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Particle Size Effect of Ordered Mesoporous Material on Non-oxidative Coupling of Methane in a Dielectric Barrier Discharge (DBD) Plasma Reactor

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Highlights

- A DBD plasma bed was successfully operated to generate C2 chemicals
- Compositions could be controlled by using size-controlled particles
- Characterization of OMM was conducted
- Productivity per discharge power was rigorously computed

1. Introduction

Typical non-oxidative methane coupling reaction in thermochemical reactor requires very high temperature (over 1,000 °C) to thermally activate C-H bond to produce methyl radicals. In this work, we use a dielectric barrier discharge (DBD) plasma reactor for non-oxidative coupling of methane. Such a DBD plasma reaction is usually conducted at atmospheric pressure and near room temperature. In the bed, we filled with ordered mesoporous materials (OMMs) such as ordered mesoporous silica (OMS) and ordered mesoporous alumina (OMA). In addition, we use more than two chemical compounds to prepare packed materials such as ordered mesoporous aluminosilicate and MgO/OMMs. This reaction system can activate C-H bond without additional thermal energy and oxidant molecules to produce methyl radical. It was found that the effect of OMM size was significant as illustratively shown in Figure 1. In the Figure, it seems quite possible to control the compositions of ethane, ethylene, and acetylene just by adjusting OMM particle size.

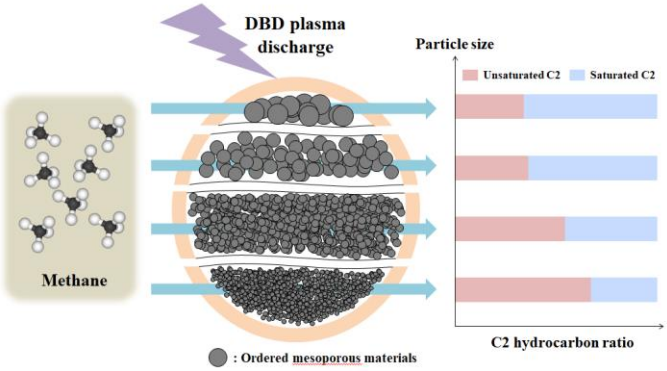

Figure 1. Variation of C2 product compositions due to the size difference of ordered mesoporous materials in a DBD plasma reactor.

2. Methods

Considering typical recipe [1], OMS in this study was prepared by a slightly modified method. Triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$, MW = 5800 g/mol) was dissolved in distilled water and concentrated HCl. Then alcohol was added to the mixture and stirred for a couple of hours. Silica precursor, tetraethyl orthosilicate was then slowly added to the mixture and stirred for one day. Then, the mixture was hydrothermally treated at 100 °C, followed by washing and drying. The dried sample was calcined at 550 °C. Synthesized OMS (denoted by M) were separated to four groups (A, B, C, and D) in terms of particle size. Non-oxidative methane coupling reaction was conducted in a lab-made DBD plasma reactor system by feeding methane mixture (CH_4: N_2 = 1:1). The discharge power was calculated by Lissajous method with voltage (V) and charge (Q). In addition, the energy yield of product *i* (Y_i) which is defined as ratio of the mass flow rate of product *i* and the corresponding discharge power was rigorously computed in table 1 [2]. The applied voltage to the reactor was 15 kV and the frequency was 1 kHz for every reaction.

Sample	Discharge Power (W)	$Y_{total\ C2}$ (g/kWh)	$Y_{unsaturated\ C2}$ (g/kWh)
A	36.6	3.69	2.32
B	32.9	6.56	3.92
C	37.2	5.86	2.44
D	35.1	5.51	1.61

Table 1. Calculated discharge power by Q-V Lissajous method and calculated energy yield of total C2 and unsaturated C2 hydrocarbon product from the reaction with each sample and the corresponding discharge power.

Sample	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
A	898	1.10	6.18
B	892	1.04	6.15
C	777	0.972	5.99
D	766	0.967	6.11
M	861	0.958	6.07

Table 2. Physisorption result of each sample

3. Results and discussion

Table 2 indicates that BET surface area and pore volume increases as particle size decreases. Figure 2 shows detailed performance of each sample in the DBD plasma bed. It was found that the smaller particles were more suitable for the production of unsaturated C2 (ethylene and acetylene), while the larger ones showed higher selectivity towards saturated C2 (ethane). It should be also noted that CH_4 conversion was found lower when small particles were packed. Reportedly [3], the surface hydroxyl group (-OH) induces the production of methyl radical and this is important for coupling reaction. The oxygen atoms on the surface of inorganic oxides such as OMS or OMA can be oxidized to surface O^- under similar discharge condition. The oxidized oxygen species chemisorbs the methane to form methyl radical, and it changes itself back to surface hydroxyl group. Therefore the larger surface area of OMM results in the more surface oxygen atoms and hydrogenated hydroxyl groups. It is believed that the high surface area of small particles lead to the higher unsaturated C2 hydrocarbon selectivity. It was also found that the medium sized-OMS particles showed higher efficiency in terms of C2 productivity. In the case of particle B, the highest amounts of unsaturated C2 and total C2 were generated when the same amount of discharge power was applied.

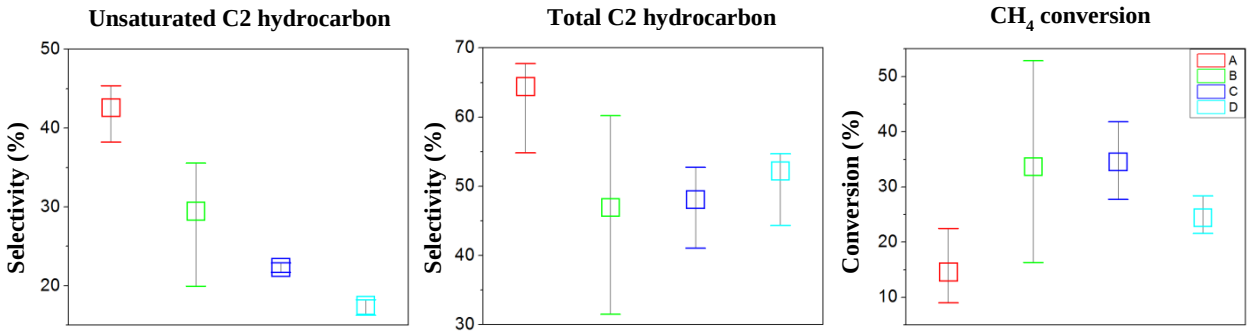

Figure 2. Min-max diagram of detailed performance of each sample in the DBD plasma bed

4. Conclusions

By adjusting OMM particle size, it was possible to control the compositions of ethane, ethylene, and acetylene. From the viewpoint of C2 generation rate per discharge power, the medium sized-OMS particles (B) were found more productive.

References

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Keywords
"Methane coupling" ; "Dielectric barrier discharge plasma reactor" ; "Ordered mesoporous material"