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# One-step reforming of CO<sub>2</sub> and CH<sub>4</sub> to high-value liquid chemicals and fuels at room temperature via plasma-driven catalysis

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**Abstract:** Conversion of  $CO_2$  with  $CH_4$  into liquid fuels and chemicals in a single-step catalytic process bypassing the production of syngas remains a challenge. In this study, one-step synthesis of liquid fuels and chemicals (e.g. acetic acid, methanol, ethanol and formaldehyde) from  $CO_2$  and  $CH_4$  has been achieved at room temperature (30 °C) and atmospheric pressure for the first time using a novel plasma reactor with a water electrode. The total selectivity to oxygenates was ca. 50-60%, with acetic acid the major component at 40.2% selectivity, the highest value reported for acetic acid so far. Interestingly, direct plasma synthesis of acetic acid from  $CH_4$  and  $CO_2$  is an ideal reaction with a 100% atom economy, but it is almost impossible via thermal catalysis due to the significant thermodynamic barrier. The combination of plasma and catalyst in this process shows great potential for manipulating the distribution of different liquid chemicals.

Chemical transformation of CO<sub>2</sub> into value-added chemicals and fuels has been regarded as a key element of creating a sustainable low-carbon economy in the chemical and energy industry. A particularly significant route currently being developed for CO<sub>2</sub> utilization is catalytic CO<sub>2</sub> hydrogenation. This can produce a range of fuels and chemicals including CO, formic acid, methanol, hydrocarbons and alcohols; however, high H<sub>2</sub> consumption (CO<sub>2</sub> + 3H<sub>2</sub>  $\rightarrow$  CH<sub>3</sub>OH + H<sub>2</sub>O) and high operating pressure (~30-300 bar) are major challenges facing this process.

Instead of using H<sub>2</sub>, direct conversion of CO<sub>2</sub> with CH<sub>4</sub> (dry reforming of methane, DRM) to liquid fuels and chemicals (e.g. acetic acid) represents another promising route for both CO<sub>2</sub> valorisation and CH<sub>4</sub> activation. CH<sub>4</sub> is an ideal H-supplier to replace H<sub>2</sub> in CO<sub>2</sub> hydrogenation as CH<sub>4</sub> has a high H density and is available from a range of sources (e.g. natural gas, shale gas, biogas and flared gas). Moreover, it is a cheap carbon source which can increase the atom utilization of CO<sub>2</sub> hydrogenation due to the stoichiometric ratio of C and O atoms, as well as reducing the formation of water.

Recently, Ge et al. investigated the direct C-C coupling of  $CO_2$  and  $CH_4$  to form acetic acid on a Zn-doped ceria catalyst using density functional theory (DFT) modeling <sup>[1]</sup>; this is an

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attractive route as direct converting of CO<sub>2</sub> and CH<sub>4</sub> to acetic acid is a reaction with 100% atom economy (R1). However, this reaction is thermodynamically unfavorable under practical conditions. The conventional indirect catalytic process often proceeds through two steps (Scheme 1): (1) DRM to produce syngas (CO and  $H_2$ ) at high temperatures (> 700 °C); (2) conversion of syngas to liquid fuels and chemicals at high pressures. Such an indirect route for CO<sub>2</sub> valorisation and CH<sub>4</sub> activation is inefficient as the DRM process for syngas production is highly endothermic and requires high temperatures and energy input (R2). Catalyst deactivation due to carbon deposition is another challenge limiting the use of this reaction on a commercial scale. It is almost impossible to directly convert two stable and inert molecules (CO<sub>2</sub> and CH<sub>4</sub>) into liquid fuels or chemicals in a one-step catalytic process bypassing the production of syngas. A step-wise method was proposed to convert  $CO_2$  and  $CH_4$  into acetic acid over Cu/Co-based catalysts <sup>[2]</sup>, Pd/C, Pt/Al<sub>2</sub>O<sub>3</sub> <sup>[3]</sup>, Pd/SiO<sub>2</sub> and Rh/SiO<sub>2</sub> <sup>[4]</sup> via heterogeneous catalysis. The catalyst was first exposed to CH4, forming CH<sub>x</sub> species on the catalyst surface. Subsequently, the feed gas was changed from CH<sub>4</sub> to CO<sub>2</sub>, forming acetic acid through the reaction of CO<sub>2</sub> with CH<sub>x</sub> over the catalyst. This indirect process was complicated as a periodic change of reactant and collection of products was required <sup>[5]</sup>.

 $CO_2 + CH_4 \rightarrow CH_3COOH, \Delta G_{298 K} = 71.17 \text{ kJ/mol}$  (R1)

CH<sub>4</sub> + CO<sub>2</sub> → 2CO + 2H<sub>2</sub>,  $\Delta$ H<sub>298 K</sub> = 247 kJ/mol

Non-thermal plasma (NTP) offers a unique way to enable thermodynamically unfavorable chemical reactions to occur at low temperatures due to its non-equilibrium character: the overall gas temperature in a NTP remains low, while the generated electrons are highly energetic with a typical electron temperature of 1-10 e; sufficient to activate inert molecules (e.g. CO<sub>2</sub> and CH<sub>4</sub>) into reactive species, including radicals, excited atoms, molecules and ions. These energetic species are capable of initiating a variety of chemical reactions. Although much effort has been expended on the use of NTP for the destruction of gas pollutants, far less has been done in regard to their use in the synthesis of fuels and chemicals <sup>[6]</sup>. Previous works on DRM using NTP mainly focused on syngas production <sup>[7]</sup>, while very limited efforts have been devoted to this challenging reaction - one-step conversion of CH<sub>4</sub> and CO<sub>2</sub> to liquid fuels and chemicals [8]-[9]. A few groups reported the formation of trace oxygenates (e.g., alcohols and acids) as byproducts in plasma DRM for syngas production <sup>[10]</sup>. So far, the use of NTP for the direct conversion of CO2 and CH4 into oxygenates has shown poor selectivity and yield.

(R2)

## COMMUNICATION



Scheme 1. Direct and in-direct processes for the conversion of CO<sub>2</sub> and CH<sub>4</sub> to liquid fuels and chemicals

In this work, a novel dielectric barrier discharge (DBD) reactor with a ground water electrode (Schemes S1 and S2) has been developed for one-step conversion of CO<sub>2</sub> and CH<sub>4</sub> to oxygenates at room temperature (30 °C) and atmospheric pressure. This setup is unique and has not before been reported. Figure 1 shows that no reaction occurred in the 'catalyst-alone' mode at 30 °C without plasma. However, the use of a NTP enables this thermodynamically unfavorable reaction to occur at room temperature and produces liquid chemicals including acetic acid, methanol, ethanol and acetone, with acetic acid being the major product. Trace amounts of formic acid, propanol and butanol were also detected in the condensed liquid. In the plasma process without a catalyst ('plasma-alone'), a total liquid selectivity of 59.1% was achieved with 33.7%, 11.9%, 11.9% and 1.6% for acetic acid, ethanol, methanol and acetone, respectively (Figure 1a). The CO selectivity was limited at ca. 20.0% (Figure 1b), together with  $CH_4$  and  $CO_2$  conversions of 18.3 % and 15.4 %, respectively (Figure 1c).

Coupling the plasma process with a catalyst shows great potential to manipulate the production of different oxygenates at ambient conditions. Clearly, packing the Cu/y-Al<sub>2</sub>O<sub>3</sub> catalyst in the DBD enhanced the selectivity of acetic acid to 40.2%, compared to the 'plasma-alone' mode and the plasma reaction using y-Al<sub>2</sub>O<sub>3</sub> only (20.2%). Acetic acid was the major product regardless of the catalyst used, followed by methanol and ethanol (Figure 1a). Note HCHO was formed only when using the supported noble metal catalysts in the plasma reaction and the Pt/y-Al<sub>2</sub>O<sub>3</sub> catalyst showed the highest selectivity to HCHO. Compared to the 'plasma-alone' mode, placing the catalysts in the DBD showed similar gaseous products, with H<sub>2</sub>, CO and  $C_2H_6$  being the major gas products (Figure 1b). However, coupling the NTP with the catalysts enhanced the H<sub>2</sub> selectivity by 10-20% (except for Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), and slightly increased C<sub>2</sub>H<sub>6</sub> production, but had a weak effect on CO selectivity (except Cu/y-Al<sub>2</sub>O<sub>3</sub> which decreased CO selectivity to 13.5%) and other  $C_xH_y$  (i.e.,  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_8$  and  $n-C_4H_{10}$ ). In addition, compared to the 'plasma-alone' mode, the conversion of CO2 and CH<sub>4</sub> slightly decreased with packing catalysts. This phenomenon can be attributed to the change in discharge behavior induced by the catalyst, which had a negative effect on the reaction (Figure S1). Interestingly, acetic acid, hydroxyl-, ethyl ester was found on the reactor inner wall in the plasmacatalyst coupling mode. (Figure S2). These findings demonstrate the feasibility of using NTP for the direct conversion of CH<sub>4</sub> and CO<sub>2</sub> into higher value liquid fuels and chemicals in a single step process at ambient conditions, bypassing the formation of syngas.



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## COMMUNICATION

To understand the formation pathways of acetic acid, ethanol and methanol, optical emission spectroscopy (OES) diagnostics was used to investigate the species produced in the  $CH_4/CO_2$  DBD (Figure 2). Reactive species, including CH,  $H_a$ , O radical,  $C_2$ ,  $CO_2^+$ ,  $CO_2$ , and CO Angstrom band, were identified, with CO, CH and H being the major species (Table S2).

CO is mainly derived from reaction S1-S3 (table S3) in the DBD. Our simulation showed electron impact CO<sub>2</sub> reactions produced ~95% vibrational excited CO2 (CO2(V)) compared to electronically excited CO2 (CO2(E)), as shown in Figure S3 and table S4. O radicals generated from CO<sub>2</sub> dissociation can attack CO<sub>2(V)</sub> molecules to produce CO (S1-S2)<sup>[11]</sup>. Different from CH, CH<sub>3</sub>-derived from CH<sub>4</sub> dissociation cannot be detected using OES, but recent simulation revealed that electron impact dissociation of CH<sub>4</sub> leads to 79% CH<sub>3</sub> formation, whereas only 15% and 5% CH<sub>2</sub> and CH formation, respectively <sup>[12]</sup>. Therefore, CH<sub>3</sub> is the dominant specie in the CH<sub>4</sub>/CO<sub>2</sub> DBD. In addition to electrons (S4 in table S3), reactive species such as OH, O and H can also react with CH<sub>4</sub> to produce CH<sub>3</sub> radicals (S5-S7) in the CH<sub>4</sub>/CO<sub>2</sub> DBD. Additionally, OH is an important specie, especially for alcohol formation. In the CH<sub>4</sub>/CO<sub>2</sub> DBD, OH could be produced indirectly via reaction S8-S13, with S8 and S9 the major channels based on the reaction rate coefficient and E<sub>a</sub><sup>[13]</sup>. Special attention was given to S10, although a very low reaction rate coefficient of 1.4E-29 and a high  $E_a$  of 111 kJ/mol were observed for ground state CO2 reacting with H radical to produce OH radical, this reaction (S10) can be accelerated by CO<sub>2(V)</sub> instead of ground state  $CO_2$  <sup>[14]</sup> and the vibrational energy of the reagents is the most effective in overcoming the activation barrier of the endothermic reaction [14-15]. Thus, the reaction  $CO_{2(V)}$  + H  $\rightarrow$  CO + OH could be one of the major routes for OH formation in this study, as CO2 mainly existed in vibrationally exited states (Figure S3).



**Figure 2.** Optical emission spectra of CH<sub>4</sub>, CO<sub>2</sub> and CH<sub>4</sub>/CO<sub>2</sub> plasmas (total flow rate 40 ml/min, CH<sub>4</sub>/CO<sub>2</sub> ratio 1:1, discharge power 10 W, 2 s exposure time).

Based on the analysis of gas and condensed liquid products combined with the OES, CO,  $CH_3$  and OH radicals were the key species in the  $CH_4/CO_2$  plasma reaction. Therefore, the possible reaction pathways for the formation of acetic acid, methanol and ethanol in this study are proposed in Scheme 2.

Acetic acid formation: Two possible reaction pathways could contribute to the formation of acetic acid. CO can react with a CH<sub>3</sub> radical to form an acetyl radical (CH<sub>3</sub>CO) via reaction S14 in table S3 with a low energy barrier of 28.77 kJ/mol <sup>[16]</sup>, followed by the recombination with OH to produce acetic acid via reaction S15 with no energy barrier <sup>[10g]</sup>, which was further confirmed by Figures 3 and S4. Clearly, the selectivity of acetic acid increased initially, then decreased with the CH<sub>4</sub>/CO<sub>2</sub> ratio, with the optimal acetic acid formation at a CH<sub>4</sub>/CO<sub>2</sub> ratio of 1:1. Correspondingly, the relative intensity of the CO band and O atomic line increased with decreasing CH<sub>4</sub>/CO<sub>2</sub> ratio from 3:1 to 1:2, while that of CH band had a reverse evolution character (Figure S4). This suggests that decreasing the CH<sub>4</sub>/CO<sub>2</sub> mole ratio decreased the generation of CH<sub>3</sub> radicals, but increased OH formation. A similar mechanism of acetic acid formation was proposed using DFT modeling <sup>[10g]</sup> and by Eliasson et al. <sup>[10i]</sup>. In addition, direct coupling of CH<sub>3</sub> and carboxyl radicals (COOH) could also form acetic acid via reaction S16, while COOH radicals may be formed from reaction S17 and S18 in table S3 [10g].



Scheme 2. Possible reaction pathways for the formation of  $CH_3COOH$ ,  $CH_3OH$  and  $C_2H_5OH$  in direct reforming of  $CH_4$  and  $CO_2$  using DBD.



Figure 3. Effect of  $CH_4/CO_2$  mole ratio on the selectivity of oxygenates without a catalyst (total flow rate 40 ml/min, discharge power 10 W).

Alcohol formation: Decreasing the CH<sub>4</sub>/CO<sub>2</sub> ratio decreased the generation of CH<sub>3</sub> radicals, but increased OH formation (Figure S4). Simultaneously, the formation of CH<sub>3</sub>OH increased initially with decreasing CH<sub>4</sub>/CO<sub>2</sub> ratio and reached a peak at a CH<sub>4</sub>/CO<sub>2</sub> ratio of 1:1. By contrast, the formation of C<sub>2</sub>H<sub>5</sub>OH decreased continuously as the CH<sub>4</sub>/CO<sub>2</sub> ratio decreased (Figure

## COMMUNICATION

3). These findings suggest that the production of CH<sub>3</sub>OH mainly depends on the generation of both CH<sub>3</sub> and OH radicals, while the formation of C<sub>2</sub>H<sub>5</sub>OH was more sensitive to the presence of CH<sub>3</sub> radicals in the plasma reaction as C<sub>2</sub>H<sub>5</sub>OH formation requires twice the amount of CH<sub>3</sub> radicals in comparison to the formation of CH<sub>3</sub>OH. As shown in Scheme 2, CH<sub>3</sub>OH can be directly formed from the coupling of CH<sub>3</sub> and OH radicals with a high rate coefficient (S19 in table S3) <sup>[17]</sup>, while C<sub>2</sub>H<sub>5</sub>OH formation required several elementary reactions (S20-S24). The recombination of CH<sub>3</sub> radical with itself forms C<sub>2</sub>H<sub>6</sub> (S20) <sup>[18]</sup>, followed by dehydrogenation to form C<sub>2</sub>H<sub>5</sub> radical via reaction S21-S23, with S21 as the primary reaction according to reaction rates <sup>[13d, 19]</sup>. C<sub>2</sub>H<sub>5</sub> radical was eventually attached by OH to form C<sub>2</sub>H<sub>5</sub>OH at a high rate coefficient of 9.34E-11 cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (S24) <sup>[20]</sup>.

Clearly, placing the catalysts in the plasma reaction can tune the distribution of oxygenates, especially for the formation of HCHO after packing the Pt and Au catalysts, revealing the occurrence of surface reactions in addition to the plasma gas phase reactions <sup>[21]</sup>. In traditional catalysis, CO hydrogenation, CH<sub>3</sub>OH oxidation and methylene (CH<sub>2</sub>) oxidation could form HCHO over noble-metal catalysts <sup>[22]</sup>. In this plasma process, packing noble-metal catalysts in the plasma had almost no influence on the CO selectivity, but decreased the selectivity of CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>COOH and increased the selectivity of HCHO and  $C_2H_6$  (Figure 1a). Considering the major species that existed in the  $CH_4/CO_2$  DBD,  $CH_x$  (x = 4, 3, and 2) could be the primary source for HCHO formation via oxidation reactions. Namely, CH<sub>x</sub> in the gas phase could be adsorbed onto the surface of the catalyst to form HCHO via the oxidation of CH<sub>2, ad</sub>  $(CH_{x, ad} + O, H, OH \rightarrow CH_{2, ad})$ , and to produce  $C_2H_6$  via selfrecombination of CH3 radical instead of converting CH3 to CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>COOH. This could explain why the presence of the Au and Pt catalysts in the plasma decreased the formation of CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>COOH, but enhanced the production of C<sub>2</sub>H<sub>6</sub> and HCHO (Figures 1a and 1b). The possible pathways for the formation of major oxygenates on the catalyst surface were proposed in Scheme S3. In addition, a range of catalyst characterization (Figures S5-S8) suggest that metal particle size and interaction of metal and support are not the determining factors for the different reaction performances (Figure 1), whereas the bonding strength of adsorbed intermediates to the catalyst surface, i.e. oxygen adsorption energy ( $\Delta E_0$ ), could be a good activity descriptor towards the formation of different products in CO<sub>2</sub> hydrogenation<sup>[23]</sup>.

In conclusion, one-step room temperature synthesis of liquid fuels and chemicals from the direct reforming of CO<sub>2</sub> with CH<sub>4</sub> has been achieved using a novel atmospheric pressure DBD reactor. The total selectivity of liquid chemicals was ca. 50-60%, with acetic acid the major product. The CH<sub>4</sub>/CO<sub>2</sub> mole ratio and type of catalyst can be used to manipulate the production of different oxygenates. These results clearly show that nonthermal plasma can overcome the thermodynamic barrier to enable the direct transformation of CH<sub>4</sub> and CO<sub>2</sub> into a range of strategically important platform chemicals, especially the production of acetic acid with a 100% atom economy. Additionally, the coupling of the DBD with noble-metal catalysts produced formaldehyde which cannot be generated in the same plasma reaction without a catalyst. This finding suggests that new research should be directed at designing a catalyst with high selectivity towards a desirable product.

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**Keywords:** CO<sub>2</sub> conversion • CH<sub>4</sub> activation • non-thermal plasma • dry reforming • liquid fuels and chemicals

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#### Entry for the Table of Contents

Layout 1:

### COMMUNICATION

Single-step synthesis of liquid fuels and chemicals from  $CO_2$  and  $CH_4$  at ambient conditions was achieved using plasma-driven catalysis.

