

Supplementary information

Acetic acid formation from methane and carbon dioxide via non-thermal plasma reactions toward an effective carbon fixation

*Naoyuki Nishimura**, *Takayuki Akaogi*, *Kazuhiro Onishi*, *Masahiro Tojo*

Corporate Research & Development, Asahi-Kasei Corporation, 3-13 Ushio-Dori, Kurashiki,
Okayama, Japan

1. Estimation of theoretical yield based on thermodynamics

The equilibrium constants (K_p) of direct CH_3COOH formation from CH_4 and CO_2 (eq.1) along with reaction temperature (T) was calculated (Fig.S1) with the following thermodynamics values (Table S1 and S2) and equation (eq.S1). As shown in Fig.S1, the theoretical yields of CH_3COOH in the equilibrium conditions are permanently negligible even with adjusting reaction temperatures. This is because in Fig.S1, the intercept ($:\Delta_rS/R$) is negative, and besides, the endotherm results in negative slope against $1/T$. Therefore, in order for efficient CH_3COOH production via this reaction to be viable, non-equilibrium conditions such as using non-thermal plasma is instrumental.

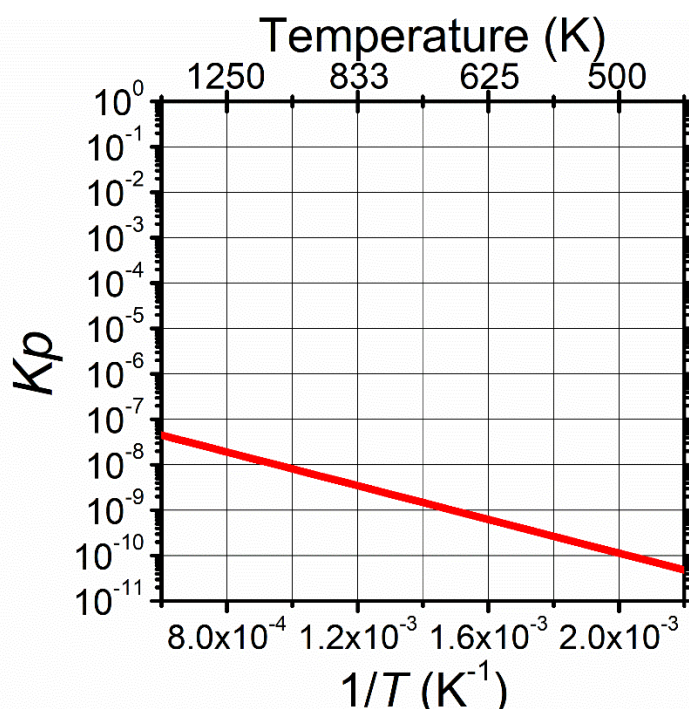


Fig. S1 The equilibrium constants of direct CH_3COOH formation from CH_4 and CO_2 along with reaction temperature

The standard enthalpy of formation ($\Delta_f H^\ominus$), standard Gibbs energy ($\Delta_f G^\ominus$) and standard entropy (S^\ominus) are described in Table S1, and besides the thermodynamic values for the reaction also estimated (Table S2) The $\Delta_r H$, $\Delta_r G$ and $\Delta_r S$ indicates thermodynamic values for the reactions.

Table S1 Thermodynamics values of parameters of the reactants¹ and product²

Substance	Chemical formula	$\Delta_f H^\ominus$ (kJ mol ⁻¹)	$\Delta_f G^\ominus$ (kJ mol ⁻¹)	S^\ominus (J K ⁻¹ mol ⁻¹)
Methane (g)	CH ₄	-74.8	-50.7	186.3
Carbon dioxide (g)	CO ₂	-393.5	-394.4	213.7
Acetic acid (g)	CH ₃ COOH	-432.8	-374	282.7

Table S2 Thermodynamics values of the target reaction

Reaction	$\Delta_r H^\ominus$ (kJ mol ⁻¹)	$\Delta_r G^\ominus$ (kJ mol ⁻¹)	$\Delta_r S^\ominus$ (J K ⁻¹ mol ⁻¹)
CH ₄ + CO ₂ → CH ₃ COOH (eq.1)	36	71	-119

The relationship between the equilibrium constant (K_p) and reaction temperature (T) is summarized in eq. S1.

$$\ln K_p = -\Delta_r G/RT = -\Delta_r H/RT + \Delta_r S/R \quad (\text{eq. S1})$$

Here, R is the ideal gas constant. Using this equation, the linear relationships between $\log K_p$ and $1/T$ were determined, as plotted in Fig. S1.

2. Experimental

2-1. Non-thermal plasma reaction

The non-thermal plasma reactions in the presence of CH₄ and CO₂ to form CH₃COOH were employed in the following reaction system (Fig. S2) and condition. The non-thermal plasma was performed with a reactor consisting of quartz tube (inside diameter: 10 mm, thickness: 1.5 mm) whose outside was covered with aluminum (Al) foil (20 mm length) and a SUS316 stick (6 mm inch) placed inside the quartz tube, and Al/ quartz and the SUS stick functioned as the electrodes. This configuration resulted in about 2 mm distance between the electrodes and 20 mm length of plasma regime along the flow direction. An alternating current between the electrodes was applied by a voltage of 3.6 kV and a frequency of 40 Hz, generating the plasma for the reaction. The reactor was heated to 373 K in a tube furnace. A mixture feed of CH₄ (99.9%), CO₂ (99.995%), and Ar (99.99%) flowed from top to bottom in the vertically placed reactor tube. The feed rates were controlled using flow meter to adjust the total rate to 77 mL min⁻¹ and the fixed value to 49 mL min⁻¹ of Ar flow (i.e., CH₄ + CO₂ = 28 mL min⁻¹). The volume of the plasma area in the reactor was estimated to be 1 mL, so the gas hourly space velocity (GHSV) for the plasma regime at 373 K was calculated to be 6300 h⁻¹. Each space time yield was estimated with the GHSV value. The CH₄/CO₂ volume ratio ranged from 0.3 to 3.0, and the optimized ratio for acid production was found to be 0.3 (Fig.2).

2-2. Investigation of the produced organic acids

The acid products were collected by bubbling into double water trap (5 mL each) placed after the plasma reactor. After the reaction and online GC investigation (described below), the reaction line was purged with 100 mL min^{-1} of Ar flow into the water traps for another 5 min in order to collect the acid products remained in the reaction line. The trap solution were measured by an offline liquid chromatography (HPLC; controller: CBM-20A, detector: CDD-10Avp from Shimadzu Co.) with a Shim-pack SCR-102H column (Shimadzu Co., operation temperature: 313 K). For the HPLC, 5 mmol L^{-1} p-toluene sulfonic acid aqueous solution and that containing EDTA (100 mmol L^{-1}) + 20 mmol L^{-1} Bis-Tris were used as a mobile phase and a buffer solution, respectively. For a reaction using an isotopic reactant ($^{13}\text{CH}_4$; 99 atm% from Taiyo Nippon Sanso Co.), the water trap solution after the reaction was also characterized by an offline mass spectroscopy: CG-MS (HP-6890/5973N from Agilent Co.) with a TC-FFAP column ($30 \text{ m} \times 0.25 \text{ mm}$, thickness: $0.25 \text{ }\mu\text{m}$, operation temperature: 323 K) The ratios of produced CH_3COOH containing isotopic carbons (^{13}C) and/or normal carbons (^{12}C) are estimated with the ratio of 60, 61, and 62 intensity in the mass spectrum.

2-3. Investigation of the gas composition

The gas composition after the reaction also measured by an online gas chromatography (GC), placed between the reactor and the water trap via a switching valve in order to estimate the conversion value of CH_4 and CO_2 . After the 5 min reaction for the acids collection with the water traps, line after the

reactor was switched from the water trap to the GC line via a switching valve, and the gas composition measurement was carried out. The online GC was GC-2010plus from Shimadzu Co. equipped with SHINCARBON ST column from Shinwakako Co. using He carrier gas. After the GC measurement started, the flow line was back to the water trap line via the switching valve to proceed with the Ar purging process.

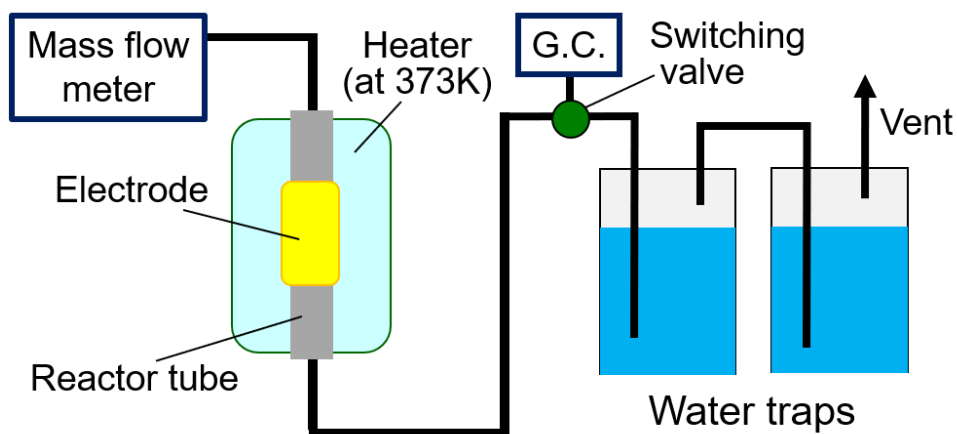


Fig.S2 Outline of the reaction system

3. Mass spectra of obtained CH₃COOH

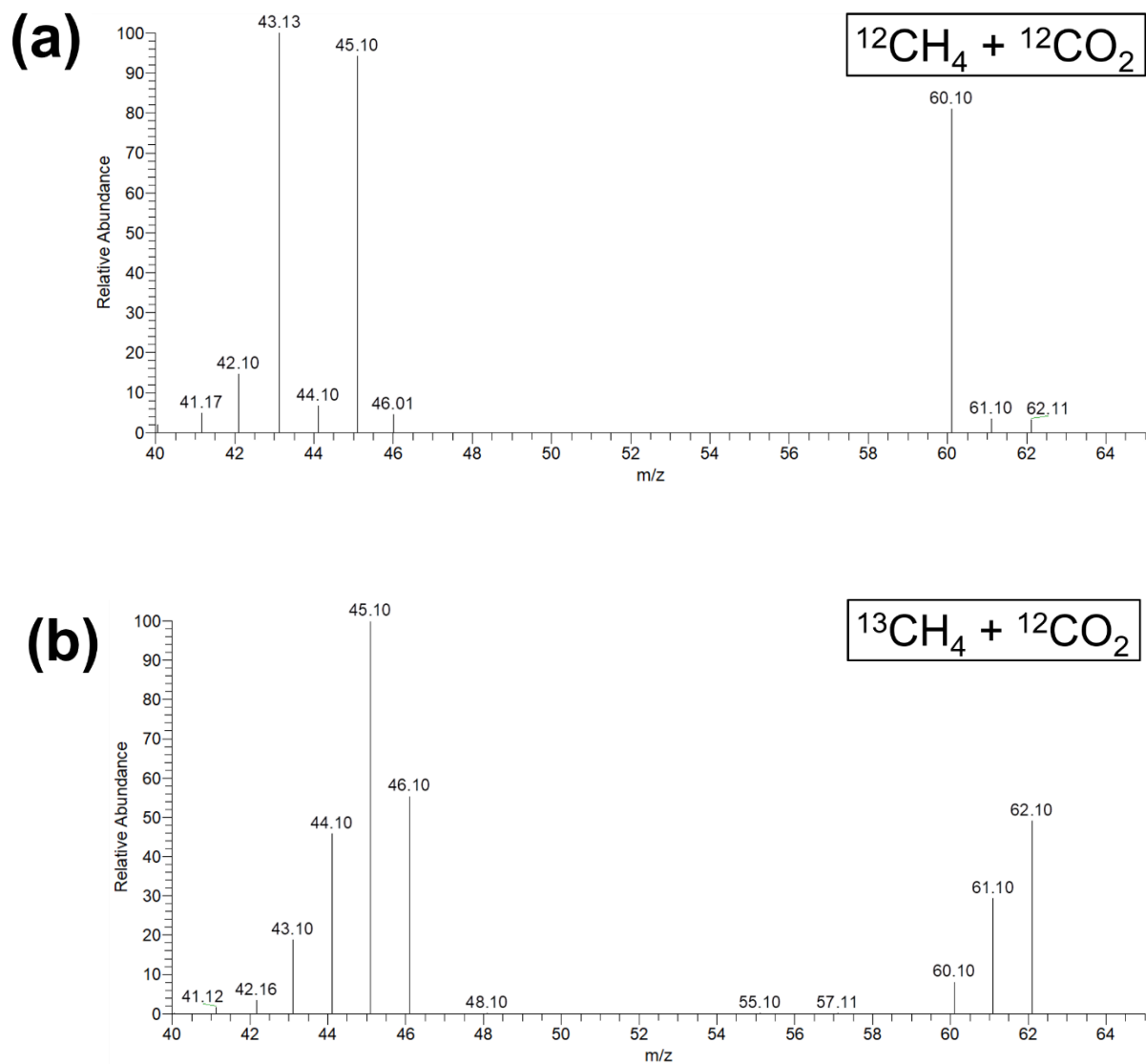


Fig. S3 Mass spectra of the CH₃COOH obtained via the reaction with (a) normal reactants ($^{12}\text{CH}_4 + ^{12}\text{CO}_2$), and (b) an isotopic CH₄ and normal CO₂ ($^{13}\text{CH}_4 + ^{12}\text{CO}_2$)

4. Yield estimation of the obtained acid

Yield, conversion, and selectivity of the obtained acid were estimated with eq.S2, S3, and S4, respectively. The gas concentrations for the conversion estimation were normalized by the Ar concentration. In the optimized condition (feed composition of CH₄/CO₂ = 0.3; Fig.2), the acid yield based on the fed CH₄ was calculated to be 0.12%, and the conversion of CH₄ and CO₂ were 19% and 28%, respectively. Accordingly, the selectivity of acid formation based on the fed CH₄ in eq.1 was estimated to be 0.6%. Besides, 1.8 vol% and 1.4 vol% of CO and H₂ was also detected in the outlet gas. Moreover, 0.3 vol% of C₂ hydrocarbons and less than 0.1 vol% of C₃ and C₄ hydrocarbons were detected in the outlet gas.

$$\text{Yield} = \frac{\text{Obtained acids (mol)}}{\text{Fed CH}_4 \text{ (mol)}} \quad (\text{eq.S2})$$

$$\text{Conversion} = 1 - \frac{\text{CH}_4 \text{ or CO}_2 \text{ after reaction (vol\%)}}{\text{CH}_4 \text{ or CO}_2 \text{ before reaction (vol\%)}} \quad (\text{eq.S3})$$

$$\text{Yield} = \text{Conversion} \times \text{Selectivity} \quad (\text{eq.S4})$$

5. Dependence of fed CH₄/CO₂ ratio on the conversions

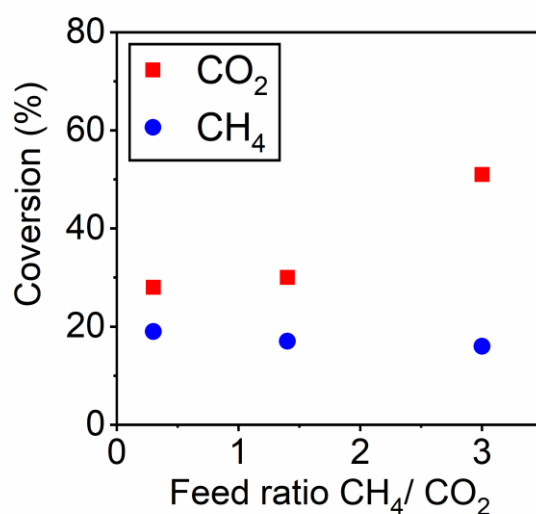


Fig. S4 The feed ratio dependence on the conversions, corresponding to Fig.2; Feed gas: total 77 mL min⁻¹ of CH₄-CO₂-Ar mixture with a fixed rate of Ar (49 mL min⁻¹), reaction temperature: 373 K, applied voltage: 3.6 kV, reaction time: 5 min

The CH₄ conversions almost unchanged with changing the feed CH₄/CO₂ ratio. Meanwhile, the CO₂ conversion increased with an increase in the fed CH₄ ratio probably because higher CH₄ concentration in the feed flow generated more activated species derived from CH₄, and the highly concentrated CH₄-derived activated species assisted the CO₂ activation more, resulting in the increase in the CO₂ conversion. This trend is in line with the fact that direct CO₂ activation (e.g., CO₂ dissociation) in the present non-thermal plasma is inefficient as elucidated in the main script.

Reference

1. Atkins, P.; Paula, J. D. *Atkin's Physical Chemistry 9th edition*; Oxford University Press: Oxford, 2010; pp 918–922.
2. The Chemical Society of Japan, *Handbook of Chemistry: Pure Chemistry, 5th edition*; Maruzen Co.: Tokyo, 2004; pp II-303