemical bonds within the water molecule.

Traditional methods like methanol pyrolysis and thermal catalysis are energy-intensive, require large equipment, and have long start-up times. In contrast, non-equilibrium plasma technology offers a promising alternative with compact equipment, mild reaction conditions, and rapid response, is highly suitable for hydrogen production in transportation [8–10]. This process generates high-energy electrons at room temperature, producing numerous excited species and reactive particles that significantly lower the initial reaction temperature of fuels [11–14].

Studies on plasma assisted methanol decomposition have been conducted in literatures. Takehiko et al. [15] investigated the methanol decomposition in non-equilibrium plasma using experimental and numerical analyses, which proved the presence of excited state atoms of O and N, as well as excited state molecules such as OH, $N_2(B^3\Pi_g)$ and N_2 ($A^3\Sigma_u^+$). Hajime et al. [16] investigated the hydrogen production characteristics of water, methane and methanol using different

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non-equilibrium plasma reactors. The results showed that the hydrogen yield was in the order of methanol > methane > water. At the fixed specific energy density, a higher gas flow rate results in a higher hydrogen yield in the reactions involving the substrates mentioned above. Shigeru et al. [17] investigated the effect of reactor type and power supply parameters on the reforming characteristics of methanol, and the results indicated that the methanol conversion rate was expressed as a function of the energy density of the reactor. Zhang et al. [18] developed a DC rotating gliding arc plasma reactor for the decomposition of methanol and discussed the possible reaction pathways during the methanol decomposition process. The experimental results showed that the plasma-assisted methanol decomposition process produces reactive components may be crucial in the methanol conversion process. Gong et al. [19] simulated the plasma-assisted methanol oxidation process and showed that O atoms play a key role in shortening the ignition delay time and that the plasma promotes the fast reaction in methanol-air mixtures. Existing experimental and simulation results have shown that the electrons and excited species are important for methanol consumption, but the mechanism and reaction pathways are not explained in detail, therefore further optimization of the kinetic model of the chemical reaction of plasma-assisted methanol decomposition is required.

The non-equilibrium plasma facilitates chemical reactions that are thermodynamically unfavorable under low temperatures. However, the selectivity of converted CH₃OH towards H_2 was found to be low with plasma, and the best results in terms of the conversion rate of CH₃OH and the selectivity of H_2 can be achieved by the combination of high efficiency of plasma and the selectivity of catalyst [20].

Catalyst research for the decomposition of methanol has focused on Cu/ZnO catalysts, which have been attributed to their effectiveness in reforming of methanol and high hydrogen selectivity at low temperature [21]. Precious metal catalysts such as Pt, Pd and Au show better thermal stability, but the expensive cost limits their application in production. Non-precious metal catalysts are cheaper, but Fe-based catalysts have much lower activity at low temperature than Cu-based catalysts, and Ni-based catalysts are also not suitable for low-temperature decomposition of methanol because of their lower hydrogen selectivity. It was demonstrated by experiment that methanol is adsorbed on the surface of the Cu catalyst and subsequently decomposed to CH₃O [22], however the pathways for the generation of CO and H₂ are still highly controversial [21]; Wang et al. [23] investigated the electron transfer behavior of adsorbed CH₃OH occurring during the photocatalytic hydrogen production from CH₃OH, where the special structure formed by CuO/WO₃ provided new activation sites (Cu₂⁺ and VOs) for the adsorption of methanol molecules. Methanol provides electrons to the catalyst surface, and the oxidation process promotes the cleavage of OH and CH bonds, a process that generates more protons and therefore promotes a significant increase in hydrogen production efficiency. Zhang et al. [24] suggested that ZnO and Al₂O₃ could increase the dispersion of copper and inhibit the sintering phenomenon during pre-reduction and hydrogen production, and that these metal oxides might affect the acid/base properties of the catalysts to promote the adsorption of methanol and its intermediates on the surface of the catalysts for stepwise dehydrogenation.

There are fewer studies on plasma-catalyst decomposition of methanol. Lee et al. [25] investigated the methanol steam reforming by coupling dielectric barrier discharge (DBD) with a Cu/ZnO/Al₂O₃ catalyst to produce non-thermal plasma on the catalyst. The effects of temperature, feed rate, voltage, frequency, and waveform on methanol conversion were investigated, and the results showed that under discharge conditions, methanol conversion increased with the increase of discharge voltage and frequency; square waves were more effective than sinusoidal waves in methanol conversion; and the electric field enhanced the intensity of the reactants' absorption at the active sites on the catalyst surface. Ge et al. [26] compared the methanol steam reforming with and without a Cu/Al₂O₃ catalyst and the result showed

that with plasma-catalyst, methanol conversion and hydrogen yield were increased by 17.9 % and 21.9 %, respectively, compared to the plasma alone, which substantially improved the energy utilization efficiency. VJ Rico et al. [27] conducted an experimental study of plasma synergistic Cu-Mn catalyst assisted methanol decomposition and showed that the methanol conversion of plasma-catalyst was higher than the sum of the methanol conversions of catalysis alone and plasma alone. Similar studies [28-33] have shown that the synergistic effect produced by plasma -catalyst improves the conversion of methanol. However, there are few studies using nanosecond pulsed discharges to stimulate, in particularly, there is a lack of data on the intermediates of methanol cracking at different voltages and frequencies, and the mechanism of the reaction between methanol and intermediates with the electrons and the excited state as well as the synergistic effect between the plasma and the catalysts under the conditions of atmospheric and low temperature is not yet clear.

Therefore, this work addresses the insufficient research on plasmacatalyst methanol decomposition under low temperature and atmospheric conditions, such as the shortage of data on species mole fractions under different electric field parameters, the insufficient validation of the plasma-promoted methanol decomposition mechanism and the insufficient kinetic analysis of the key species, as well as the lack of explanation of synergistic effects. First, DBD discharge experiments under nanosecond pulsed discharge excitation were carried out at atmospheric pressure and 453–593 K. The concentrations of products under plasma, catalyst, and plasma-catalyst were measured under different electric field parameters. Second, a novel and detailed plasma kinetic model is validated and provides path analysis for excited state and key radicals in the discharge and afterglow process. Third, based on the above pathways, the influence of CH_3O formation on H_2 selectivity under synergism effect is discussed and revealed.

2. Experimental method

2.1. Experimental setup

Fig. 1 is the schematic diagram of the experimental setup for the plasma-catalytic decomposition of methanol. The experimental setup mainly consisted of a double-layer dielectric coaxial DBD reactor, nanosecond pulsed power supply, mass flow controller, and measurement system. The reactor is composed of a quartz tube with coaxially stainless-steel electrode built in and a concentric copper electrode attached to outside of the quartz tube. The catalyst was placed inside the reactor with quartz wool in two ends. Considering the complete gasification of methanol and the optimal reaction temperature of the catalyst, an electric furnace was used to maintain a constant temperature in the reactor in this work. And the pipeline was heated to 423 K to achieve the complete gasification. Methanol was injected into the vaporizer using a infusion pump and carried by the dilution gas, argon. The purity of methanol was 99.7 %, and the Ar were supplied using cylinders with 99.999 % purity. The plasma experimental conditions are listed in Table 1. Although higher methanol concentrations are required for industrial operation, the focus of this study is to establish the underlying chemical reaction kinetics, therefore an initial concentration of 1 % methanol was set. Ar as an auxiliary gas can contribute to the enhancement of methanol decomposition and hydrogen production by generating highly reactive particles during the discharge process, participating in complex chemical reactions and providing additional reaction pathways.

This study employed a novel copper-zinc-aluminum (Cu–Zn–Al) catalyst system, which has been extensively characterized in the literature and the diagnostic results from the literature [34] can be seen in the Supplementary material. And the copper oxide (CuO) is the primary active component, supported by zinc oxide (ZnO) and aluminum oxide (Al₂O₃) as structural spacers. Through an innovative coprecipitation preparation method, the developed catalyst exhibits a significantly



Fig. 1. The schematic diagram of the flow reactor.

Table 1Experimental conditions.

CH ₃ OH(%)	Flow rate (SCCM)	T(K)	Voltage (kV)	Frequency (kHz)
1	1000	453-593	6	15
1	1000	453–593	8	10/15

larger effective copper surface area along with enhanced catalytic activity and long-term operational stability. The characterization results were referenced from Lee et al. [34] and more details are displayed in the Supplementary material. The concentrations were analyzed online by GC combined with mass spectrometry using a thermal conductivity detector (TCD) and flame ionization detector (FID). The measurement errors were 5 % for organic products such as CH₃OH, CH₄ and C₂H₄ and 10 % for CO and H₂. The CH₃OH, H₂, CO, CH₄ concentration profiles were obtained based on the calibration experiments for each species, with experimental uncertainties estimated to be within 10 %. [35]. The reactoer is composed of a quartz tube with coaxially stainless-steel electrode built in and a concentric copper electrode attached to outside of the quartz tube. The reactor is 450 mm in length, 15 mm in inner diameter, and 2 mm in wall thickness. The high-voltage electrode is 30 mm in length, 19 mm in inner diameter, and 2 mm in thickness. The diameter of the inner electrode is 3 mm as showed in Fig. 2.

The conversion ratio of methanol (*X*) and the production ratios of hydrogen, carbon monoxide and methane (*Y*), were calculated using the following equations:

$$X_{\rm CH_3OH} = \Delta C_{\rm CH_3OH} \left/ C_{\rm CH_3OH}^{\rm in} \times 100\% \right. \tag{1}$$

$$Y_{\rm H_2} = C_{\rm H_2}^{\rm out} / \left(2 C_{\rm CH_3OH}^{\rm in} \right) \times 100\%$$
 (2)

$$Y_{\rm CO} = C_{\rm CO}^{\rm out} / C_{\rm CH_3OH}^{\rm in} \times 100\%$$
(3)

$$Y_{\rm CH_4} = C_{\rm CH_4}^{\rm out} \left/ C_{\rm CH_3OH}^{\rm in} \times 100\% \right. \tag{4}$$

Where $C_{\text{H}_2}^{\text{out}}$ is hydrogen concentration from the outlet. C_i^{out} , C_i^{in} are the concentration of *i* from the outlet and inlet, respectively.

The selectivity for hydrogen, carbon monoxide, and methane (*S*) were calculated using the following equations:

$$\begin{split} S_{\rm H_2} = & C_{\rm H_2}^{\rm out} \left/ \left(C_{\rm H_2}^{\rm out} + 2C_{\rm CH_4}^{\rm out} + 2C_{\rm C_2H_4}^{\rm out} + C_{\rm C_2H_2}^{\rm out} + 3C_{\rm C_2H_6}^{\rm out} + 4C_{\rm C_3H_8}^{\rm out} \right. \\ & \left. + C_{\rm H_2O}^{\rm out} \right) \times 100\% \end{split}$$
(5)

$$S_{\rm CO} = C_{\rm CO}^{\rm out} / \left(C_{\rm CO_2}^{\rm out} + C_{\rm CO}^{\rm out} + C_{\rm CH_4}^{\rm out} + 2C_{\rm C_2H_4}^{\rm out} + 2C_{\rm C_2H_2}^{\rm out} + 2C_{\rm C_2H_6}^{\rm out} + 3C_{\rm C_3H_4}^{\rm out} \right) \times 100\%$$
(6)

$$S_{CH_4} = C_{CH_4}^{out} / \left(C_{CO_2}^{out} + C_{CO}^{out} + C_{CH_4}^{out} + 2C_{C_2H_4}^{out} + 2C_{C_2H_2}^{out} + 2C_{C_2H_6}^{out} + 3C_{C_3H_4}^{out} \right) \times 100\%$$
(7)



Fig. 2. DBD plasma-catalytic flow-tube reactor.

2.2. Electrical discharge characteristics

Chang et al. [36] showed that the introduction of easily ionizable gases such as ammonia and methane into Ar can help to trigger the Penning effect, which allows ions to be produced by collisions of moving electrons with neutral molecules, ultimately leading to the generation of a long plasma plume in the ambient environment with reactions Ar + $e^* \rightarrow e + e + Ar^+$ and $Ar^* + e^* \rightarrow e + e + Ar^+$. Compared with He, N₂ and CO₂, Ar shows the easiest ionization and produces the highest current value after breakdown [37], because of the low ionization potential (~15.8 eV). Also, in plasma-assisted CH₄ pyrolysis experiments, Ar as a dilution gas breaks down more easily than N₂ [38], and CH₄ is broken down in Ar at lower voltage than in N₂. Therefore, Ar was chosen as the dilution gas for this study. More detail information about the voltage waveforms and energy input can be found in the Supplementary material.

3. Numerical method and kinetic model

3.1. Simulation method

A coupled plasma and combustion chemistry solver (CPCC) [39] by combing the ZDPlaskin code [40] with combustion dynamics solver CHEMKIN [41] has been developed on the basis of Hybrid Plasma and Combustion code [42]. In this work, we use the CPCC code to simulate the nanosecond pulsed discharge-assisted methanol decomposition and analyze the microscopic chemical reaction kinetics. The Poisson equation is not solved in this model, so it is assumed that the deposited energy in plasma is an adjustable parameter that controls the discharge duration.

3.2. Chemical kinetic model

A detailed mechanism for the kinetics of the low-temperature atmospheric pressure plasma-assisted CH₃OH (1 %)/Ar (99 %) mixture decomposition was developed in this work. The mechanism consists of two parts, the ground state kinetic mechanism and the plasma kinetic mechanism, with 48 components (Table 2) and 333 reactions. The ground state dynamics mechanism is simplified based on GRI Mech 3.0 [43] to save computational resources, and the results show that it can predict the experimental data well. The plasma mechanism considers 114 reactions, including electron collision reactions (vibrationally excited and electronically excited reactions), relaxation reactions of excited states, and electron-ion recombination reactions. Electron collision reaction rates were obtained by solving the Boltzmann equation by the BOLSIG + solver [44]. The collision cross sections for Ar and H₂ were obtained from the Phelps database [45] in the Lxcat database, the collision cross sections for O were obtained from the Morgan database [46] in the Lxcat database. However, the electron collision cross section for CH₃OH is not yet published, so in this work, the electron collision reaction rate for methanol was estimated based on the literature [47] which is important for initial consumption of CH₃OH. For the vibrational excited state species, vibrational-translational (VT) relaxation, vibrational-vibrational (VV) energy transfer and vibrational

Table 2

Species in the plasma-assisted CH₃OH/Ar decomposition model.

Molecules	Radicals	Excited species	Charged species
H ₂ , H ₂ O, O ₂ , CH ₄ , CO, CH ₂ O, CH ₃ OH, C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₈ , CH ₂ CO, CH ₃ CHO, Ar	H, O, OH, HO ₂ , C, CH, CH ₂ , CH ₃ , HCO, CH ₂ OH, CH ₃ O, C ₂ H, C ₂ H ₅ , HCCO, HCCOH, C ₃ H ₇ , CH ₂ CHO	H ₂ (v1), H ₂ (v2), H ₂ (v3), O (1D), O (1S), Ar*	$O^+,H^+, H_2^+, Ar^+, CH_3OH^+, C^+, CH_3OH^+, CH_2^+, CH_3^+, CH_4^+, e$

excited species reacted with neutral radicals were considered. In this work, the dissociation reaction of Ar* with CH₃OH and the collisional dissociation reaction of electrons with CH₃OH have been updated for the first time based on literatures [47–49]. Levko et al. [47] determined the concentration of the components in the discharge according to a method of calculating the average introduced power based on the whole volume of the discharge, and proved the method is justified. Quenching reactions of the electronically excited state Ar* with CH₃OH, CH₄, and C₂H₆, etc., as well as ionic reactions associated with the positive ions H⁺, H⁺₂, CH⁺, CH⁺₃ and electron-ion recombination reactions were considered. The initial plasma reactions of CH₃OH renewed in this work are summarized in Table 3.

4. Results and discussion

4.1. Plasma decomposition of CH₃OH

4.1.1. Effect of discharge voltage

Fig. 3 depicts the measured mole profiles of CH₃OH under conditions of 0 V and 8000 V at the temperature range of 453–593 K. The initial reaction temperature of CH₃OH decreases significantly with plasma assisted and the concentration of methanol decreases from 8600 ppm to 7000 ppm at 8000 V from 453 K to 593 K, which contrasts with no CH₃OH consumption without plasma. This demonstrates the effectiveness of plasma on the methanol conversion. And the active particles such as electrons, excited species and reactive radicals increases the chemical reaction rate of CH₃OH consumption.

Fig. 4 illustrates the CH₃OH conversion rate and production rate of H₂ and CO at different voltages at 453–593 K. The conversion of CH₃OH and hydrogen yield increase with temperature, especially under higher voltage conditions. Methanol is decomposed under 6000 V condition, with a minimum conversion rate of 7 % and a maximum value of 10 % at the rage of 473 K–593 K. A larger increase is observed for 8000 V (17 %–29 %). This is because the mean electron energy increases with voltage, thus leading to more radicals and other active particles that promote the CH₃OH consumption.

New reaction pathways such as electron impact reactions, excited species reactions and some recombination reactions are introduced into the decomposition system due to the active species produced by non-equilibrium plasma, which promote the consumption of CH_3OH significantly. And this results in the formation of key radicals such as CH_3 , CH_2OH , CH_3O ((R1), (R2) and (R3)). During this process, reactive radicals, such as H and OH, are rapidly generated with higher field intensities.

	$CH_3OH + e \rightarrow CH_3 + OH + e$	(R1)
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 $CH_3OH + e \rightarrow CH_2OH + H + e$ (R2)

$$CH_3OH + e \rightarrow CH_3O + H + e$$
 (R3)

4.1.2. Effect of discharge frequency

Fig. 5 shows the concentrations of the primary products for different frequency parameters. The higher the frequency, the larger the energy input per unit of time into the system. The methanol conversion and

Table 3

Selected important reactions of CH3OH initial reactions renewed in present model.

No.	Reaction	Rate constant, (cm ³ s ⁻¹)	Refs.
R1	$CH_3OH + e \rightarrow CH_3 + OH + e$	4.7E-15	[47]
R2	$CH_3OH + e \rightarrow CH_2OH + H + e$	5.0E-15	[47]
R3	$CH_3OH + e \rightarrow CH_3O + H + e$	5.0E-15	[47]
R4	$CH_{3}OH + Ar^{*} \rightarrow CH_{2}OH + H + Ar$	6.6E-10	[48,49]
R5	$CH_{3}OH + Ar^{*} \rightarrow CH_{3}O + H + Ar$	6.6E-10	[48,49]
R6	$CH_{3}OH + Ar^{\star} \rightarrow CH_{3} + OH + Ar$	6.6E-10	[48,49]



Fig. 3. Measured methanol concentration at plasma and no plasma conditions.



Fig. 4. Methanol conversion rate and hydrogen production rate at different applied voltages.

yields of hydrogen and carbon monoxide increases notably with the increase of frequency. Specifically, methanol conversion rates are 13.3 % and 18.7 % at the frequency of 10 kHz and 15 kHz, respectively, at 473 K. As the temperature increases, the methanol conversion exhibits a steady rise. Overall, adjusting the voltage parameters has a greater impact on improving the efficiency of methanol consumption.

4.2. Model validation

Based on the effects of voltage and frequency on methanol decomposition above, it can be easily seen that voltage shows a greater effect, therefore the simulations for different voltages in the same temperature window were performed to verify the accuracy of the model.

Fig. 6 presents the experimental and simulation results of products and reactants concentrations in plasma-assisted methanol decomposition as a function of temperature at 8000 V. Fig. 6(a) shows that, the concentration of CH_3OH slightly decreases and the mole fraction of H_2 and CO increase with the temperature. In contrast, CH_4 shows a decline trend as the temperature rises. Regarding the overestimation of C_2H_6 prediction, it may be due to: (1) The underestimation of C_2H_6 consumption reactions in the discharge mechanism. Detailed C_2H_6 consumption reactions are considered in this kinetic model (reactions such as $H + C_2H_6=C_2H_5+H_2$, $OH + C_2H_6=C_2H_5+H_2O$ ), and the reaction rate constants of these reactions have been extensively studied. However, the mechanism of discharge particles reacting with C_2H_6 remains incomplete, thus the C_2H_6 consumption reactions are underestimated. (2) It was observed in the experiments that in addition to products such as CH_4 and C_2H_6 , other organic compounds were also generated, most likely products such as methyl formate. But the subset of reactions is complex and lacks high accurate reaction rate constants, which limits the accuracy of the model.

Overall, the formation of species obtained by present model agrees well with the experimental measurements of most species, which indicates that the kinetic model is suitable to calculate other parameters.

4.2.1. Methanol decomposition chemistry

To investigate the effect of plasma on the products, a rate of production (ROP) analysis has been conducted in Supplementary materials. With the effect of plasma, active species like Ar^* and high-energy electrons are generated, which collide with methanol to produce CH₂OH, CH₃O, and CH₃, accompanied by radicals H and OH that also react with methanol. Plasma reduces the activation energy of the reactions by providing new reaction pathways to generate radicals faster, thus significantly enhances the CH₃OH conversion.

 $CH_3OH + Ar^* \rightarrow CH_2OH + H + Ar$ (R4)

$$CH_3OH + Ar^* \rightarrow CH_3O + H + Ar$$
 (R5)

$$CH_3OH + Ar^* \rightarrow CH_3 + OH + Ar \tag{R6}$$

$$CH_3OH + H = CH_2OH + H_2 \tag{R7}$$

$$CH_3OH + H = CH_3O + H_2 \tag{R8}$$

$$CH_3OH + OH = CH_2OH + H_2O$$
(R9)

 CH_2OH and CH_3O are formed by the H-abstraction reaction to produce CH_2O , which is eventually dehydrogenated to HCO, accompanied by the production of H_2 . Therefore, the electrons and Ar^* generated by the discharge are effective in initiating the reaction and building up the radical pool at low temperatures.

$$CH_2OH + OH = CH_2O + H_2O \tag{R10}$$

$$CH_2OH + H = CH_2O + H_2 \tag{R11}$$

$$CH_2OH + H = CH_2 + H_2O \tag{R12}$$

$$CH_3O + H = CH_3 + OH \tag{R13}$$

$$CH_3O + H = CH_2O + H_2$$
 (R14)

$$CH_3O + H = CH_2 + H_2O$$
 (R15)

$$CH_2O + OH = HCO + H_2O \tag{R16}$$

$$CH_2O + H = HCO + H_2 \tag{R17}$$

To illustrate the initial reactions in plasma-assisted CH_3OH decomposition, time evolutions of excited species, radicals and electron mole fractions at 493 K and 8000 V is carried out in Fig. 7. In the discharge stage, electron impact reactions are the primary process to the formation of various species, then the electronically excited species start to quench which promotes the production of radicals and ions and the later dissociative recombination of electrons and fuel ions.

4.2.2. Effect of voltage

Fig. 8 compares the pathway fluxes for the detailed reaction kinetics of plasma-assisted CH_3OH consumption under different voltages at initial temperature of 493 K. The increased electric field promotes the



Fig. 5. Methanol conversion rate and hydrogen production rate at different discharge frequencies.



Fig. 6. Measured (symbols) and simulated (lines) mole fraction profiles of plasma-assisted methanol decomposition Kinetics analysis of plasma on CH_3OH decomposition.

collisional dissociation reaction between Ar* and methanol, leading to a rapid increase in the concentration of radicals H, O and OH in the system, which further promotes the reaction between H and OH with CH₂OH, CH₃O and CH₂O ((R10)-(R17)). Therefore, increasing the voltage significantly increases the methanol conversion. The number density of H, O and OH is calculated and displayed in Fig. 9(a), indicating that increasing the voltage has a significant influence on active radicals (H, O and OH). The number density of H of 8000 V is 3 times higher than that of 6000 V condition, because the electron energy increases with field tensity (Fig. 9(b)), which promotes the collision of electron and neutral species, therefore, radical concentrations such as H, O, and OH exhibit an upward trend.

The electronically excited species Ar* also plays an important role in the system, therefore, the pathway flux of Ar is investigated in Supplementary materials. Ar* is produced by reaction (R18), and as the voltage increases from 6000 V to 8000 V, the flux increases from 92 % to 96 %, which implies that the increased electrical tensity improves the energy deposed in (R18), which promotes the initial consumption of CH₃OH.

$$Ar + e \to Ar^* + e \tag{R18}$$

4.2.3. Effect of initial temperature

Fig. 6 has showed the effects of different initial temperatures on methanol decomposition at 8000 V. At a given electric field, the conversion of CH₃OH and the yield of H₂ increase with initial temperature. To further explore the mechanism of temperature, a rate of product analysis is conducted under different initial temperature conditions. As shown in Fig. 10(a), (R7) exhibited only 4.3 % flux of methanol consumption at low temperature (493 K) but 15 % flux at high temperature (593 K) which has been demonstrated to be the mainly pathway in forming H₂, therefore increasing the voltage results in the increase of H₂. And Fig. 11(a) compares the H-abstraction reaction rate of methanol (R7) at different temperatures. The reaction rate increases by a factor of 2–3 with a temperature rise of 100 K, which greatly facilitates the initial consumption of methanol and the production of hydrogen.

For the decrease of methane with temperature, it is related to the main reaction that produces methane (R19). Fig. 10(b) compares the production pathways at 493 K and 593 K of methane, and (R19) accounts for 98 % and 82 % flux, respectively. The flux decreases at higher temperature because of the decline rate of (R19) which indicates that the increase of temperature is unfavorable for the conversion from methanol to methane, leading to the methane concentration drops with



Fig. 7. Time evolutions of excited species, radicals and electron mole fractions at 493 K and 8000 V.

temperature. As depicted in Fig. 11, reaction (R7) and (R19) compete with each other, and as temperature increases, H radicals are more likely to react with methanol rather than methane which results in the different concentration trends of CH_3OH , H_2 and CH_4 .

$$H + CH_3(+M) = CH_4(+M)$$
 (R19)

4.3. Plasma-assisted catalyst decomposition of methanol

4.3.1. Production of H_2 and consumption of CH_3OH

The trend of H_2 and CH_3OH mole fraction with temperature is shown for plasma, catalyst and plasma-catalyst in Supplementary materials. The H₂ production under plasma synergistic catalysis increases dramatically compared with the other two, and the consumption of methanol shows a similar trend. The mole fraction of methanol consumption under the catalyst alone shows a slight up trend with temperature, and the conversion is low. At the initial stage, both the yield of H₂ and consumption of CH₃OH increases with temperature, and this trend reverses with continually increasing temperature. This may due to that as temperature rises, the catalyst activity increases and a large number of radicals and intermediates generated by the plasma undergo Eley-Rideal reaction (reactions between chemisorption reactants and gas phase reactants), at this time, the synergistic effect of catalyst and plasma is positive and methanol consumption is increased; when the catalytic activity is further increased, the adsorption reactions and the primordial radical generation reactions compete with each other, which induces a negative effect resulting in lower methanol conversion rates and hydrogen yield rates as the study mentioned by Lee et al. [34]. And we will continue this study in the future to explain the mechanism.

4.3.2. The synergistic effect of plasma and catalyst

The synergistic effect of plasma with the catalyst is analyzed next, with an initial temperature of 493 K. As shown in Fig. 12, the selectivity of H_2 and CO is the lowest under plasma only, while CH_4 has the highest selectivity and CO_2 mole fraction is zero. For the catalyst alone, it results in 100 % H_2 selectivity, higher selectivity for both CO and CO_2 than plasma, and 0 methane selectivity, but the lowest conversion of methanol at 11 % only. Under the synergistic effect of plasma and catalysis, both CH_3OH conversion and H_2 selectivity behaves well, and the H_2 yield value is greater than the sum of plasma and catalyst alone. Therefore, at this initial temperature, the synergistic effect is shown as positive, which maintains a better product selectivity and significantly improves the methanol conversion and hydrogen production.

As mentioned before, plasma decomposition of methanol is mainly through the following reaction chains $CH_3OH \rightarrow CH_2OH/CH_3O \rightarrow CH_2O \rightarrow CH_2CO \rightarrow CH_2CHO \rightarrow HCO \rightarrow CO$. When the catalyst is introduced, the reaction pathway changed ((R20)-(R30), where S is the active site,



Fig. 8. The pathway of the decomposition process of CH₃OH at 493 K, 6000 V and 8000 V.



Fig. 9. Time evolution of (a) H, O, OH and (b) electron of different voltage.



Fig. 10. Pathways of (a) CH₃OH, (b) CH₄ at different initial temperatures of 8000 V.



Fig. 11. Comparison of reaction rate over time of different initial temperature. (a) H-abstraction reaction from CH₃OH. (b) The key reaction of forming CH₄.

which consists of two types: the S2 is the active site for methanol decomposition, and the S_{2a} is the site for adsorption of H [34]. Greeley et al. [50] conducted self-consistent periodic DFT-GGA calculations to investigate methanol decomposition pathways on the Cu(111) surface. Their study revealed the most stable molecular configuration during methanol decomposition as shown in Supplementary material. CH₃OH exhibits weak binding to the Cu(111) surface, with a binding energy of 0.16 eV. The O-H bond aligns approximately parallel to the surface which indicates that $CH_3O^{(2)}$ and $H^{(2)}$ is the primary intermediate formed via O–H bond cleavage. And CH₃O⁽²⁾ adopts a configuration with the C-O axis perpendicular to the surface with binding energy of 2.08 eV. These computational results conclusively establish CH₃O⁽²⁾ formation as the initial step in the methanol decomposition mechanism. Wang et al. [51] calculated the activation potential for methanol reactions on Ni surfaces and concluded that free radical substances can interact with metal surfaces much stronger than molecules due to the unpaired electrons of the free radicals. This work reported the adsorption energy to be $OH > H > CH_3O > HCO > CO > CH_3 > CH_2OH \gg CH_3OH$ as shown in

Supplementary material. Based on above studies, it is reasonable to hypothesize that adsorption occurs throughout the process and the generated radicals with higher binding energies are also adsorbed on the metal surface to facilitate the chain reaction.

After the series of H-abstraction reaction of methanol, CH₂O is produced in the reaction system which adsorbs on the active site of catalyst and reacts with CH₃O to generate CH₃OCH₂O (R22). And after a series of reactions ((R23)-(R29)), CO is generated with part of that further oxidized by O to form CO₂ (R30). For the production of H₂, a large amount of H is produced and then adsorbed at the active site to form $H^{(2a)}$ by reactions (R20)-(R28) and ultimately $H_2^{(g)}$ is generated by reaction (R31) and re-enter the system.

$$S_2 + S_{2a} + CH_3OH = CH_3O^{(2)} + H^{(2a)}$$
(R20)

$$CH_3O^{(2)} + S_{2a} = CH_2O^{(2)} + H^{(2a)}$$
(R21)

$$CH_3O^{(2)} + CH_2O^{(2)} = CH_3OCH_2O^{(2)} + S_2$$
(R22)



Fig. 12. Comparison of product selectivity and methanol conversion by plasma, catalyst and plasma-catalyst.

$$CH_3OCH_2O^{(2)} + S_{2a} = CH_3OCHO^{(2)} + H^{(2a)}$$
(R23)

 $CH_3OCHO^{(2)} = CH_3OCHO + S_2$ (R24)

 $CH_3OCHO^{(2)} + S_2 = CH_3O^{(2)} + CHO^{(2)}$ (R25)

 $CH_2O^{(2)} = CHO^{(2)} + H^{(2a)}$ (R26)

 $CHO^{(2)} + S_{2a} = CO^{(2)} + H^{(2a)}$ (R27)

 $CHO^{(2)} = CO^{(2)} + H^{(2a)}$ (R28)

 $CO^{(2)} = CO^{(g)} + S_2$ (R29)

 $CO^{(g)} + O^{(2)} = CO_2^{(g)} + S^{(2)}$ (R30)

$$2H^{(2a)} = H_2^{(g)} + 2S^{(2a)}$$
(R31)

Combined with plasma-assisted methanol decomposition reactions, the possible pathways for plasma-catalyst decomposition of methanol are shown in Fig. 13. On the on hand, part of methanol reacts with active particles such as high-energy electrons and excited states to be dissociated into CH₂OH, CH₃O, and CH₃. As for the catalysis, CH₃O⁽²⁾ is the primary product. Wang et al. [51] calculated the bond energies of CH₃OH and arrived at energy barriers of 120 kJ/mol for the C–H bond breaking, 169 kJ/mol for the C–O bond breaking, and the energy barrier of the O–H bond breaking for 39 kJ/mol, the O–H bond breaking being much smaller than the former two as shown in Supplementary material.

Then intermediates CH₂OH and CH₃O are dehydrogenated by

plasma to produce radicals such as CH₂O and CH₂, while CH₃O⁽²⁾ is adsorbed on the active site with H^(2a). Through a series of chains reactions in plasma both CH₃O and CH₂OH eventually converts to CO, and for catalyst pathway, CO adsorbed on the active sites of the catalyst reacts with O radicals to generate CO₂, which is mutually verified with the experimental results in this work. As for the hydrogen generation, H₂ is firstly generated by CH₃OH + H=CH₂OH + H₂ and CH₃OH + H=CH₃O + H₂ and other H-abstraction reactions of H produced by plasma. On catalyst surface, the oxygen atom in methanol bonds with Cu of the catalyst and at the same time, the H^(2a) is formed through the reaction sequence ((R20)-(R29)), resulting in the generation of H₂^(2a), which rapidly desorbs from the Cu surface (R31) and converts to H₂^(g) [52].

Overall, the plasma converts methanol to CH₂OH, CH₃O, and CH₃ at the beginning of the reaction, while the catalyst reaction channel is more homogeneous, which breaks the O-H bond of methanol by a weak bond adsorption of O to form CH₃O. As a result, the new path created by the plasma generates multiple products, resulting in poor H₂ selectivity. The catalyst shows a good H₂ selectivity but low conversion. With plasmacatalyst, which combines the high energy and high conversion of plasma with the high selectivity of catalyst, the H₂ yield and selectivity can be effectively balanced. As for the plasma-catalytic synergy, Gadkari et al. [53] proved that the type of discharge is transformed from filamentary discharge to a combination of micro discharge and surface discharge, and similar phenomena are observed in the experiments. Bal et al. [54] found that the apparent free energy barrier of the dissociation chemistry decreases due to the vibrational imbalance, promoting the dissociation of CH4. And Joule heating generates "hotspots" at high-resistance particle contact surfaces enhancing methanol conversion as Zhou et al. [55] shown. Also, Wang et al. [56] studied the synergistic effect of Fe-based catalysts on ammonia decomposition by synergistic plasma. NH3* species produced by plasma could adsorb on the catalyst surface with higher adsorption capacity and stronger strength in comparison with ground-state NH3. More details are shown in Supplementary material.

5. Conclusion

In this study, an experimental investigation combined with kinetic modeling was performed on plasma-catalytic methanol decomposition in a DBD reactor. Species profiles of key intermediates were measured and the kinetic model explicitly integrating collisional reactions of methanol and radicals with energetic electrons and excited species is presented for the first time.

Under the non-equilibrium plasm, the methanol cracking reaction can be efficiently triggered at a low temperature of 453 K, realizing a low-temperature conversion process that cannot be carried out under conventional thermodynamic conditions. By increasing the voltage from 6 kV to 8 kV, the energetic electron density is increased by a factor of 2–3. In the range of 453–593 K, the methanol conversion is driven to



Fig. 13. The possible reaction sequence of the CH₃OH system (orange: plasma pathway; green: catalytic pathway and blue: plasma-catalyst pathway). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

jump from the baseline value of 7 %–10 % to the interval of 17 %–29 %, and the hydrogen yield increases from 3 %-5 % to 8.5 %-10 % at the same time. Within the experimental temperature region (453-593 K), both methanol consumption and hydrogen production show a significant positive temperature trends, whereas the concentration of the main by-product methane paradoxically decreases by 40 ppm. This phenomena is attributed to differences in the kinetic parameters of the competing reaction pathways: radical pathway analysis shows that the addition reaction of CH_3 with H ($CH_3+H\rightarrow CH_4$) exhibits a negative temperature-dependent properties, with its rate constant decreasing by about a factor of 2 as the temperature increases from 493 K to 593 K. In contrast, the rate constant of the key H-abstraction pathway of methanol $(CH_3OH + H \rightarrow CH_2OH/CH_3O + H_2)$ is elevated by a factor of 2, leading to kinetic inhibition of the methane production at higher temperature. During the discharge, methanol is initially decomposed by electrons, Ar* and radicals such as H to form CH₂OH and CH₃O. These intermediates undergo chain reactions, generating key products such as CH₂O and CH₂CHO, which ultimately decompose into CO while releasing substantial H₂.

On this basis, experiments were conducted to investigate methanol decomposition using Cu/ZnO/Al₂O₃ catalysts and plasma-catalyst systems. This study demonstrates the synergistic plasma-catalyst effects at 453–573 K. Based on that, we propose a potential pathway for methanol decomposition via plasma catalysis. At 493 K, 15 % increase in H₂ selectivity and 12 % increase in CH₃OH conversion are achieved compared with plasma alone. During the initial plasma stage, methanol decomposes into both CH₂OH and CH₃O. In contrast, methanol preferentially converts to CH₃O on the active sites of the Cu/ZnO/Al₂O₃ catalyst.

In this paper, the catalyst-assisted methanol decomposition process is limited to experimental phenomena, in future we will focus on the catalyst characterization, by combining DFT calculations. The effects of different kinds of catalysts on the reaction, especially the electronic interactions and the effects on the free energies of the intermediate products, will be studied continually. The effects of catalysts on hydrogen selectivity and conversion will be explored, as well as the optimization of catalysts for thermal stability and anti-poisoning properties in practical applications.

CRediT authorship contribution statement

Shuming Li: Writing – original draft, Resources, Investigation, Formal analysis, Data curation. Erjiang Hu: Writing – review & editing, Validation, Supervision, Methodology, Funding acquisition. Geyuan Yin: Writing – review & editing, Validation, Methodology. Zuohua Huang: Writing – review & editing, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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