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Supplementary Information

Leveraging Oxygen Mobility with Zirconia in Low-Temperature Plasma for Enhanced Methane Reforming to Syngas

FNU Gorky, [a] Levi Pile, [a] Grace Jones, [a] Apolo Nambo, [b] Mourad Benamara, [c] and Maria L. Carreon[a,†]

[a]*Ralph E. Martin Department of Chemical Engineering, University of Arkansas, 3202 Bell Engineering Center Fayetteville, AR 72701-1201, USA.*

[b]*Bert Thin Films, LLC., 625 Myrtle St, Louisville, KY 40298, USA.*

[c]*Materials Science and Engineering Program, Institute for Nanoscience and Engineering, University of Arkansas, Fayetteville, AR, 72701 USA*

Corresponding author e-mail address: mc138@uark.edu (Maria L. Carreon).

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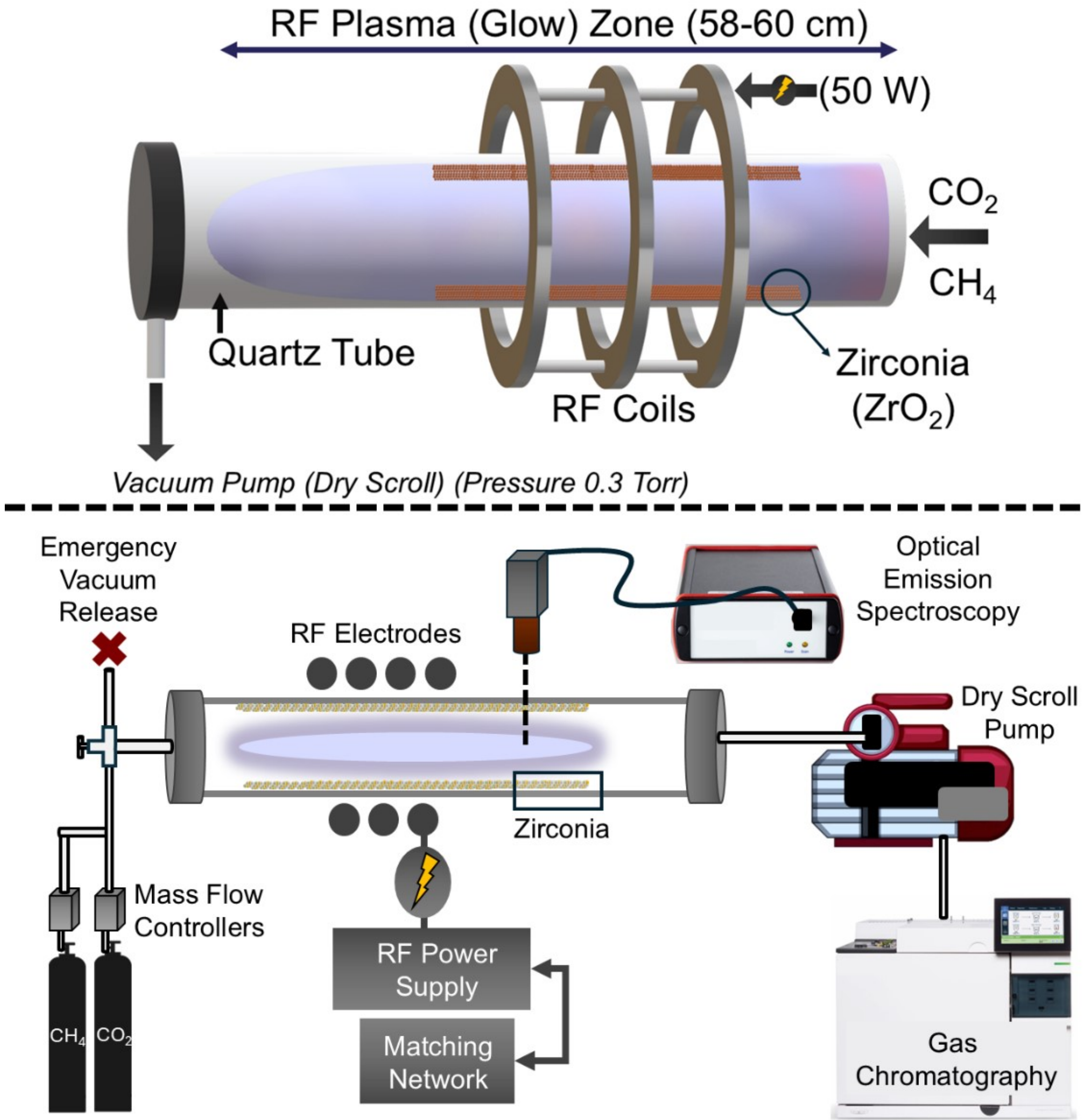


Figure S1. RF-plasma reactor schematics.

Zirconia textural properties (XRD)

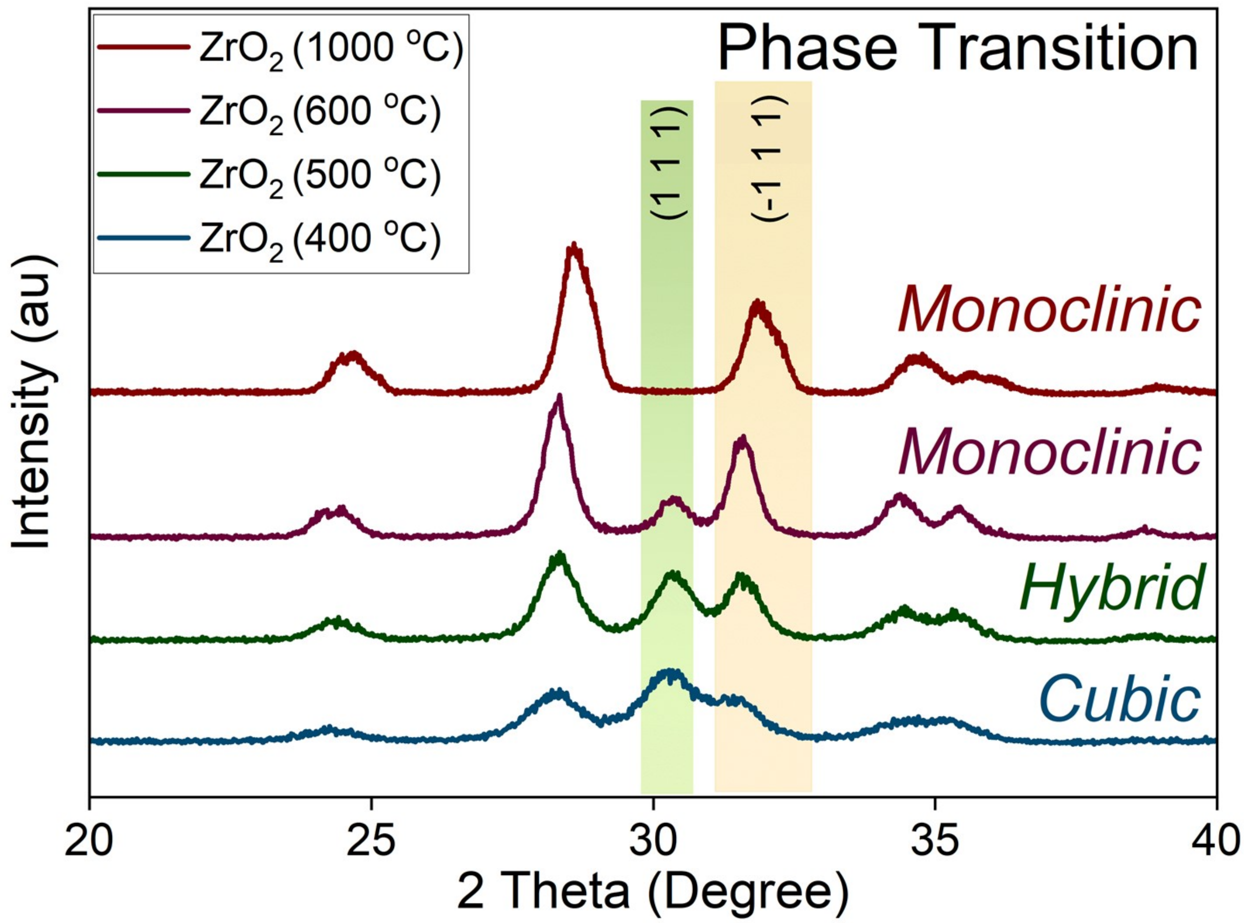


Figure S2. XRD revealing effect of calcination temperature on ZrO_2 phases.

Effect of Calcination temperature on Pore Size Distribution

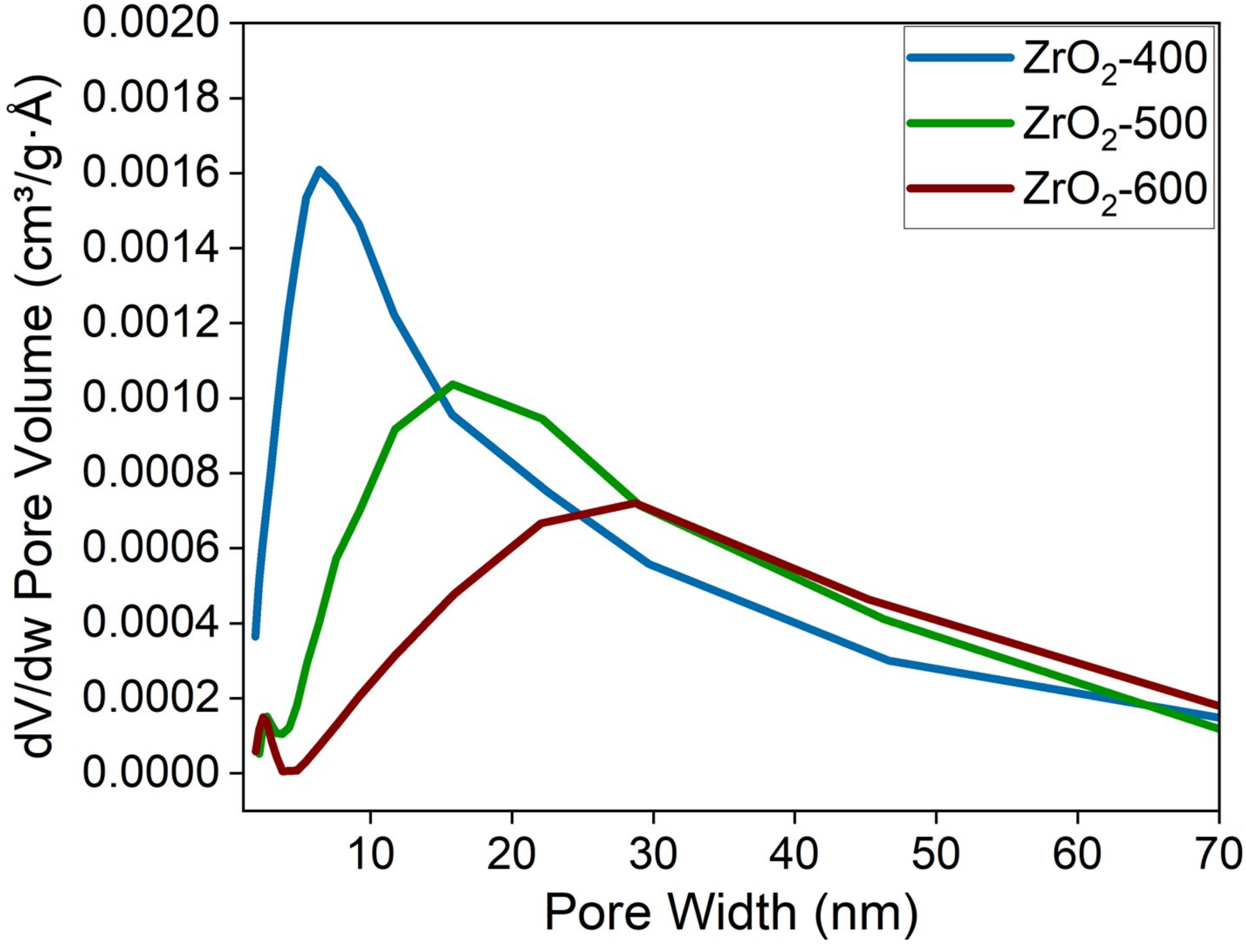


Figure S3. Effect of calcination temperature on pore-size distribution.

Effect of cooling fan on electrode area

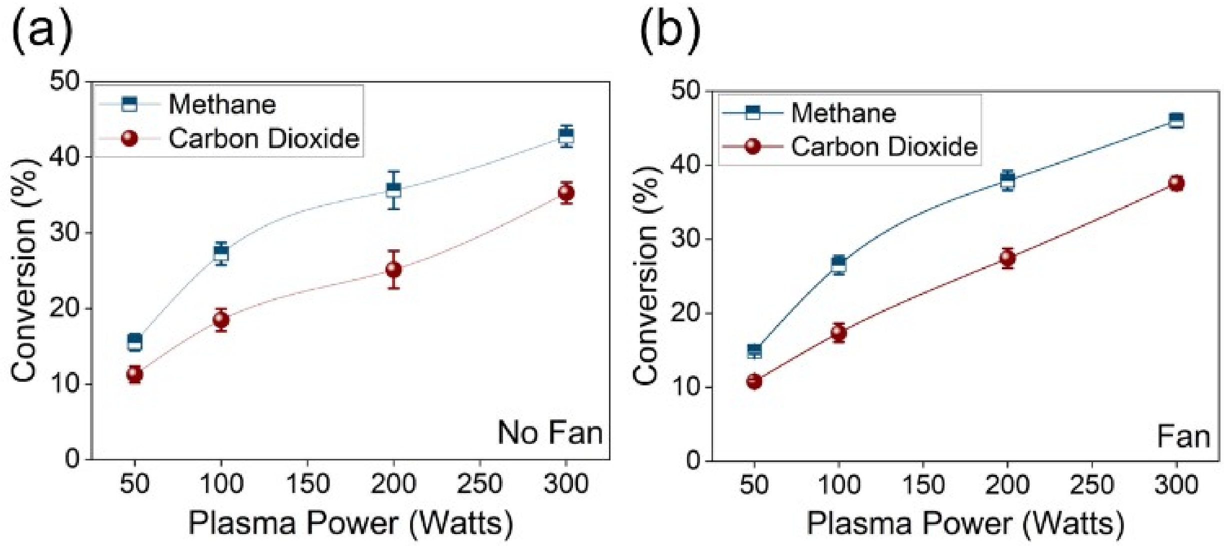


Figure S4. Effect of Plasma Power on Methane and Carbon Dioxide Conversion, Total Flow Rate: 25 sccm, Feed Ratio: 1:1 (CH_4:CO_2), Plasma Power: Varied, Temperature: Not Applied, Results: Averaged from Triplicate Measurements, Reaction Time: 2 Hours

Zirconia State of the art (Thermal Catalysis)

Table S1. Zirconia performance in thermal catalysis literature.

Catalysis Route	Support	Impregnation	Temperature	Conversion (%)		Ref.
	Zirconia	*(Metal)*	*°C*	*CH_4*	*CO_2*	
Thermal	ZrO_2	Ni	750	65.0	-	1
Thermal	ZrO_2	Ni–CeO_2	700	59.0	-	2
Thermal	ZrO_2	Pt	700	79.0	86.0	3
Thermal	ZrO_2	Rh	800	65.9	74.2	4
Thermal	ZrO_2	Pt	800	83.0	94.0	5
Thermal	CeZr	Ni	750	41.0	-	6
Thermal	$Ce_{0.75}Zr_{0.25}O_2$	Ni	750	5.8	8.3	7
Thermal	$Ce_{0.75}Zr_{0.25}O_2$	Ni–Rh	750	6.9	11.8	7
Thermal	$Ce_{0.8}Zr_{0.2}O_2$	Ni	800	78.0	77.0	8
Thermal	$Ce_{0.8}Zr_{0.2}O_2$	Ni–MgO	800	95.0	96.0	8
Thermal	$Ce_{0.75}Zr_{0.25}O_2$	Ni	850	92.0	95.0	9
Thermal	Al_2O_3–ZrO_2	Ni	850	80.0	81.0	10
Thermal	MgO–ZrO_2	Ni	750	80.0	-	11
Thermal	MgO–ZrO_2	Ni + K (promoter)	750	88.0	-	11
Thermal	ZrO_2	Ni (promoter: Zr)	700	73.0	76.7	12
Thermal	ZrO_2	Pt	700	80.1	84.6	3
Thermal	MCM-41	Ni + Zr (promoter)	600	91.0	-	13
Thermal	ZrO_2–SiO_2	Ni	750	79.0	-	14
Thermal	MgO–ZrO_2	Ni	750	70.0	73.0	15
Thermal	$Ce_{0.75}Zr_{0.25}O_2$	Ni	800	64.0	75.0	9

Comparing product distribution with Silica

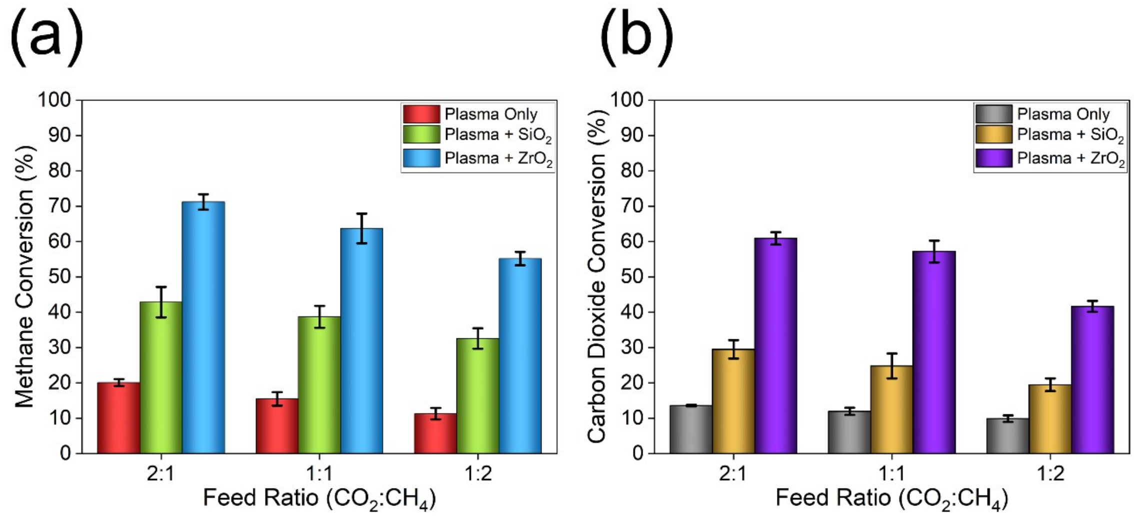


Figure S5. Comparing (a) Methane and (b) Carbon Dioxide conversions with Plasma only Vs. Packed bed reactor with Silica and Zirconia at a total flow rate: 25 sccm, at different feed ratios (CO_2:CH_4), Plasma Power: 50 Watts, reaction time: 2 hours.

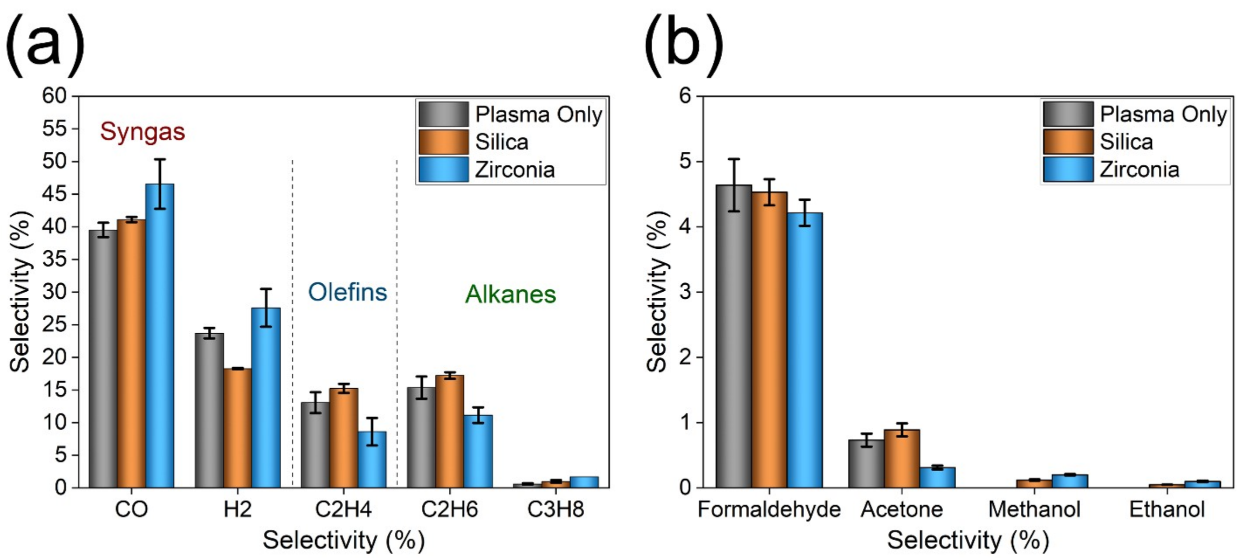
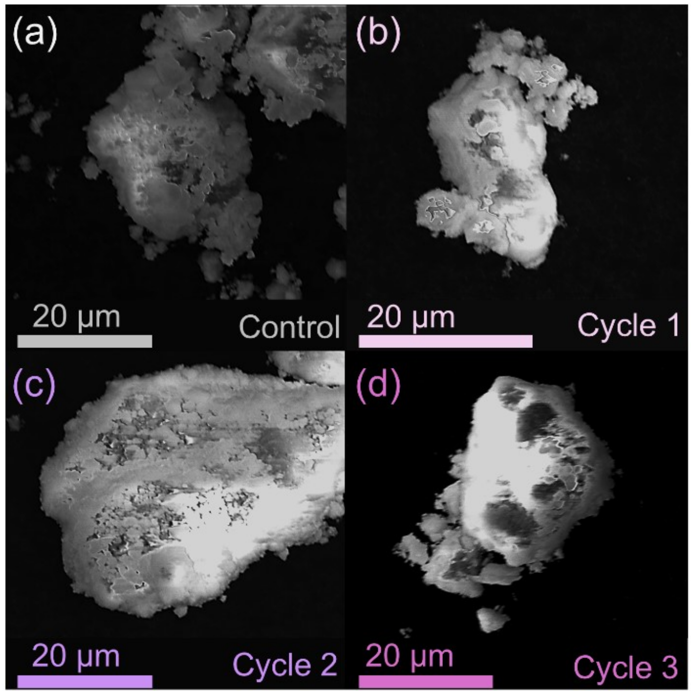


Figure S6. Dry methane reforming product distribution: (a) Gases product distribution (*syngas, olefins, alkanes*), (b) Oxygenates product distribution (aldehydes, ketones, alcohols) at rich methane feed ratio (1:1 CO_2:CH_4); Plasma Power: Varied, Temperature: Not Applied, Results: Averaged from Triplicate Measurements, Reaction Time: 2 Hours

SEM images of Zirconia after plasma exposure



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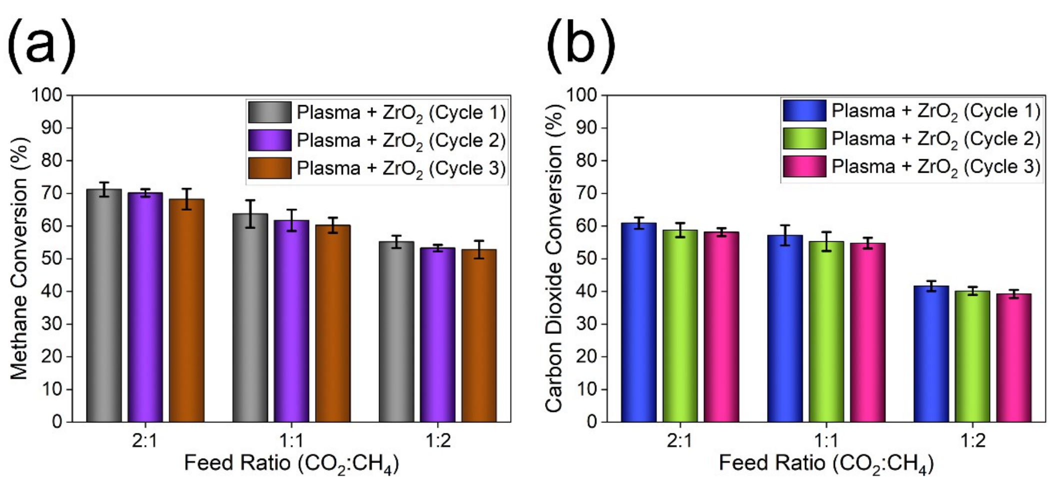

Figure S8. Zirconia stability test with Methane and Carbon Dioxide conversion (%).

Optical Emission Spectroscopy (Gas Phase for Pure CO_2, DRM (CO_2 + CH_4), and Pure CH_4)

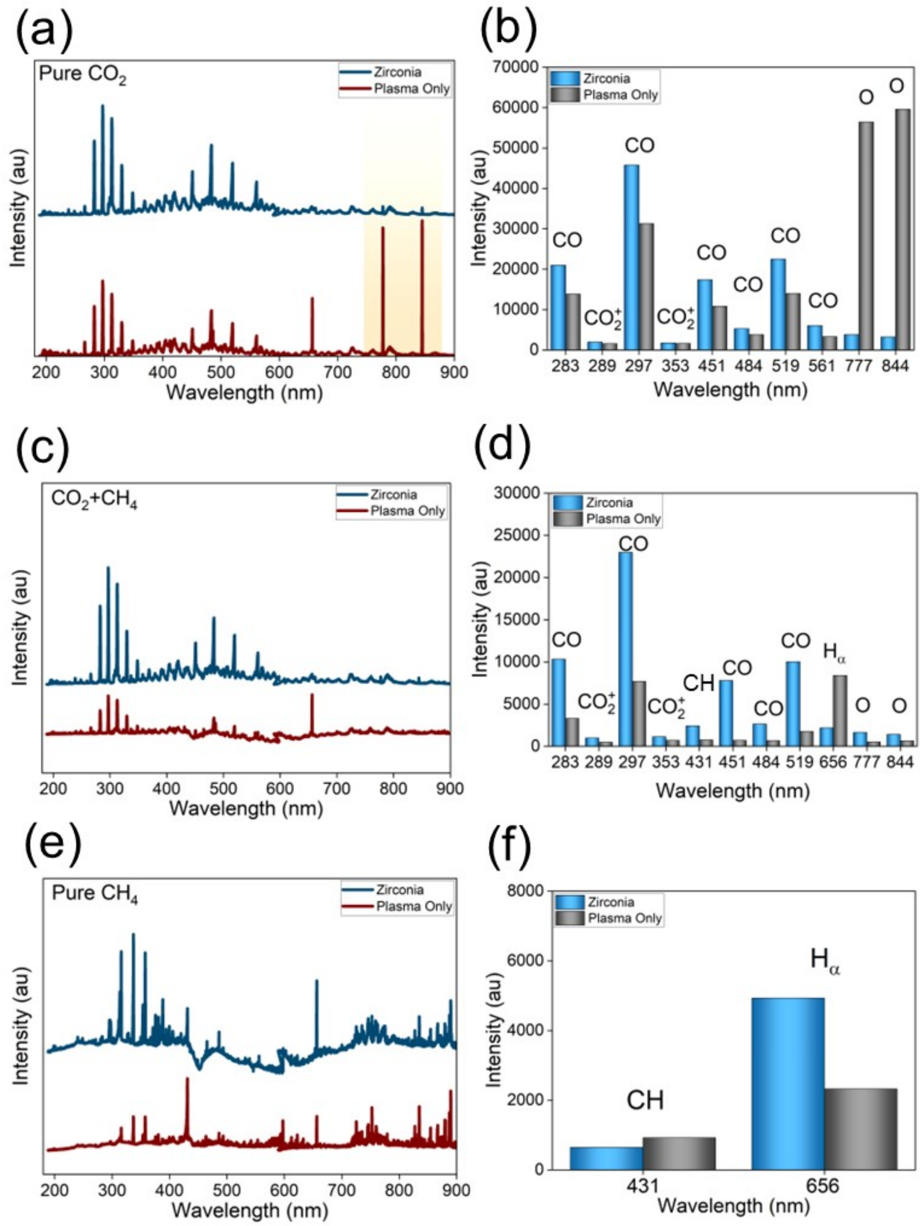

Figure S9. (a) Pure Carbon Dioxide OES (12.5 sccm); (b) Pure Carbon Dioxide OES (12.5 sccm) important plasma species;(c) Methane + Carbon Dioxide OES (25 sccm) DMR important plasma species with Feed Ratio: 1:1 (CO_2:CH_4),; (d) Methane + Carbon Dioxide OES (25 sccm) DMR; (e) Pure Methane OES (12.5 sccm);(f) Pure Methane OES (12.5 sccm); Plasma Power:50 Watts, Reaction Time: 2 Hours

Zirconia XPS Literature

Table S2. Binding energy (eV) for zirconia based on literature.

Species	Location	Binding Energy Range (eV)	Literature Review			*This work*
			Bumajdad, A. *et al.* (2018)[26]	Gu, H. *et al.* (2019)[27]	Teeparthi, S. R. *et al.* (2018)[28]	
O1s						
Zr–O (lattice oxygen)	Oxygen atoms in the ZrO_2 lattice (bulk oxide)	529.7 – 530.0	529.7 – 530.0	529.6	529.7 – 529.9	529.11-529.39
Zr–OH (surface hydroxyls)	Hydroxyl groups bonded to zirconium	531.5 – 532.0	531.3 – 531.5	Oxygen vacancies assigned at 531.2 eV, not explicitly for OH	531.7 – 531.9	530.51-530.93
C–O	carbon–oxygen	-	assigned together with $OH/H_2O/CO_x$	532.4 chemically adsorbed oxygen species, OC	534.2 – 535.8	532.65
Zr3d						
$Zr3d_{5/2}$	Zirconium 3d5/2 core level for Zr^{4+} sites	182.0 eV	181.7 –182.0	-	182.0	181.39-181.59
$Zr3d_{3/2}$	Zirconium 3d3/2 core level for Zr^{4+} sites	184.4 eV	184.3–184.4	-	184.0	183.74-183.92

State of the art (Plasma Catalysis)

Table S3. Plasma catalysis state of the art for Dry Methane Reforming (DRM) at equimolar feed

Plasma Route	Catalyst	Power	External Heating	CH_4	CO_2	Ref
		Watts	^0C	*Conversion (%)*	*Conversion (%)*	
DBD	*No Catalyst*	10	30	18	15.4	[16]
DBD	*No Catalyst*	9.45	60	44	29	[17]
DBD	*No Catalyst*	7	60	1.1	0.3	[18]
DBD	*No Catalyst*	10	20	24	22	[19]
DBD	*No Catalyst*	40	20	42	35	[19]
MW	*No Catalyst*	1000	-	67	49	[20]
MW	*No Catalyst*	1000	-	63	49	[20]
MW	*No Catalyst*	1000	-	58	46	[20]
MW	*No Catalyst*	1000	-	55	46	[20]
MW	*No Catalyst*	3000	-	44	33	[21]
GA	*No Catalyst*	165	-	13.1	8.4	[22]
DC Corona	*No Catalyst*	45	-	80	70	[23]
RF	*No Catalyst*	25	-	34	-	[24]
RF	*No Catalyst*	50	-	45	-	[24]
RF	*No Catalyst*	75	-	50	-	[24]
RF	*No Catalyst*	100	-	55	-	[24]
RF	*No Catalyst*	150	-	60	-	[24]
RF	*No Catalyst*	50	-	16.5	11.9	This work
DBD	γ-Al_2O_3	10	30	15.5	10.5	[16]
DBD	Cu/γ-Al_2O_3	10	30	16	7.5	[16]
DBD	Au/γ-Al_2O_3	10	30	16.5	15	[16]
DBD	Pt/γ-Al_2O_3	10	30	17.2	12.5	[16]
DBD	SiO_2	9.45	60	47	31	[17]
DBD	Co/SiO_2	9.45	60	50	38	[17]
DBD	Fe/SiO_2	9.45	60	46	41	[17]
DBD	Al_2O_3	20	240	37.1	20.2	[25]
DBD	Fe/Al_2O_3	20	240	33.9	17.5	[25]
DBD	NaY	20	240	31.2	13.2	[25]
DBD	Na-ZSM-5	20	240	47.5	26.8	[25]
DBD	MOF-177	7	-	18.4	14.7	[18]
MW	$CaAl_4O_7$	3,000	-	81	69	[21]
RF	Fumed SiO_2	50	-	38.4	23.4	This work
RF	Commercial ZrO_2	50	-	63.7	57.1	This work
DBD = Dielectric Barrier Discharge Plasma; MW = Microwave Plasma; GA = Gliding Arc; DC = Direct Current Corona Plasma; RF = Radiofrequency Plasma.						

CH_4: CO_2 (1:1).

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