Supplementary Information

Effects of Dielectric Particles on Non-Oxidative Coupling of Methane in a Dielectric Barrier Discharge Plasma Reactor

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Table S1

The molar balances on hydrogen and carbon in each test.

Sample	Blank	α-Al_2O_3			sea sand			KIT-6		
Size	**-**	**S**	**M**	**L**	**S**	**M**	**L**	**S**	**M**	**L**
TOS 60 min										
CB (%) [a]	94.22	98.18	82.70	86.68	79.97	75.02	81.10	96.84	75.86	85.72
HB (%) [b]	97.01	98.57	93.51	93.65	95.46	95.09	92.41	99.77	92.03	94.47
TOS 300 min										
CB (%) [a]	93.50	94.00	95.44	95.89	99.12	98.09	90.61	98.71	97.49	94.12
HB (%) [b]	96.09	93.33	95.11	97.19	100.00	99.79	97.43	99.06	98.77	97.14

[a] Carbon Balance (CB) (%) = $\frac{\text{Moles of } CH_4 \text{ not converted} + \sum(x \times \text{Moles of } C_xH_y \text{ produced})}{\text{Moles of } CH_4 \text{ in the feed}} \times 100$

[b] Hydrogen Balance (HB) (%) = $\frac{4 \times \text{Moles of } CH_4 \text{ not converted} + 2 \times \text{Moles of } H_2 \text{ produced} + \sum(y \times \text{Moles of } C_xH_y \text{ produced})}{4 \times \text{Moles of } CH_4 \text{ in the feed}} \times 100$

Table S2

Various non-oxidative methane coupling reaction performances in a DBD plasma reactor.

Temperature / Pressure	Feed	Packing material	Voltage/Frequency/Power	CH_4 conversion (%)	Product selectivity (%)					Reference
					C_2H_2	C_2H_4	C_2H_6	C3	C4	
25 °C / 1 atm	40 sccm of CH_4/N_2 = 1	SiO_2, Al_2O_3	15 kV / 1 kHz / 36.1 – 44.1 W	19.9 – 58.4	11.2 – 46.5	4.70 – 12.7	9.56 – 21.8	6.43 – 10.7	3.86– 25.2	This study
20 °C / 1 atm	30 sccm of 90 % CH_4, 10 % Ar	Blank	7.2 kV / 2 kHz / 9.6 W	9.7	Not included	3.3	24.6	8.3	2.6	[1]
Not included	200 sccm of 10 % CH_4, 90 % Ar	MgO/Al_2O_3	6 kV / 3 kHz / 3.2 – 3.5 W	9.5 – 23	10.5 - 28	18.6 – 30.3	27.4 – 48.1	8.7 – 23.7	0.3 – 0.7	[2]
25 °C / 1 atm	30 sccm of 100 % CH_4	Blank	20 kV / 60 W	13.8	1.23	3.26	14.8	6.74	5	[3]

Table S3

Maximum experimental errors in packed bed tests with various packing materials

Packing material	Maximum error (%) [a]						
	CH_4 conv.	C_2H_2 sel.	C_2H_4 sel.	C_2H_6 sel.	C2 HC sel.	C3 HC sel.	C4 HC sel.
KIT-6	0.15	5.69	2.43	11.92	5.59	8.45	4.25
α-Al_2O_3	1.22	7.67	6.87	1.90	6.31	3.19	0.86
γ-Al_2O_3	0.17	10.35	12.00	3.16	8.58	5.17	3.33

[a] $\text{Maximum error (\%)} = \max\left(\left|\frac{\text{experimental value} - \text{mean experimental value}}{\text{mean experimental value}}\right|\right) \times 100$ (%)

Table S4

Physisorption result of each sample.

Sample	BET Surface Area (m^2/g)
α-Al_2O_3 (S)	22.8
α-Al_2O_3 (M)	18.0
α-Al_2O_3 (L)	12.9
sea sand (S)	n.d.
sea sand (M)	n.d.
sea sand (L)	n.d.
KIT-6 (S)	898
KIT-6 (M)	892
KIT-6 (L)	777

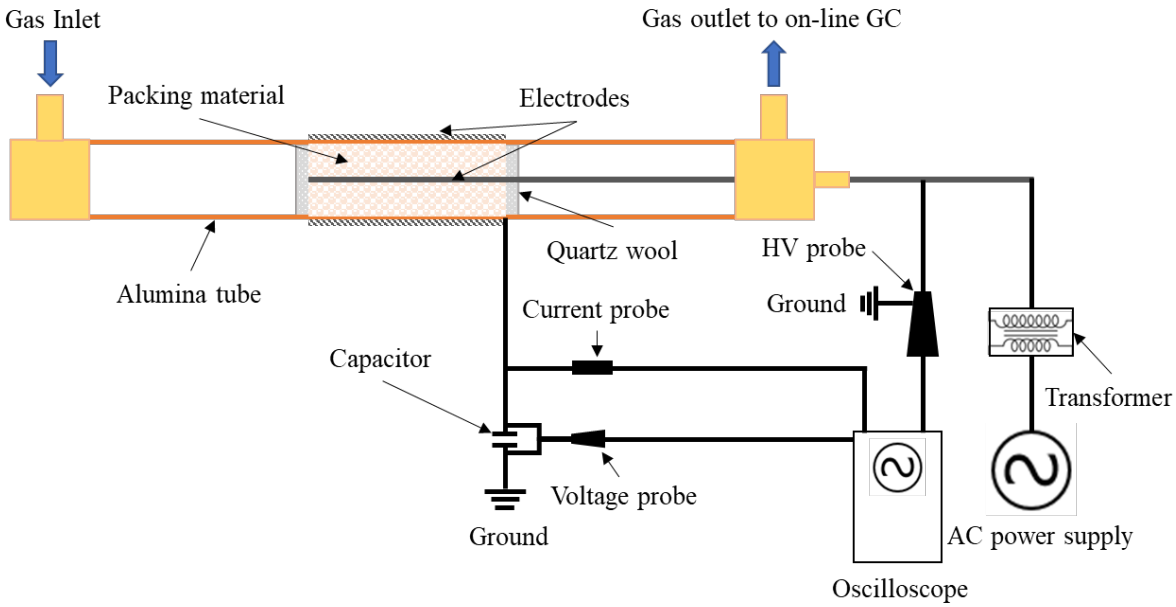

Figure S1. Schematic diagram of packed bed DBD plasma system.

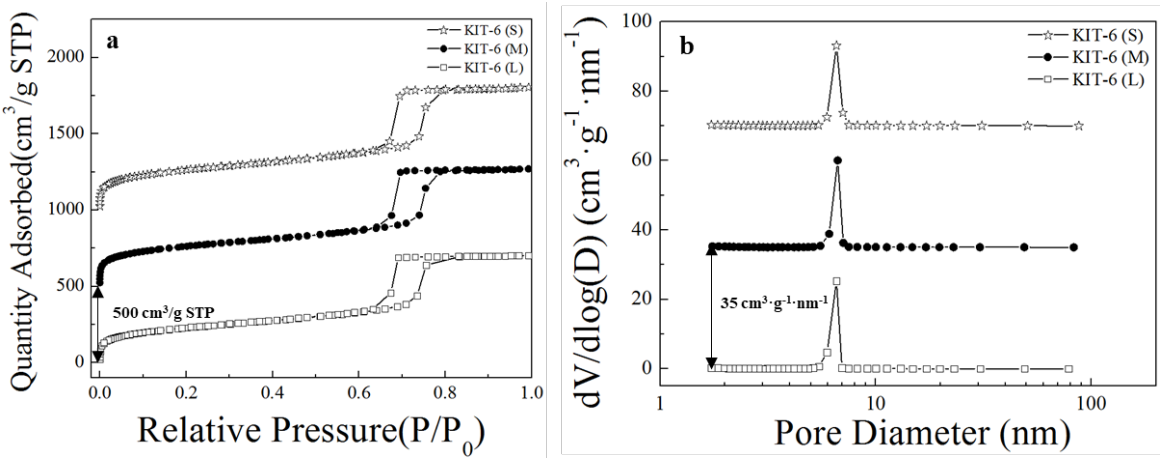

Figure S2. N_2 physisorption results; (a) Isotherms (b) BJH pore size distribution curves of the fresh KIT-6 samples.

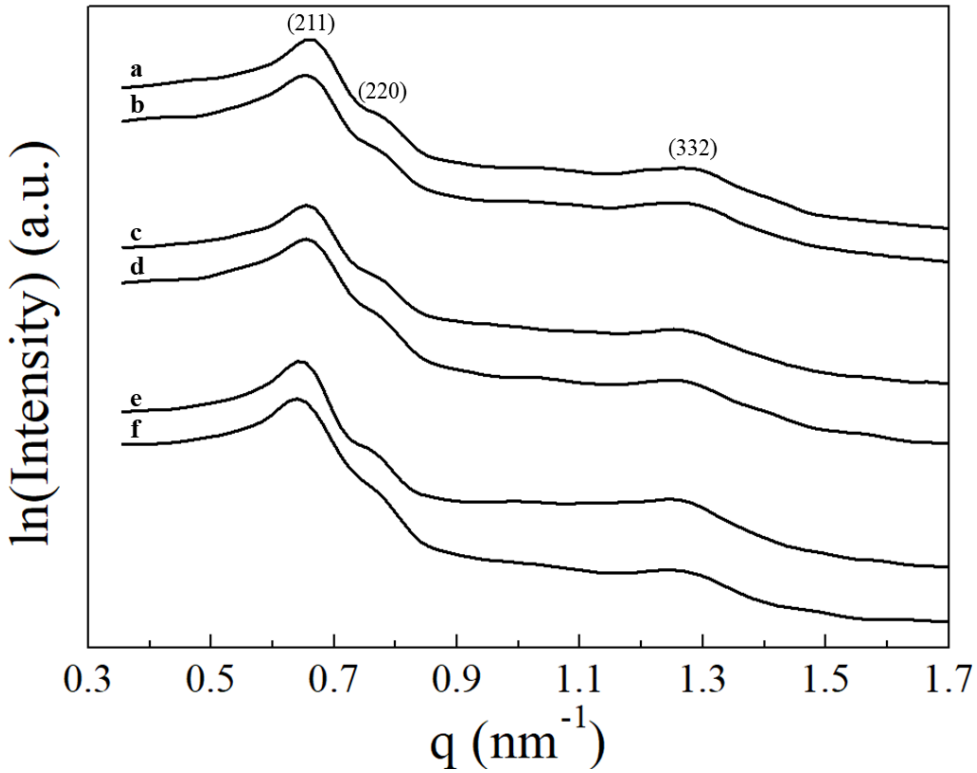

Figure S3. Small-angle X-ray scattering patterns of (a-b) fresh & spent KIT-6 (S), (c-d) fresh & spent KIT-6 (M), and (e-f) fresh & spent KIT-6 (L).

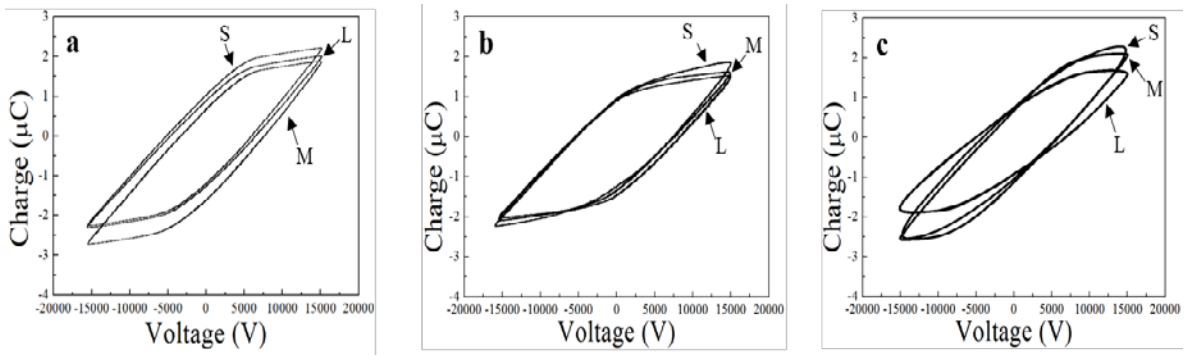

Figure S4. Q-V Lissajous plots of (a) α-Al_2O_3 samples, (b) sea sand samples, and (c) KIT-6 samples. (S), (M), and (L) denote the size of each sample.

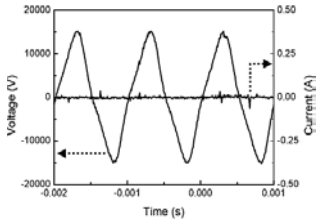

Figure S5. Voltage-current profiles in the blank DBD reactor.

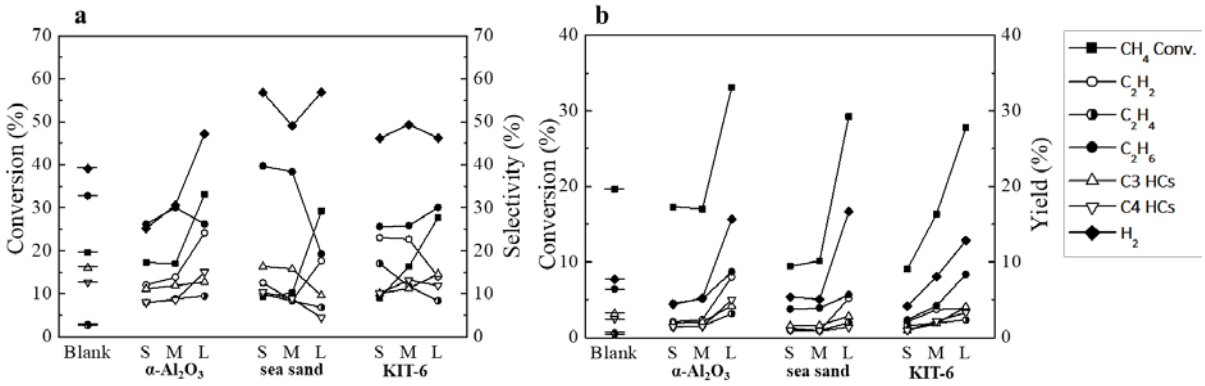

Figure S6. Reaction performances when no particles (blank), α-Al_2O_3, sea sand, and KIT-6 were used at TOS 380 min; (a) CH_4 conversion and product selectivity (b) CH_4 conversion and product yield.

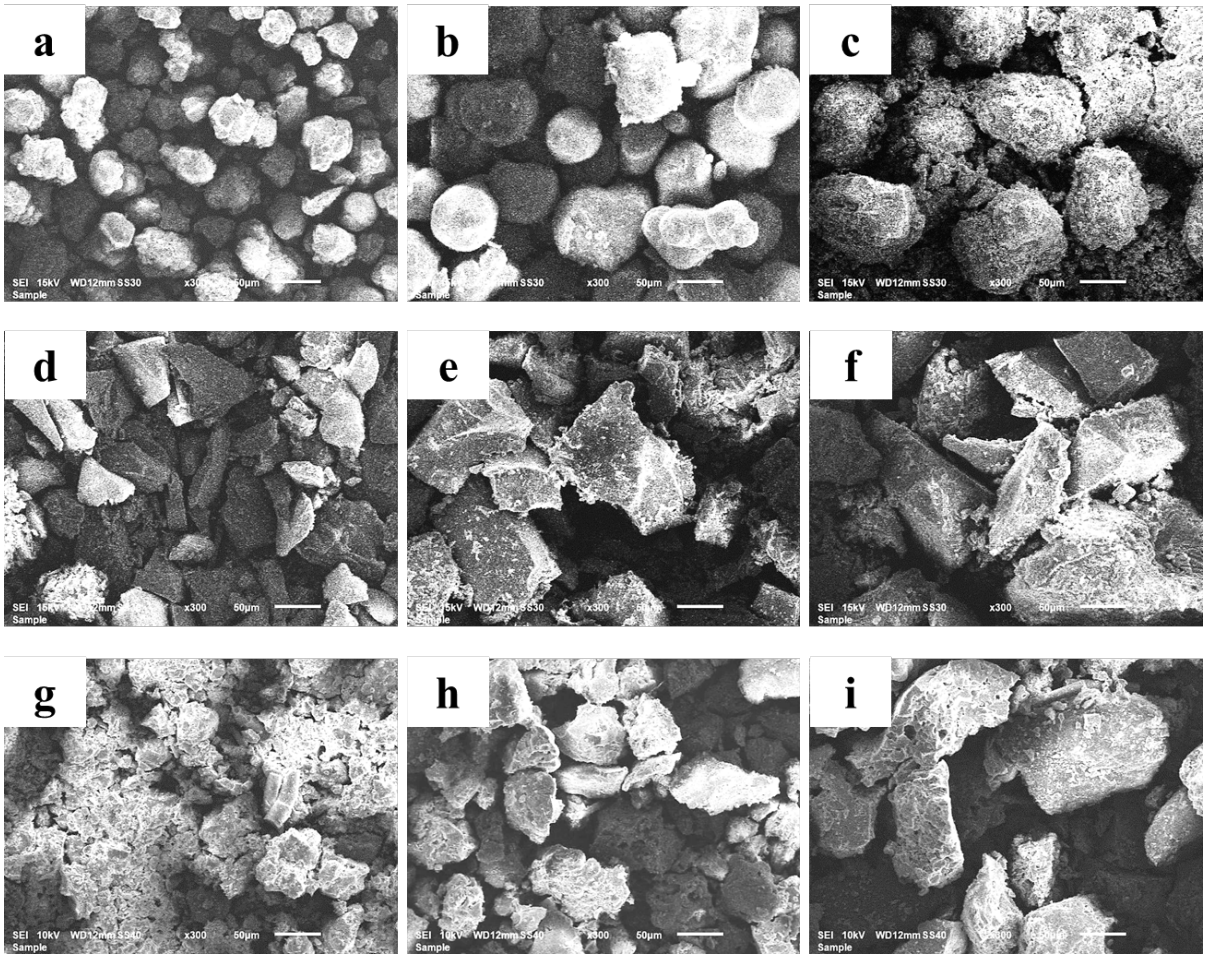

Figure S7. SEM image of (a) spent α-Al_2O_3 (S), (b) spent α-Al_2O_3 (M), (c) spent α-Al_2O_3 (L), (d) spent sea sand (S), (e) spent sea sand. (M), (f) spent sea sand (L), (g) spent KIT-6 (S), (h) spent KIT-6 (M), and (i) spent KIT-6 (L).

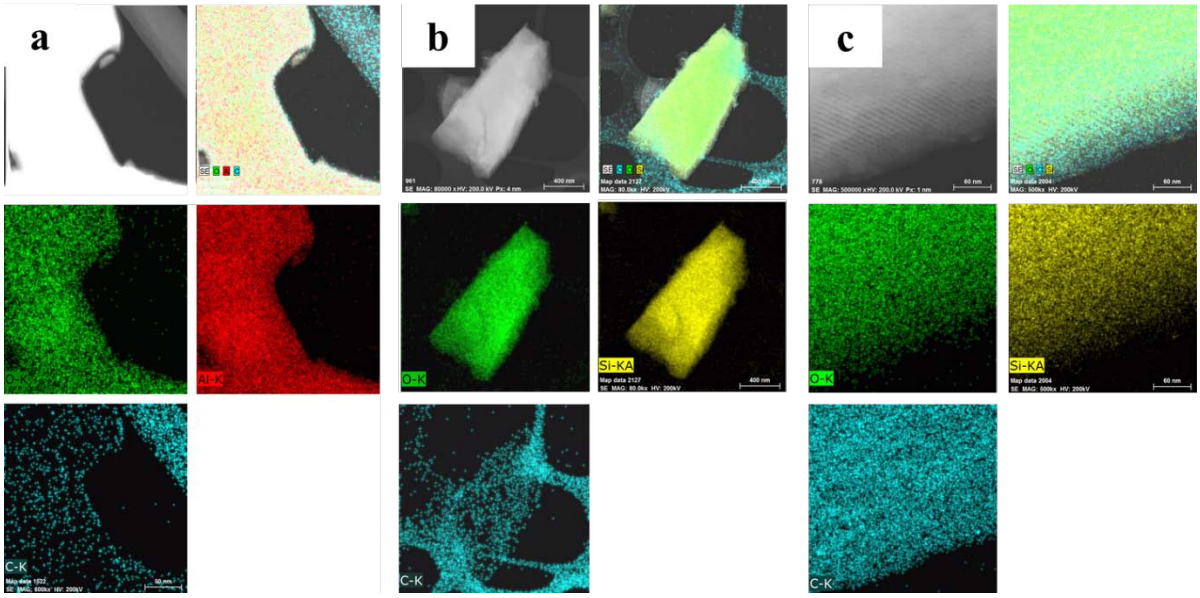

Figure S8. TEM imaging analyses with EDS of (a) spent α-Al_2O_3, (b) spent sea sand, and (c) spent KIT-6.

References for Supplementary Information

[1] S. Kudryashov, A. Ryabov, G. Shchyogoleva, A new approach to the non-oxidative conversion of gaseous alkanes in a barrier discharge and features of the reaction mechanism, Journal of Physics D: Applied Physics 49 (2015) 025205.

[2] P. Kasinathan, S. Park, W.C. Choi, Y.K. Hwang, J.-S. Chang, Y.-K. Park, Plasma-Enhanced Methane Direct Conversion over Particle-Size Adjusted MO x/Al 2 O 3 (M= Ti and Mg) Catalysts, Plasma Chemistry and Plasma Processing 34 (2014) 1317-1330.

[3] A. Indarto, N. Coowanitwong, J.-W. Choi, H. Lee, H.K. Song, Kinetic modeling of plasma methane conversion in a dielectric barrier discharge, Fuel Processing Technology 89 (2008) 214-219.