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Supplementary information

Exothermic methane coupling with ethylene as a hydrogen accepter toward two-step methane conversion to ethylene

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1. *Estimation of thermodynamic values*

The equilibrium constants employed in this work were obtained from thermodynamic parameters for the individual reactants and products. The standard enthalpy of formation ($\Delta_f H^\ominus$), standard Gibbs energy ($\Delta_f G^\ominus$) and standard entropy ($S^\ominus$) values are provided in Table S1.

Table S1. Thermodynamic values for the reactants and products.[1]

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	CH_4	–74.81	–50.72	186.26
Ethane	C_2H_6	–84.68	–32.82	229.60
Etylene	C_2H_4	52.26	68.15	219.56
Moleculer hydrogen	H_2	0	0	130.68
Moleculer oxygen	O_2	0	0	205.14
Water vapor	H_2O	–241.82	–228.57	188.83
Propane	C_3H_8	–103.85	–23.49	269.91
1-Butene	C_4H_8	–0.13	71.39	305.71

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

$$ln\ Kp = -\Delta_r G/RT = -\Delta_r H/RT + \Delta_r S/R \qquad \text{(S1)}$$

Here, R is the ideal gas constant. Note that the subscript 'r' in $\Delta_r H$, $\Delta_r G$ and $\Delta_r S$ indicates thermodynamic values for the reactions. Using this equation, the linear relationships between log Kp and $1/T$ were determined, as plotted in Fig. 1.

This equation also explains the importance of a positive, large $\Delta_r S$ for an endothermic reaction with regard to obtaining a high yield of the target product. Since $\Delta_r S/R$ is the y-intercept in Fig. 1, endothermic reactions with positive $\Delta_r S$ values (such as the dehydrogenation of ethane: eqn (3)) will exhibit high Kp values (e.g., $Kp \geq 1$ and $\Delta_r G < 0$) at high reaction temperatures, and thus can be industrially viable. In contrast, endothermic reactions with negative $\Delta_r S$ values (such as direct methane coupling to form ethane: eqn (2)) will not show high Kp and positive $\Delta_r G$ values even when adjusting the reaction temperature. Consequently, a large $\Delta_r S$ allows an endothermic reaction to generate a high yield of the target product.

2. Oxidative methane coupling with molecular oxygen

Oxidative methane coupling with molecular oxygen (O_2) proceeds according to the reaction in eqn (S2). The thermodynamic parameters for this reaction are presented in Table S2.

$$2\ CH_4 + O_2 \rightarrow C_2H_4 + 2\ H_2O \qquad \text{(S2)}$$

Table S2. Thermodynamic values for oxidative methane coupling.

Reaction	$\Delta_r H^\ominus$ (kJ mol^{-1})	$\Delta_r G^\ominus$ (kJ mol^{-1})	$\Delta_r S^\ominus$ (J K^{-1} mol^{-1})
$2\ CH_4 + O_2 \rightarrow C_2H_4 + 2\ H_2O$ (S2)	–282	–288	20

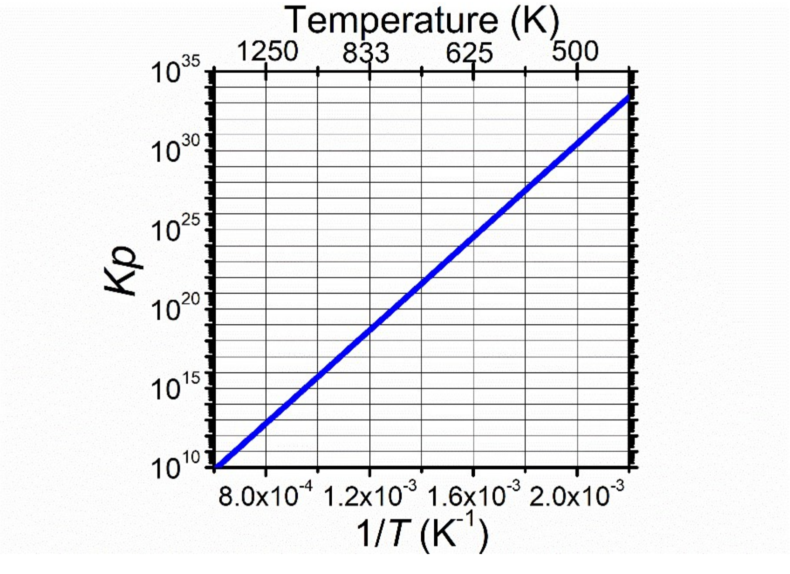

Figure. S1 Relationships between the equilibrium constants (*Kp*) and reaction temperature (*T*) for oxidative methane coupling with molecular oxygen ($2\ CH_4 + O_2 \rightarrow C_2H_4 + 2\ H_2O$: eqn (S2))

3. Ethane generation via methane coupling in the presence of ethylene

3-1. Estimation of turnover frequency over the platinum catalyst

The turnover frequency (TOF) for each product over the platinum (Pt) catalyst was determined using the following equation.

$$\mathrm{TOF} = \frac{v_{\mathrm{product}}}{S_{\mathrm{Pt}}} \qquad \text{(S3)}$$

Here, v_{product} and S_{Pt} represented the generation rate of each product and the relative surface area of Pt catalyst placed in the reactor (0.97 m^2), respectively.

3-2. Estimation of the theoretical maximum in ethane generation via direct methane coupling

The theoretical maximum amount of ethane generation via direct methane coupling was estimated based on eqn (S4), using the equilibrium constant (*K*) obtained from eqn (2).

$$K = \frac{[C_2H_6]\ \ [H_2]}{[CH_4]^2} \qquad \text{(S4)}$$

According to Fig. 1, the theoretical *K* value at 473 K (the temperature employed in the experimental work) was 1.52×10^{-8}. Based on the methane concentration of 50 vol% used in the experiment of Fig. 3, the theoretical maximum amount of ethane generated via direct methane coupling (as in eqn (3)) was calculated to be 2.7×10^{-7} mol min^{-1}, which is corresponding to TOF of 2.8×10^{-7} mol $\mathrm{min}^{-1}\ \mathrm{m}^{-2}$ in the employed condition.

5. Thermodynamic calculation of side reactions

Thermodynamics values of side reactions were calculated. Propane generation via combining methane and ethylene (eqn (S5)) and ethylene oligomerization forming 1-butene (eqn S6) were considered to be major side reactions since these reactions likely occur in light of their thermodynamics. (Fig. S2 based on Table S3) Although theoretical yields of these reactions are slightly higher than the methane coupling with ethylene (eqn (4)), butene including the isomers and propane obtained in the present reaction were a little (Fig. S3), which suggesting that the catalyst that efficiently proceeds with ethylene hydrogenation is a key to suppressing the side reactions.

$$CH_4 + C_2H_4 \rightarrow C_3H_8 \qquad (S5)$$

$$2\ C_2H_4 \rightarrow C_4H_8 \qquad (S6)$$

Table S3. Thermodynamic values for side reactions

Reaction	$\Delta_r H^\ominus$ (kJ mol^{-1})	$\Delta_r G^\ominus$ (kJ mol^{-1})	$\Delta_r S^\ominus$ (J K^{-1} mol^{-1})
$CH_4 + C_2H_4 \rightarrow C_3H_8$ (S5)	–81	–41	–136
$2\ C_2H_4 \rightarrow C_4H_8$ (S6)	–105	–65	–133

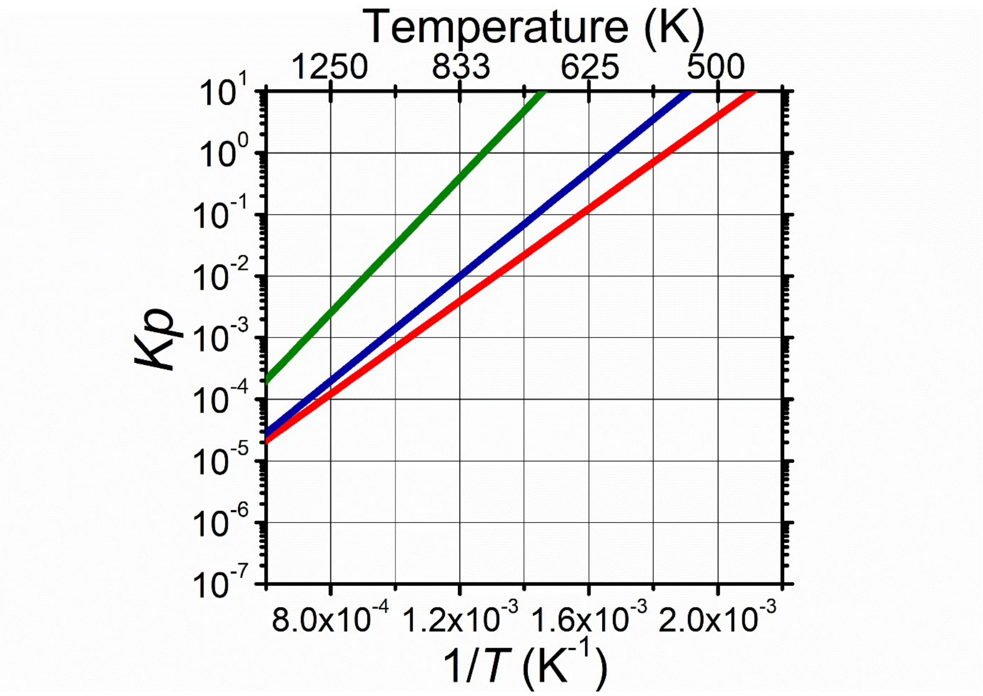

Figure. S2 Relationships between the equilibrium constants (*Kp*) and reaction temperature (*T*) for the target reaction and side reactions. Legend; red: methane coupling with ethylene to generate ethane ($2\ CH_4 + C_2H_4 \rightarrow 2\ C_2H_6$: eqn (4)), blue: propane generation via combining methane and ethylene ($CH_4 + C_2H_4 \rightarrow C_3H_8$: eqn (S5)), green: ethylene oligomerization forming 1-butene (2 $C_2H_4 \rightarrow C_4H_8$: eqn (S6))

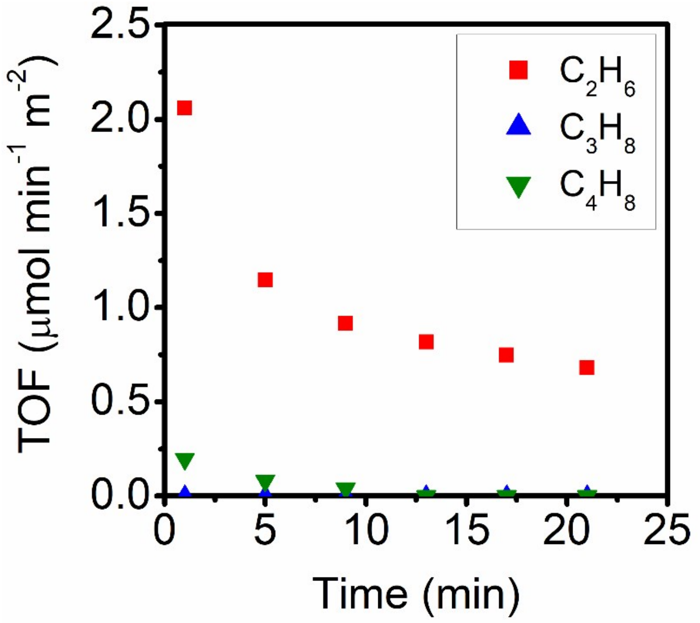

Figure. S3 TOF of ethane, propane, and butene generation via methane coupling in conjunction with ethylene as a function of time. Reaction conditions as same as Fig. 3: catalyst = 5 wt% platinum loaded on alumina (0.5 g), reactant gas = a 2:1 mixture of methane and ethylene, or methane (without ethylene). Both flows were diluted with argon to adjust the flow rate to 100 mL min^{-1}, atmospheric pressure, reaction temperature = 473 K.

6. Investigation in regeneration feature of the catalyst

In order to investigate regeneration features of the employed catalyst, a periodic reaction including a regeneration process was employed. The periodic reaction consisted of four process: (1) a reaction under flow of the methane-ethylene mixture for 120 s, (2) flushing the gases in the reactor with an argon flow for 20 s, (3) regeneration of catalyst under flow of hydrogen diluted with argon for 60 s, and followed by (4) flushing gases in the reactor with an argon flow for 40 s. (please see the experimental section for the details) It was confirmed that after the present regeneration process, catalytic activity was back to be close to the original (approximately 93–97%, Fig. S4), indicating that the deactivation in the ethane generation over time in Fig.3(a) was mainly due to accumulation of the reactant species absorbed on the catalyst.

For further investigation of accumulated species on the Pt/Al_2O_3 catalyst under the flow of methane-ethylene mixture, short-interval sampling with the periodic reaction was implemented. While sampling span of the used GC was longer than several minutes, the periodic reaction enables detection in short time interval of several seconds in the regeneration process owing to the regeneration feature of the catalyst. Thus, time for the whole cycle of the periodic reaction (i.e., process (1)-(4)) was 240 s, while sampling was carried out every 248 s, so that sampling interval of 8 s is available and was applied to investigation of generated gases under the regeneration process. Fig. S5 plots generated gases under regeneration, indicating that both methane and ethane were generated under the regeneration. Accordingly, the reaction process under flow of a methane-ethylene mixture led to the accumulation of activated methane and C2 hydrocarbon species, leading to deactivation of the ethane generation.

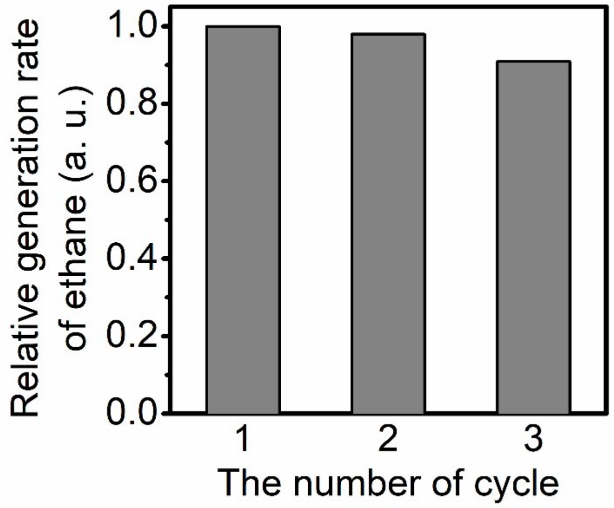

Figure S4. Relative generation rate of ethane under a flow of the methane-ethylene mixture after cycles of regeneration via exposing the catalyst under flow of hydrogen diluted with argon at 473 K.

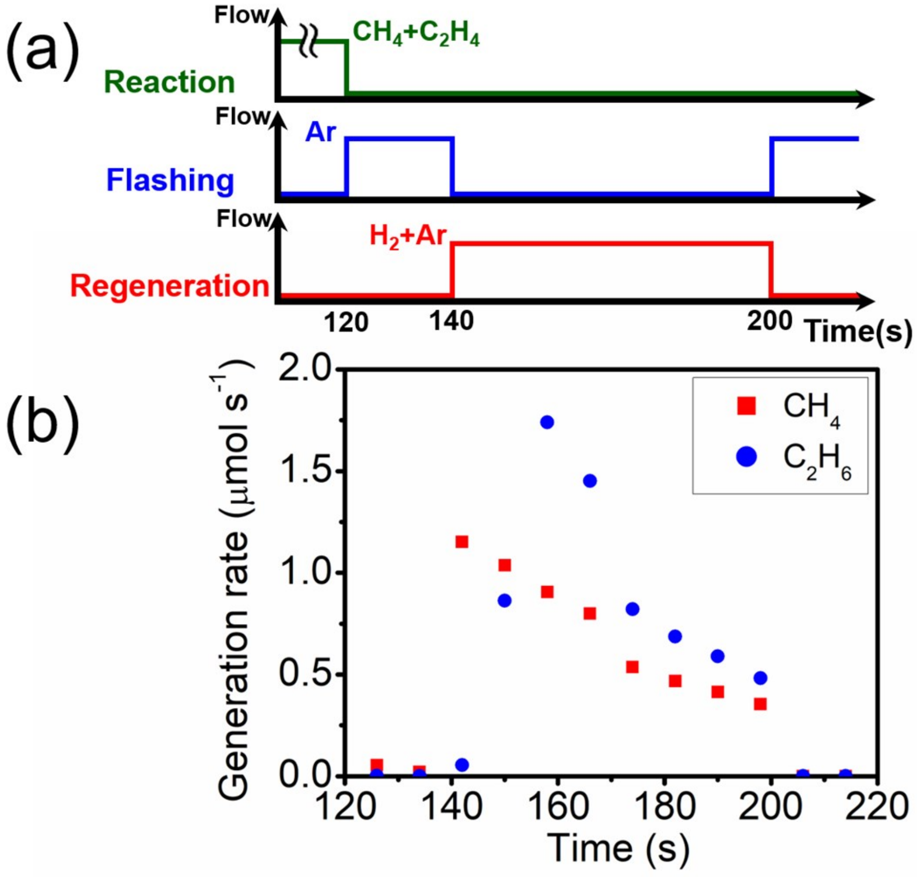

Figure S5. (a) Schematic describe of the change in flow under the periodic reaction, (b) generation rate of the detected gases under the regeneration process

7. Experimental

7-1. Preparation of the catalyst

Pt catalyst was loaded on an alumina support (α -phase Al_2O_3; Wako Co., Wako special grade) by stirring 10 g of the alumina power in 100 mL of a 25 mM aqueous solution of chloroplatinic acid ($H_2[PtCl_6]$) for 2 h, followed by evaporation of the water and calcination of the product at 773 K for 1 h. The resulting power was ground in a mortar for 30 min, pelletized at a pressure of 20 MPa and subsequently graded by size to obtain particle sizes between 0.25 and 0.50 mm. The resulting material (5 wt% Pt/Al_2O_3) was employed as the catalyst. The surface area of the loaded Pt with pretreatment of hydrogen reduction at 673 K was estimated to be 1.93 m^2 g^{-1} by chemisorption of hydrogen at 318 K with a surface characterization analyzer (3Flex, Shimazu Co.), and the surface area value was used for the estimation of TOF.

7-2. Gas flow reactor for methane coupling in the presence of ethylene

The experimental reactions were carried out in a gas flow reactor by placing 0.5 g of the prepared catalyst between portions of quartz wool at the center of a quarter inch diameter reaction tube made of SUS steel. A thermometer was placed in the center of the catalyst zone in the tube to monitor the reaction temperature. The reaction tube was then transferred into a thermostatic chamber and connected to a gas flow reactor with an online gas chromatography apparatus (490GC, Agilent Co.), situated such that it received the effluent from the reaction tube, and was equipped with a CP-Sil5 CB column (Agilent Co.) for ethane detection and a Molsieve 5Å PLOT column (Agilent Co.) for hydrogen detection. The CP-Sil5 CB column was heated to 313 K, and helium was used as the carrier gas, while for the Molsieve 5ÅPLOT, a column temperature of 373 K and an argon carrier gas were employed. The reactant gas comprised a mixture of methane (99.99% pure) and ethylene (99.9% pure) and the individual flow rates of these gases were controlled with calibrated flow meters.

7-3. A trial of methane coupling in the presence of ethylene

Methane coupling in the presence of ethylene to generate ethane was carried out using the flow reactor described above. In addition, a reaction without the ethylene feed was also examined as the reference. Prior to each reaction, the catalyst was reduced under a 100 mL min^{-1} flow of hydrogen at 673 K for 30 min. Following this, a 500 mL min^{-1} flow of argon was applied for longer than 60 min to allow the temperature of the apparatus to stabilize at 473 K, which was the desired reaction temperature. After confirming a stable temperature, the mixture of methane, ethylene, argon was supplied at atmospheric pressure, with respective flow rates of 50, 25, and 25 mL min^{-1} (100 mL min^{-1} in total), as the reactant gas for the methane coupling with ethylene. As for the reference reaction, the same condition as above except a reactant gas comprising mixture of methane and argon with both flow rates of

50 mL min^{-1} (100 mL min^{-1} in total) was employed. The resulting ethane, hydrogen, propane, and butene were quantified using the online gas chromatography system at 3 min intervals.

7-4. Periodic reaction for detection of generated gases under regeneration of the catalyst

A periodic reaction was employed to detect generated gases under regeneration process. The periodic scheme comprised the following four processes in atmospheric pressure at 473 K with changing flows. (1) reaction process: flowing mixture of methane and ethylene at atmospheric pressure, with respective flow rates of 50 and 5 mL min^{-1} for 120 s, (2) flushing process: flowing argon with a rate of 500 mL min^{-1} for 20 s, (3) regeneration process: flowing hydrogen (10 mL min^{-1}) diluted with argon (90 mL min^{-1}) for 60 s, (4) flushing process: flowing argon with a rate of 500 mL min^{-1} for 40 s. Hence, time for the cycle (i.e., process (1)-(4)) was 240 s. While the repeating process underwent, sampling was carried out every 248 s, and so sampling interval of 8 s is available and was applied to investigation of generated gases under the regeneration process.

Reference

1 P. Atkins, J. D. Paula, *Atkin's Physical Chemistry 9th edition;* Oxford University Press, Oxford, 2010.