Communication

# A Brief Catalyst Study on Direct Methane Conversion Using a Dielectric Barrier Discharge

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A series of metal catalysts was used for methane conversion to higher hydrocarbons and hydrogen in a dielectric barrier discharge. The main goal of this study is to identify the metal catalyst components which can influence the reactions in room-temperature plasma conditions. The catalysts supported by  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and zeolite (ZSM 5x) were prepared by the incipient wetness method with solutions containing the metal ions of the second component. Among the catalysts tested, only Pt and Fe catalysts showed a unique result of catalytic reaction in a reactor bed packed with glass beads.

Keywords: Plasma; Dielectric barrier discharge; Metal catalyst; Methane conversion.

# INTRODUCTION

The identification of catalysts showing high activity and selectivity for the direct conversion of methane to higher hydrocarbon or hydrogen is the major purpose of this research. Many different catalyst systems have been investigated and varying degrees of success have been achieved; however, until now none of them have demonstrated outstanding performance.<sup>1,2</sup> Generally, catalysts operate under conditions where temperature of the process reaches an appropriate point so that a catalyst can be active. Some references claim that it is possible to activate the metal catalyst in near-room temperature using some alternative methods, e.g. plasma.<sup>3-5</sup>

However, different plasma conditions in each experiment make it difficult to confirm and compare the real activity of the catalysts on the reactions. In order to overcome this problem, a comprehensive study was done by comparing the catalyst activity in the same plasma system. Experiments were done using a dielectric barrier discharge (DBD) at room temperature and atmospheric pressure. Among non-thermal plasmas, DBD has a better future to be applied at an industrial level for chemical synthesis. Flexibility to be used in liquid<sup>6-7</sup> or gas<sup>8-9</sup> environment condition is an advantage. The activation of a catalyst was investigated by studying its effects on methane conversion and the distribution of products.

## **EXPERIMENTAL SETUP**

Fig. 1 shows a schematic diagram of the experimental setup. Methane was introduced into a cylindrical reactor at room temperature and atmospheric pressure. The products were analyzed by gas chromatography. Details of each part of the system are described in the next sections.

#### Reactor

The reactor is a cylindrical Pyrex tube (ID of 7.5 mm) with 2 parallel-straight wires (0.2-mm diameter, stainless steel) as the inner metal electrode and silver film coated around the tube as the outer electrode. A high frequency alternating current (AC) power supply was connected to the electrodes. The effective volume and length of the reactor were 8.8 mL and 200 mm, respectively. In order to maintain a similar reactor configuration, e.g. gap distance, the reactor capacitance was checked by a RCL meter (Fluke PM6304) before and after experiments. The reactor capacitances were in the range of 9.5-10.0 pF in air-filled gap conditions.

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## **Power Supply**

The maximum voltage and frequency of the AC power supply (Auto Electric, model A1831) were 10 kV and 20 kHz, respectively. To measure the total supplied power to the reactor, a digital power meter (Metex, model M-3860M) was inserted into the electric line of the power supply. The general waveform of voltage and current used during experiments is shown in Fig. 2.

#### Materials

All experiments were carried out by introducing methane (CH<sub>4</sub>, purity > 99.99%) to the reactor at room temperature and atmospheric pressure. The gas flow rate was controlled by a calibrated mass flow controller (Milipore, model FC-280SAV). Analysis of the products was carried out using a gas chromatograph (YoungLin, model M600D) with a thermal conductivity detector (TCD, Column: Hayesep D 80/100) for measuring H<sub>2</sub> and CH<sub>4</sub>, and a flame ionized



Fig. 1. Schematic diagram of experimental set up.



Fig. 2. Voltage and current profile.

detector (FID) for measuring  $CH_4$  and higher hydrocarbons.

The evaluation of system performance was done based on product selectivity and methane conversion which are formulated as:

Selectivity of 
$$H_2 = \frac{\text{moles of } H_2 \text{ produced}}{2 \times \text{moles of } CH_4 \text{ converted}} \times 100\%$$
 (1)

Selectivity of 
$$C_x H_y = \frac{x \times \text{moles of } C_x H_y \text{ produced}}{\text{moles of } CH_4 \text{ converted}} \times 100\%$$
 (2)

$$Conversion of CH_4 = \frac{moles of CH_4 converted}{moles of initial CH_4} \times 100\%$$
(3)



Fig. 3. XRD spectra of (a) Al<sub>2</sub>O<sub>3</sub> and (b) zeolite (ZSM 5x)-supported catalyst.

A series of metal catalysts was prepared by incipient wetness impregnation method with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (purchased from Junsei Chemical, Japan) and zeolite 5x (ZSM 5x, Junsei Chemical, Japan) used as the supports. The aqueous solutions of metal catalyst were made by dissolving precursors in distillate water. All catalysts were dried at 388 K for 2 h, followed by calcination at 873 K for 3 h in O<sub>2</sub>-rich gas conditions. Reduction of catalyst was done by flowing hydrogen at 673 K for 2 h. Amounts of metal loaded were all settled to be 3 wt% of the catalyst.

Fig. 3 shows the XRD spectra of each catalyst. The XRD characterization was done after the reduction step. In order to measure the exact amount of metal doped on the catalyst support, energy dispersive spectroscopy (EDS) analysis was conducted and the spectra example of 3% Ni over  $Al_2O_3$  is shown in Fig. 4. In these experiments, 0.5 gram of catalyst was packed at the end of the plasma zone to prevent the decomposition of products by plasma.

#### **RESULTS AND DISCUSSION**

#### Non-catalytic plasma process

In order to investigate the effects of catalyst existence in the DBD, a non-catalytic plasma process was conducted as a comparison. All experiment ranges were done at atmospheric pressure and ambient temperature. The total flow rates were varied from 5 mL/min to 40 mL/min while the supplied power was set at 50, 60, and 80 watts. Some parts of these works have been presented before where we compared the plasma process with the thermal process.<sup>8</sup> It was concluded that the plasma process has better results for higher hydrocarbons production.

Fig. 5a shows the effect of flow rate and voltage variation on the methane conversion. Higher conversion of methane can be achieved by supplying higher power to the reactor or lowering the flow rates. Higher supplied power means an increase in the concentration of higher energetic species in the plasma zone which are able to decompose the chemical bond of methane. The maximum point of the conversion reaches 80% at the flow rate of 5 mL/min and the supplied power of 80 watts. Fig. 5b presents the product distribution of methane conversion by non-catalytic plasma process. The highest selectivity of H<sub>2</sub> was produced at the lowest input flow rate. It is believed that fragmentation of methane into smaller molecules, e.g. H<sub>2</sub> and C, is more favorable than recombinant reactions to produce higher hydrocarbons.<sup>8,10-11</sup> This condition will lead to re-decomposition reactions of higher hydrocarbons which were previously produced during plasma reaction, e.g. coupling reactions of methyl radicals.

An electron which has an important role in the cold plasma process, e.g. DBD,<sup>12</sup> will initiate the radical reactions:



Fig. 4. EDS spectra of 3%Ni/γ-Al<sub>2</sub>O<sub>3</sub>.

$$CH_4 + e \rightarrow CH_4$$
 (4)

$$CH_4 \rightarrow CH_3 + H + e$$
 (5)

Recombinant reactions of higher hydrocarbons could occur by coupling reactions of methyl radicals ( $CH_3$ ·). However, the existence of hydrogen in the reactor will give the opposite effect because the hydrogen radical (H·) has a tendency to become a reducer species or reactant decomposer for higher hydrocarbons.

$$CH_{3} + CH_{3} \rightarrow C_{2}H_{6} \tag{6}$$

$$CH_3 \cdot + CH_3 \cdot \to C_2H_4 + H_2 \tag{7}$$

$$CH_{3'} + C_2H_{3'} \rightarrow C_3H_6 \tag{8}$$

$$C_x H_y + H \cdot \rightarrow C_x H_{y-1} \cdot + H_2 \tag{9}$$



Fig. 5. Effects of flow rates on (a) methane conversion and (b) products distribution.

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Instead of H·, re-decomposition of higher hydrocarbon could be caused by electrons. Electron collision with molecules is faster than molecule collision with ions or radicals.<sup>13</sup> Longer resident time of molecules in the plasma reaction will reduce the concentration of higher hydrocarbons and produce more H<sub>2</sub> molecules compared to the shorter resident time reactions. In this experiment, very small amounts of solid carbon were found and they can be ignored.

# Catalyst-assisted plasma process

In order to convert methane to the desired products (such as ethylene and benzene) with high selectivity, the combination of plasma with catalyst has been explored separately in many different plasma conditions.4,14-15 However, this situation results in difficulty to make a direct comparison of the activity among those catalysts. Some research papers also show ambiguous arguments, e.g. different results. To overcome these problems, we investigated the plasma methane conversion over various  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and zeolite (ZSM 5x)-supported metal catalysts. Table 1 shows the effects of catalysts in the discharge plasmas on methane conversion and the selectivity of C2, C3, C4, and H2. Generally, catalysts supported by zeolite (ZSM 5x) produce higher acetylene and ethane compared to non-catalytic process. On the other hand, this condition will influence the selectivity of higher hydrocarbons, e.g. C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>, that is lower compared to a non-catalytic process. It can be concluded that the existence of zeolite in the plasma reaction leads to the formation of lighter hydrocarbons rather than higher hydrocarbons. This idea is supported by previous investigations which showed the same tendency of increasing selectivity of acetylene and ethane.<sup>15</sup>

However, from Table 1, we can draw a conclusion that the activity of the metal catalysts for methane conversion prepared by incipient wetness of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and zeolite (ZSM 5x)-supported catalyst are somewhat disappointing. Although sometimes the existence of metal catalysts in the plasma process gives diverse results, the product distribution is relatively the same, and the difference selectivity values are not significant compared to the non-catalytic process. In dielectric barrier discharge where the temperature is equal to the room temperature, most metal catalysts supported by  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and zeolite (ZSM 5x) were not activated only by the existence of energetic species, such as electrons and ions. It is believed that activation temperature is still the most important factor to activate the metal cata-

		2		1			
catalvst	run <sup>1</sup>	CH <sub>4</sub> conv.	selectivity (%)				
oataryot		(%)	He	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	n-C4H10
empty	1	7.51	34.52	5.13	35.73	11.73	4.81
	2	18.05	23.99	7.73	33.83	17.59	9.73
	3	21.11	34.63	6.93	35.37	19.59	0.00
Al <sub>2</sub> O <sub>3</sub>	1	8.69	39.69	7.62	26.31	15.85	5.74
	2	14.23	27.19	9.82	38.64	15.78	0.00
	3	20.16	41.51	6.80	40.06	18.05	0.00
3% Fe/Al <sub>2</sub> O <sub>3</sub>	1	5.93	24.74	0.00	58.70	10.26	0.00
	2	12.11	34.39	11.40	44.79	16.53	0.00
	3	25.10	34.13	9.77	41.33	19.74	11.85
3% Cu/Al <sub>2</sub> O <sub>3</sub>	1	6.79	25.63	5.98	27.46	13.65	1.25
	2	19.09	21.52	6.26	29.32	11.58	0.00
	3	24.92	28.93	6.50	28.00	12.10	0.00
1% Pt/Al <sub>2</sub> O <sub>3</sub>	1	9.91	35.79	4.83	47.80	20.34	0.00
	2	13.57	41.05	3.15	50.68	20.38	0.00
	3	21.06	38.67	4.95	42.96	17.50	4.53
3% Pt/Al <sub>2</sub> O <sub>3</sub>	1	8.25	33.53	2.14	45.68	10.65	0.00
	2	17.56	35.12	1.58	48.95	14 65	2.63
	3	27.01	32.92	0.00	44 87	16.36	5 51
3% Ni/Al <sub>2</sub> O <sub>3</sub>	1	8 45	37 14	6.12		10.46	4.32
	2	15.64	30.49	5.46	32.87	13.65	0.00
	2	20.98	38.89	5.23	27.97	14.02	5 31
5% Mn/Al <sub>2</sub> O <sub>3</sub>	1	10.36	29.94	12.42	39.54	0.00	0.00
	2	15.24	30.26	10.26	36.45	5.62	4.16
	2	35.63	30.16	7.36	32.24	8.70	4.10 8.70
3% Ru/Al <sub>2</sub> O <sub>3</sub>	1	9.54	34.34	1/ 89	30.35	18.28	0.70
	2	15.63	30.25	8.63	29.63	11.25	2.36
	2	38.20	40.70	6.06	23.00	14.00	2.00 8.01
zeolite		7.56	20.85	10.56	38.06	8.07	0.21
	2	12.20	29.00	10.00	26.27	7.67	0.00
	2	10.29	42.00	10.03	40.57	7.07	0.00 E 74
2º/ Eo/zoolito		0.54	42.90			9.65	1.02
5% Fe/2eone		0.02	30.23	2.39	60.30 E2.0E	9.07	1.20
	2	15.20	38.87	0.20	53.25	19.53	0.00
	3	22.01	34.32	10.23	58.43	7.70	0.00
3% U/Zeolite	0	8.89	47.10	9.57	37.89	4.97	0.00
	2	15.67	30.03	13.83	30.59	1.37	1.94
3% Pt/zeolite	1	7.65	38.10	4 91	50.52	10.56	0.00
	2	11.67	33.22	1.20	45.58	6 52	0.00
	2	20.16	31.04	5 11	46.05	0.02 1 02	0.00
8% Ni/zoolito	1	6.56	/0.22	6.28	30.00	5 10	0.00
3% NI/Zeone	י ר	16.00	40.00	12.00	36.00	J. 12 1 60	0.00
	2	10.20	40.40	15.20	00.92 20 71	4.00	0.00
20/ Du/zoolite	ں ۱	6.00	25.57	0.00		0.00	0.00
3% Ru/zeolite	1	0.22	30.07 40.50	0.04	01.94 01.61	2.10	0.00
	2	14.33	40.50	8.09	31.61	5.63	0.00
	3	22.89	38.95	12.92	42.10	3.11	0.00

Table 1. Effects of catalysts on methane conversion and products selectivity

Note: <sup>1</sup>Run 1 is flow rate: 30 mL/min, power: 35 W; run 2 is flow rate: 30 mL/min, power: 50 W; run 3 is flow rate: 15 mL/min, power 50 W.

lyst. Further studies of these effects and catalyst characterization analysis are underway. Among metal catalysts, only Pt and Fe show a unique result on the selectivity of hydrocarbons. Pt and Fe sup-

ported by both  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and zeolite (ZSM 5x) increase the selectivity of ethane by a factor of 1.2-1.4 compared to the non-catalytic process. Increasing ethane selectivity affects the selectivity of acetylene which is lower than that of the non-catalytic process. The reverse phenomenon shows that the hydrogenation process of acetylene to ethane occurs during plasma reaction when Pt and Fe exist. Low activation energy (~0 kJ/mol) of acetylene adsorption on the surface of Pt and Fe<sup>16</sup> can be the reason for this case. Acetylene will be attached easily on the surface of the catalyst. Hydrogen atoms which are numerously produced by collision between CH<sub>4</sub> and electrons will initiate the series of hydrogenation reactions of attached acetylene into ethane.

- $C_2H_{2(surf)} + H_{(surf)} \rightarrow C_2H_{3(surf)}$ (10)
- $C_2H_{3(surf)} + H_{(surf)} \rightarrow C_2H_{4(surf)}$ (11)
- $C_2H_{4(surf)} + H_{(surf)} \rightarrow C_2H_{5(surf)}$ (12)
- $C_2 H_{5(surf)} + H_{(surf)} \rightarrow C_2 H_{6(surf)}$ (13)

# CONCLUSION

Catalytic and non-catalytic processes of direct conversion of methane using a dielectric barrier discharge were experimentally investigated at ambient temperature and atmospheric pressure. The maximum conversion of the non-catalytic process was 80% at a flow rate of 5 mL/min and supplied power of 80 watts. The products were dominated by acetylene, ethane, and propane. The immersion of the zeolite (ZSM 5x)-supported catalyst in the plasma reaction exhibits a positive effect on increasing lighter hydrocarbons, such as acetylene and ethane, by reducing the yield of  $C_3$  and  $C_4$  products. Among all metal catalysts, only Pt and Fe can be activated by plasma by showing a unique characteristic on the product distribution. Pt and Fe can be active site materials for the hydrogenation process of acetylene in ethane.

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