

Research Article

Effect of Coexistent Hydrogen on the Selective Production of Ethane by Dehydrogenative Methane Coupling through Dielectric-Barrier Discharge under Ordinary Pressure at an Ambient Temperature

Katsuya Konno,^{1,2} Kaoru Onoe,¹ Yasuyuki Takiguchi,¹ and Tatsuaki Yamaguchi¹

¹ Department of Life and Environmental Sciences, Faculty of Engineering, Chiba Institute of Technology, Narashino 2-17-1, Chiba, Japan

² Hitachi Automotive Systems, Ltd., Development Division Drive Control Systems Division 6-3, 1 Chome, Fujimi, Kanagawa, Japan

Correspondence should be addressed to Tatsuaki Yamaguchi; tatsuaki.yamaguchi@it-chiba.ac.jp

Received 14 June 2013; Accepted 25 September 2013; Published 1 January 2014

Academic Editors: S. Kambara, D. H. Lee, and O. Senneca

Copyright © 2014 Katsuya Konno et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The effect of coexistence of hydrogen on the product selectivity to ethane from methane by dielectric-barrier discharge (DBD) reactor was examined experimentally under ordinary pressure without use of catalyst and external heating. By the dilution of methane with hydrogen, both the increase of methane conversion and the decrease of alkene production were observed, improving the selectivities to ethane by *ca.* 70%.

1. Introduction

To make use of natural gas as an alternative feedstock for petrochemical products, we have tried to synthesize C₂ hydrocarbons by nonoxidative, that is, dehydrogenative coupling of methane, because this process produces hydrogen as a sole byproduct. The dehydrogenative coupling could become one of the green chemistry processes generating no waste materials without use of catalysts. Our previous performances were the synthesis of acetylene from methane (reaction (1)) by the microwave plasma reaction [1] and ethylene from methane (reaction (2)) by the thermal diffusion column [2–8], both with the acceptable high selectivities of the main product, being the maximum acetylene selectivity of 97.4% with the methane conversion (X_{CH_4}) of 92.7% and also the ethylene selectivity of 91.5% with the X_{CH_4} of 9.4%, respectively,



The high selectivity is principally attributable to the local high energy supply to the reactant molecule under a reduced pressure in case of the microwave plasma reaction and also the steep temperature gradient between the center and the wall of the reactor column in case of the thermal diffusion reaction. Although the highest selectivity should be possible for these techniques, the low energy efficiency and the peculiar reactor setup give rise to be a stumbling block to the further progress for practical usages.

Subsequently, intensive investigations on dehydrogenative (nonoxidative) coupling of methane have been conducted in atmospheric nonthermal plasmas generated by spark discharge or dielectric-barrier discharge (DBD) without catalysts [9–11] and by DBD with special catalysts [12–15]. Ethane is the main product of these methane activation techniques, and the selectivity was as much as 60%, accompanying unsaturated and C₃₊ hydrocarbons. In our previous paper on the methane conversion by DBD [16], it has been clarified that the product distribution is greatly affected by the introduced gas pressure. Under a reduced pressure (12 kPa) acetylene was given in the highest selectivity of 40%, but it get

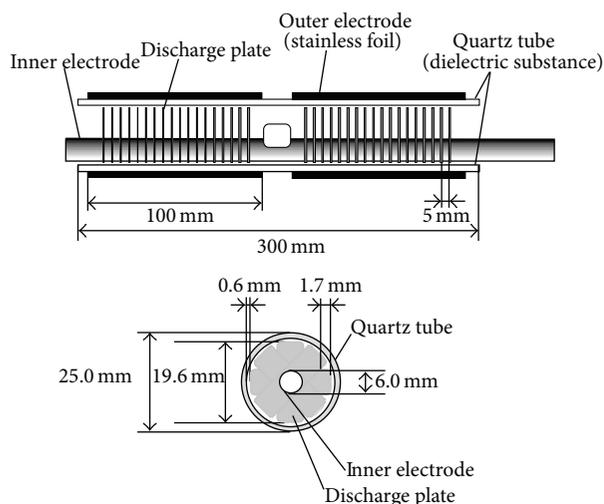
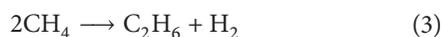


FIGURE 1: Detail of dielectric-barrier discharge reactor.

down to 5% at the atmospheric pressure (101 kPa), resulting in the increase of the selectivity to ethane up to 57% and propane to 24%.

The objective of the present paper is to increase the product selectivity to ethane by a convenient DBD-driven plasma reactor, reducing the production of alkenes and C3+, by means of the coexistence of hydrogen, the main byproduct of the reaction (reaction (3)). The coexistence of helium was also examined as a reference,



2. Experimental

The schematic diagram of the experimental apparatus of dielectric-barrier discharge reactor, which consists of five sections (gas supply, high voltage power supply, radiator, reactor and analysis equipment), is similar the previous paper [16]. The detail of the reactor, which is basically available as an ozonizer, is illustrated in Figure 1. A Pyrex tube (25 mm i.d. with 300 mm length) was used as the dielectric barrier between outer and inner electrodes. Aluminum was pasted on the outer wall of the reactor tube as the outer electrode. The discharge occurred in the gap between the edge of disks and the inside wall of the tube. Two stainless steel rods (100 mm length) were connected, and the disk of 36 sheets (total) were arranged in a regular interval (5 mm) between the upper and lower parts of the tube.

The power level of the primary (V_1) and the secondary (V_2) voltages were varied from 0 to 100 V and 9.0 kV, respectively. The voltage and current were measured by using a high voltage probe and a current probe with an oscilloscope. Very low electric power (3~32 W) is required to make discharge with this reactor. All the experiments were carried out under atmospheric pressure.

High purity gas of CH_4 (99.9999%) was used as a sole reactant gas. And also high purity gases of H_2 (99.99%) or helium (99.9999%) were added to methane as coexistent gas

at prescribed rate by volume. The reactant gas was supplied to the DBD reactor at the total feed rate of 50 mL/min.

After the discharge had been employed for 240 sec in the plasma state the outlet gas was sampled and analyzed using gas chromatographs (SHIMADZU, GC-14B) with a thermal conductivity detector (TCD) and a flame ionization detector (FID) using SHINCARBON S (2 m \times 3 mm ϕ) and SHINCARBON T (6 m \times 3 mm ϕ) as the separation column, respectively.

The conversion of the reactant methane defined as follows:

$$\begin{aligned} \text{Methane conversion } (X_{\text{CH}_4}, \%) \\ = 100 \times \frac{\text{carbon moles of methane consumed}}{\text{carbon moles of methane introduced}}. \end{aligned} \quad (4)$$

And the carbon selectivity of the products were defined as follows:

$$\begin{aligned} \text{Product selectivity } (\%) \\ = 100 \\ \times \frac{\text{carbon moles of the product}}{\text{total carbon moles of all products excepting methane}}. \end{aligned} \quad (5)$$

3. Results and Discussion

3.1. The Effect on the Methane Conversion. The main product of the thermal decomposition of methane (thermal diffusion reactor, 800–1200°C) is ethene [2–8] and the polymerized oil [5]. A steep temperature gradient in this reactor was elucidated to give a higher conversion to ethene over the thermodynamic data calculated for the temperature uniform system. The key action of the so-called thermal diffusion effect by temperature gradient system is the mass separation of CH_3 (or CH_2) radical and H, evolved at the first stage of the decomposition of methane at the high temperature surface of the reactor.

It has been proposed as a possible DBD reaction mechanism that the collision of methane molecule with electron affords CH_3 radical which gives birth to ethane by simple coupling. In our previous report [16], the methane conversion is limited to 9.5%, but the main product is ethane (nearly 60%) followed by propane (around 20%). The distributions of these main products by DBD are also similar values to the other reports [9–15], improving the methane conversion by use of catalysts, although the increase of C_2 selectivities has been limited by ca. 20%. This means that the catalyst action seems hard to regulate the plasma state but promotes the further decomposition of the initial activated state.

As it was shown in our former paper [3], some coexistent gases promote the conversion of methane by retarding of the recombination of the dissociated methyl radical to methane. In the present study, the expected main byproduct with dehydrogenative methane coupling, namely hydrogen, was selected to be introduced to the discharge zone as a coexistent gas with methane to make simpler components of outlet gases from the practical standpoint.

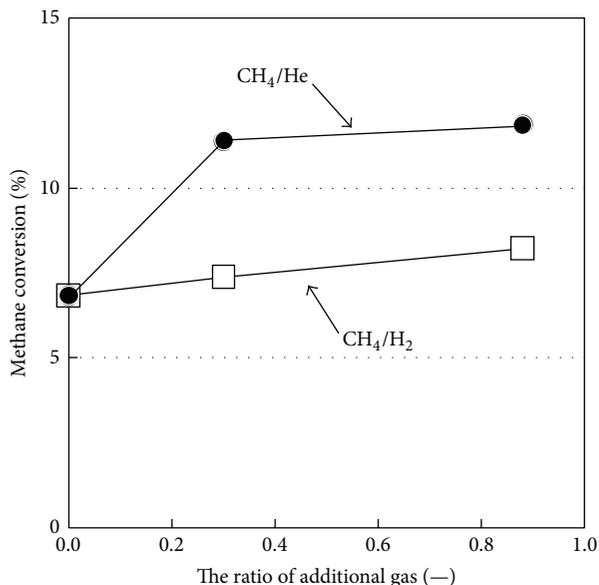


FIGURE 2: Comparison of methane conversion obtained from CH₄/He or CH₄/H₂ at various ratios of coexistent gas (power: 44 W).

As for the purpose to increase the X_{CH_4} , the dilution with coexistent gas was also effective in this case. The experimental results of the effect on the X_{CH_4} with the dilution gases are shown in Figure 2. The increase effect with helium coexistence was larger than that with hydrogen. This tendency was observed more clearly with the increase of the supplied power to the reactor (Figure 3).

The retarding effect against the recombination of CH₃ and H is obvious with helium even at the gas ratio with methane is 0.3, but it is limited with respect to hydrogen. The reason might be the possibility of hydrogen to afford H to CH₃ radical by the dissociation of itself, although it is not so much as methane (as shown in the case without coexistent gas).

3.2. The Effect on the Ethane Selectivity. The initial step, the C–H bond cleavage of methane, has the lowest exciting energy threshold of *ca.* 9.0 eV followed by the formation of CH₂ (10 eV), CH (11 eV), and C (12 eV) [17]. This means that the attack of lower energy electron on methane molecule is favorable for the increase of CH₃ radical concentration in the reaction zone, preventing the further decomposition to CH₂, CH, and so forth, which are intermediate species to unsaturated hydrocarbons. It is favorable to apply as low energy to methane molecule as possible.

As it has been reported previously, the methane conversion with a high energy supply by microwave-induced plasma in a reduced pressure affords ethyne in extremely high yield [1], and the presence of a sort of catalyst in the similar situations promotes further dehydrogenations and results in the formation of carbon nanotube [18, 19]. Contrary to these, the low energy supply to methane molecule by DBD resulted in the product distributions to alkanes, ethane, and propane, with high rates of selectivity [16].

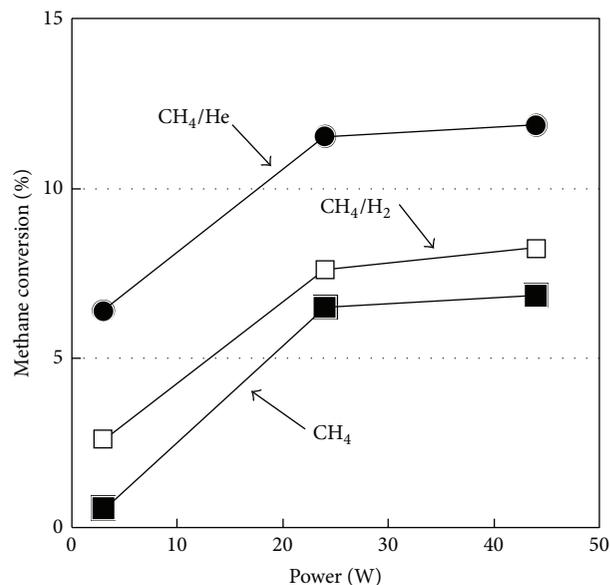


FIGURE 3: Comparison of methane conversion obtained from CH₄/He or CH₄/H₂ at various electric powers (ratio of coexistent gas: 0.88).

As for the effect of coexistent gas on the selectivities, it was shown that hydrogen worked to reduce unsaturated products compared with helium in the whole experimental conditions (Table 1). This phenomenon could also be supported by the promoting effect of added rare gas, which has been reported by Indarto et al. [20], on the methane conversion to hydrogen and solid carbon in the arc discharge. The opposite effect on the dehydrogenation was observed with the hydrogen addition. In the presence of excess hydrogen, no carbon deposition was observed and the production of ethene or ethyne was decreased greatly, resulting in higher selectivities to ethane and propane, *ca.* 70% and 20%, respectively. The reason might be attributable to the hydrogenation of the activated intermediates for ethane and propane, preventing them from the further dehydrogenations.

4. Conclusion

In the dehydrogenative coupling reaction of methane by DBD reactor, the coexistent hydrogen is effective for both the increase of the methane conversion rate and the increase of the product selectivity to ethane. The former can be explained by the dilution effect retarding the recombination of methyl radical with H, and the latter by the hydrogenation of unsaturated products or active intermediates. It is required to balance these conflicting effects for sake of increasing the yield of ethane.

In practical way of doing, ethane and propane would be converted to ethene and propene, both the petrochemical feedstock, by the conventional method at the present time. Byproduced hydrogen could be recycled on the site to the reactor with the recovered methane.

TABLE 1: Effect of coexistent gases on the carbon selectivity, in comparison with the other methods of dehydrogenative methane coupling.

Method	Coexistent gas	Ratio (v/v)	Power (w)	Product carbon selectivity (mol%)								
				C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	C ₃ H ₈	(CH ₃) ₂ CHCH ₃	n-C ₄ H ₁₀	others		
DBD	None	0	3	46.9	16.1	5.6	19.1	6.6	3.6	2.0		
			24	49.8	5.1	3.9	21.7	5.2	5.4	8.9		
			44	50.4	3.6	3.1	21.5	5.1	5.9	10.4		
		0.3	3	45.8	8.7	9.2	12.0	3.3	4.7	16.3		
			24	53.0	2.6	3.8	19.9	4.6	6.7	9.4		
			44	51.1	2.2	3.1	20.3	4.9	6.8	11.6		
	H ₂	0.88	3	63.3	0.0	4.1	20.3	5.6	6.7	0.0		
			24	67.1	0.0	0.8	19.1	4.4	4.4	4.1		
			44	69.4	0.0	0.7	19.0	3.9	4.1	3.0		
		0.3	3	47.2	11.5	6.6	17.9	4.5	5.3	7.0		
			24	47.5	4.1	3.5	22.1	5.4	6.6	10.8		
			44	48.0	3.2	5.7	22.2	6.6	1.1	13.2		
	He	0.88	3	50.1	9.7	4.0	22.7	4.8	6.0	2.8		
			24	50.7	6.4	2.7	24.7	4.6	6.8	4.1		
			44	50.4	5.4	2.0	24.3	4.7	8.9	5.4		
		MW ^a Plasma [16]	None	0	10	25.5	31.9	41.9	0.3	—	—	0.3
					30	10.7	21.4	66.5	0.3	—	—	1.0
					50	2.4	6.3	90.2	0.2	—	—	0.9
100	1.2				4.2	92.9	0.3	—	—	0.3		
150	0.6				2.9	95.1	0.3	—	—	1.0		
200	0.5				2.5	95.9	0.2	—	—	0.9		
TDCR ^b [5]	None	0	250	0.4	2.4	95.2	0.2	—	—	0.8		
			300	0.2	2.2	84.8	0.3	—	—	12.6		
			1220 K ^c	39.2	60.8	—	—	—	—	—		
			1300 K ^c	19.1	63.9	10.1	6.9	—	—	—		
			1400 K ^c	1.2	65.4	31.1	2.3	—	—	—		

^a Microwave, ^b thermal diffusion column reactor, ^c surface temperature of Pt-loaded carbon rod.

Highlights

There have been intensive investigations on dehydrogenative coupling of methane without catalyst at ambient conditions. The effect of coexistence of hydrogen on the methane conversion and the product selectivity of ethane was examined experimentally. The methane conversion was increased by the dilution of methane with hydrogen. The selectivity of ethane was improved up to 70%.

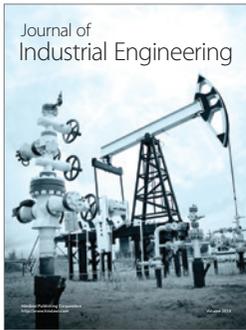
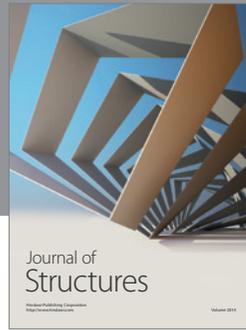
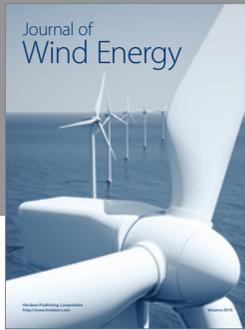
Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- [1] K. Onoe, A. Fujie, T. Yamaguchi, and Y. Hatano, "Selective synthesis of acetylene from methane by microwave plasma reactions," *Fuel*, vol. 76, no. 3, pp. 281–282, 1997.
- [2] T. Yamaguchi, A. Kadota, and C. Saito, "Dehydrogenative coupling of methane by use of thermal diffusion column," *Chemistry Letters*, vol. 17, pp. 681–682, 1988.
- [3] T. Yamaguchi and C. Saito, "Selective synthesis of ethylene by dehydrogenative coupling of methane by use of thermal diffusion column," *Bulletin of the Chemical Society of Japan*, vol. 61, pp. 2649–2650, 1988.
- [4] T. Yamaguchi, C. Xianghao, and G. Zhiming, "Dehydrogenative coupling in thermal diffusion reactor with the function of hydrogen separation," *Journal of the Japan Petroleum Institute*, vol. 35, pp. 292–295, 1992.
- [5] K. Suzuki, R. Takahashi, K. Onoe, and T. Yamaguchi, "Dehydrogenative methane homologation to C₂ hydrocarbon and aliphatic oil by a thermal diffusion column reactor with platinum-loaded pyrogen," *Energy and Fuels*, vol. 13, no. 2, pp. 482–484, 1999.
- [6] K. Suzuki, V. J. Wargadalam, K. Onoe, and T. Yamaguchi, "CO₂ reforming of methane by thermal diffusion column reactor with Ni/carbon-coated alumina tube pyrogen," *Energy and Fuels*, vol. 15, no. 3, pp. 571–574, 2001.
- [7] Z. Gao, M. Kobayashi, H. Wang, K. Onoe, and T. Yamaguchi, "Methane conversion in thermal diffusion column reactor with carbon rod as pyrogen," *Fuel Processing Technology*, vol. 88, no. 10, pp. 996–1001, 2007.
- [8] S. Kawakami, T. Kanaguchi, H. Tagami, and T. Yamaguchi, "The effect of coexistent gases on the thermal reaction of toluene or methane in a Clusius-Dickel type diffusion column," *Bulletin of the Chemical Society of Japan*, vol. 65, pp. 3434–3438, 1992.

- [9] S. Kado, Y. Sekine, T. Nozaki, and K. Okazaki, "Diagnosis of atmospheric pressure low temperature plasma and application to high efficient methane conversion," *Catalysis Today*, vol. 89, no. 1-2, pp. 47-55, 2004.
- [10] X.-S. Li, A.-M. Zhu, K.-J. Wang, Y. Xu, and Z.-M. Song, "Methane conversion to C₂ hydrocarbons and hydrogen in atmospheric non-thermal plasmas generated by different electric discharge techniques," *Catalysis Today*, vol. 98, no. 4, pp. 617-624, 2004.
- [11] A. Indarto, N. Coowanitwong, J.-W. Choi, H. Lee, and H. K. Song, "Kinetic modeling of plasma methane conversion in a dielectric barrier discharge," *Fuel Processing Technology*, vol. 89, no. 2, pp. 214-219, 2008.
- [12] S.-S. Kim, H. Lee, J.-W. Choi, B.-K. Na, and H. K. Song, "Methane conversion to higher hydrocarbons in a dielectric-barrier discharge reactor with Pt/ γ -Al₂O₃ catalyst," *Catalysis Communications*, vol. 8, no. 9, pp. 1438-1442, 2007.
- [13] Q. Wang, B.-H. Yan, Y. Jin, and Y. Cheng, "Dry reforming of methane in a dielectric barrier discharge reactor with Ni/Al₂O₃ Catalyst: interaction of catalyst and plasma," *Energy and Fuels*, vol. 23, no. 8, pp. 4196-4201, 2009.
- [14] A. Górska, K. Krawczyk, S. Jodzis, and K. Schmidt-Szałowski, "Non-oxidative methane coupling using Cu/ZnO/Al₂O₃ catalyst in DBD," *Fuel*, vol. 90, no. 5, pp. 1946-1952, 2011.
- [15] A. Indarto, J.-W. Choi, H. Lee, and H. K. Song, "Methane conversion using dielectric barrier discharge: comparison with thermal process and catalyst effects," *Journal of Natural Gas Chemistry*, vol. 15, no. 2, pp. 87-92, 2006.
- [16] K. Konno, M. Kobayashi, K. Onoe, and T. Yamaguchi, "Conversion of methane by dielectric-barrier discharge plasma method—comparison with microwave plasma method," *Journal of the Japan Petroleum Institute*, vol. 53, no. 3, pp. 144-151, 2010.
- [17] S. Kado, K. Urasaki, Y. Sekine, K. Fujimoto, T. Nozaki, and K. Okazaki, "Reaction mechanism of methane activation using non-equilibrium pulsed discharge at room temperature," *Fuel*, vol. 82, no. 18, pp. 2291-2297, 2003.
- [18] K. Konno, K. Onoe, and T. Yamaguchi, "The effect of changes in catalyst temperature produced by direct plasma heating on the preparation of carbon nanotube," *Tanso*, no. 241, pp. 2-5, 2010.
- [19] K. Konno, K. Onoe, Y. Takiguchi, and T. Yamaguchi, "Direct preparation of hydrogen and carbon nanotubes by microwave plasma decomposition of methane over Fe/Si activated by biased hydrogen plasma," *Green and Sustainable Chemistry*, no. 3, pp. 19-25, 2013.
- [20] A. Indarto, J.-W. Choi, H. Lee, and H. K. Song, "Effect of additive gases on methane conversion using gliding arc discharge," *Energy*, vol. 31, no. 14, pp. 2650-2659, 2006.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

