Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

A single-stage methane to methanol: A step forward to the synthesis of oxygenates

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1. Table S1. Formula of standard concentration curves.

Sample	Equation	Adj. R square
Methanol	y = 1.37235E-7 × x – 0.0005599	0.99981
Ethanol	y = 6.58505E-8 × x – 0.01202	0.99898
Acetic acid	y = 1.09359E-7 × x + 0.01624	0.99993
Acetone	y = 4.78846E-8 × x – 0.00307	0.99871
Formaldehyde	y = 2.06717E-5 × x + 0.08029	0.99855
Formic acid	y = 1.47165E-5 × x – 0.02457	0.99967

2. The standard formulas to calculate the conversion of reactant, yields (Y) and selectivity of the gaseous products (S) and liquid oxygenates (S_i):

$$CH_4\ conversion\ (\%) = \frac{No.\ of\ moles\ of\ CH_4\ converted}{No.\ of\ moles\ of CH_4\ input} \times 100 \quad (1)$$

$$Selectivity\ of\ CO_x(\%) = \frac{No.\ of\ moles\ of\ CO_x\ produced}{No.\ of\ moles\ of\ CH_4\ converted} \times 100 \quad (2)$$

$$Selectivity\ of\ C_2H_6\ (\%) = \frac{2\ \times\ No.\ of\ moles\ of\ C_2H_6\ produced}{No.\ of\ moles\ of\ CH_4\ converted} \times 100 \quad (3)$$

$$Selectivity\ of\ H_2\ (\%) = \frac{No.\ of\ moles\ of H_2\ produced}{2\ \times\ No.\ of\ moles\ of\ CH_4\ converted} \times 100 \quad (4)$$

The selectivity of the liquid products can be calculated as:

$$Total\ liquid\ oxygenates\ selectivity\ (\%) = 100 - (S_{CO}\ +\ S_{CO_2}\ +\ S_{C_2H_6}) \quad (5)$$

$$S_i(\%) = \frac{n_i C_i}{\sum n_i C_i} \times eq\ (5)$$

n_i = Carbon number in the liquid oxygenate, i

C_i = moles of Carbon containing liquid oxygenate

$$Yield\ of\ products\ (\%) = Selectivity\ \times\ CH_4\ conversion\ (\%) \quad (7)$$

$$Energy\ efficiency\ for\ CH_4 conversion\ (mmol/kJ) = \frac{CH_4\ converted\ (mmol/min)}{Discharge\ power\ (W)} \times \frac{1000}{60} \quad (8)$$

3. Particle distribution curves for all the materials

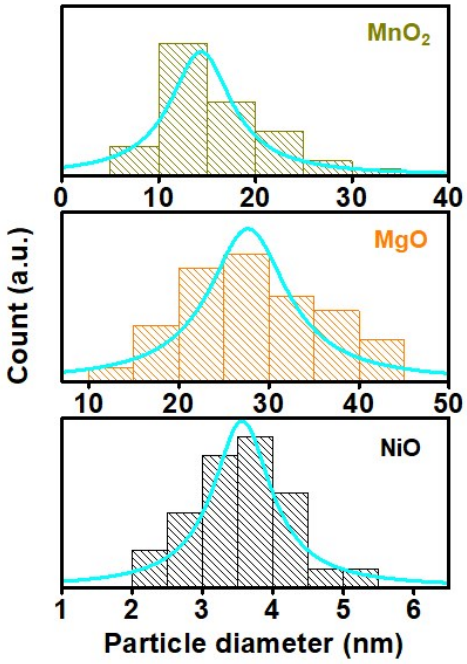

Fig. S1. Particle size distribution curves for NiO, MgO and MnO_2 nanoparticles.

4. Discharge parameters calculation

All the discharge parameters are calculated from Fig. S2 [1-2]. Here the cell capacitance can be presented as

$$\frac{1}{C_{cell}} = \frac{1}{C_d} + \frac{1}{C_g} \quad (1)$$

The break-down voltage can be calculated as

$$U_b = \frac{1}{1 + (C_g / C_d)} \times V_{min} \quad (2)$$

The average electric field for plasma only and catalyst packed plasma DBD system can be defined as

$$E\ (kV/cm) = \frac{U_b}{d_{gap}} \quad (3)$$

$$E_{cat}(kV/cm) = \frac{U_b}{d_{cat-gap}} \quad (4)$$

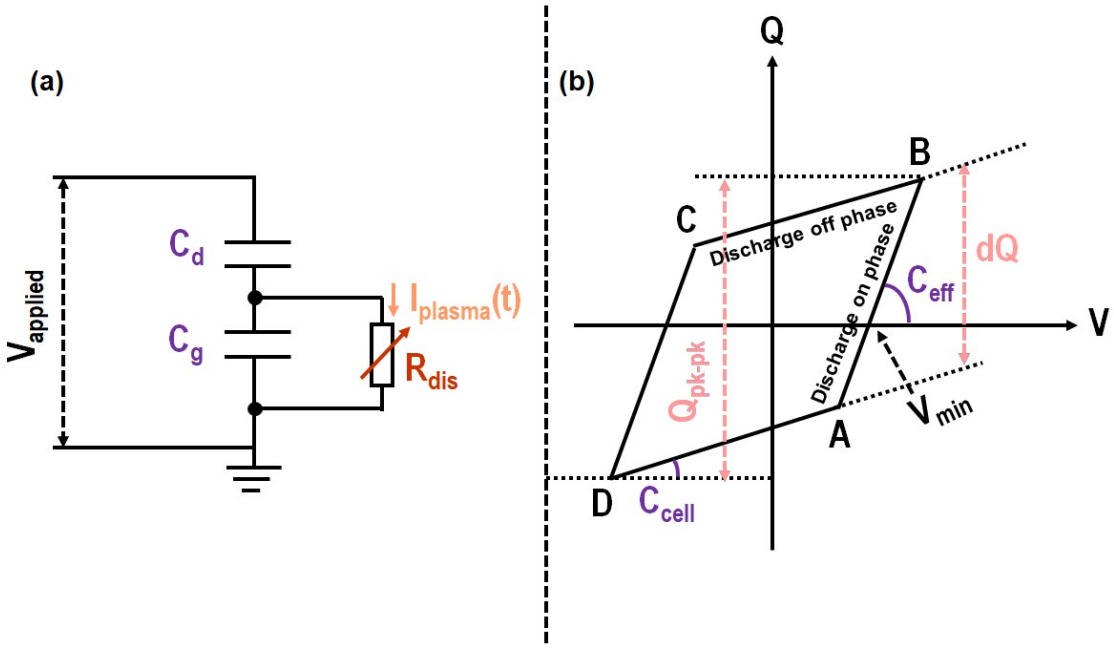

Fig. S2. (a) DBD circuit and (b) the corresponding Q-V Lissajous diagram.

5. Dielectric constant value measurement

An Impedance analyzer (Wayne Kerr 6500B) instrument was used to find out the dielectric constant of the synthesized materials. The measurement was performed at room temperature in the frequency range of 20 Hz -1 MHz.

Figure S3 shows the frequency dependent dielectric constant plot where the dielectric constant value of synthesized materials gets lower with increasing frequency and becomes almost constant

at higher frequency range. This effect can be attributed to the space charge polarization and dipolar polarization which cease with moving from lower to higher frequency range.

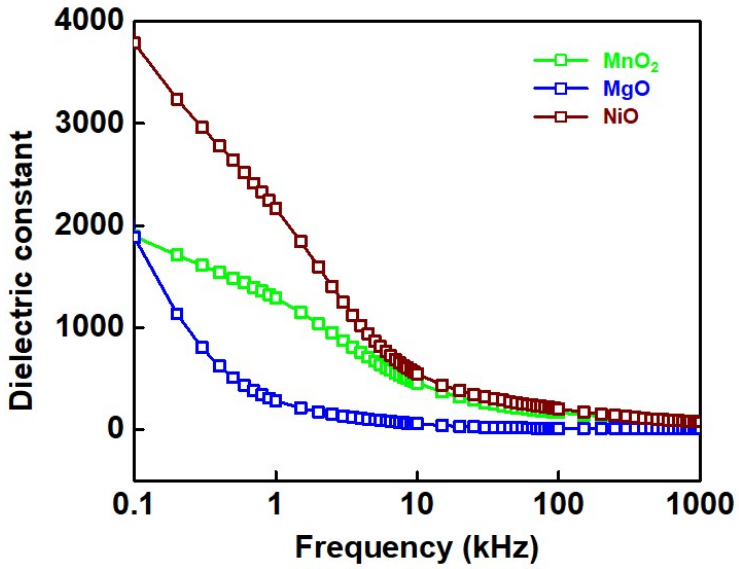

Fig. S3. Dielectric constant variation with frequency.

Table S2. Dielectric constant values of the synthesized materials with different frequency range.

Sample	Frequency (kHz)	Dielectric constant
MnO_2	100	166
	1000	70.7
MgO	100	12.6
	1000	6.4
NiO	100	203
	1000	75.8

6. CH_4 TPD study

CH_4 TPD experiment was also studied to measure the interaction between CH_4 and MO_X nanoparticles and the onset temperature for CH_4 desorption (T_{onset}) was taken into consideration in this purpose. As observed from Fig. S4 the T_{onset} follows the order of NiO> MgO> MnO_2, which implies that CH_4 is more strongly bound to the NiO surface as compared to other two, which may

increase the residence time of adsorbed CH_4 in the reaction zone. Therefore, the interaction probability of CH_4 increases which affects both the CH_4 conversion and products distribution.

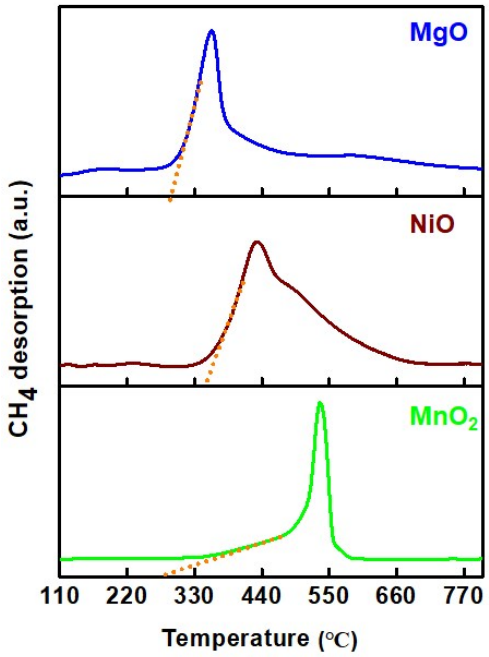

Fig. S4. CH_4 TPD profile of the MO_X nanoparticles.

7. Long term reaction stability

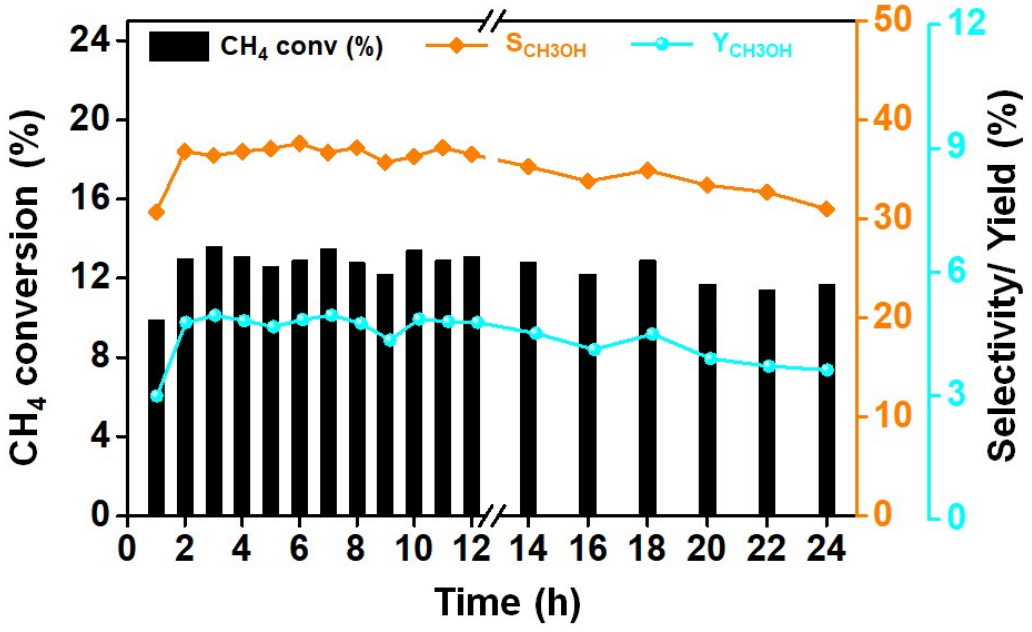

Fig. S5. The stability run of the reaction (CH_4:O_2 = 5:1, SIE = 3.8 J/mL).

8. Spent NiO sample analysis

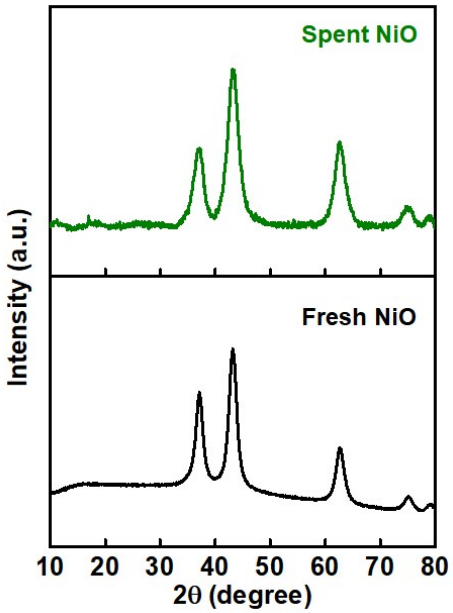

Fig. S6. XRD profiles of both fresh and spent NiO.

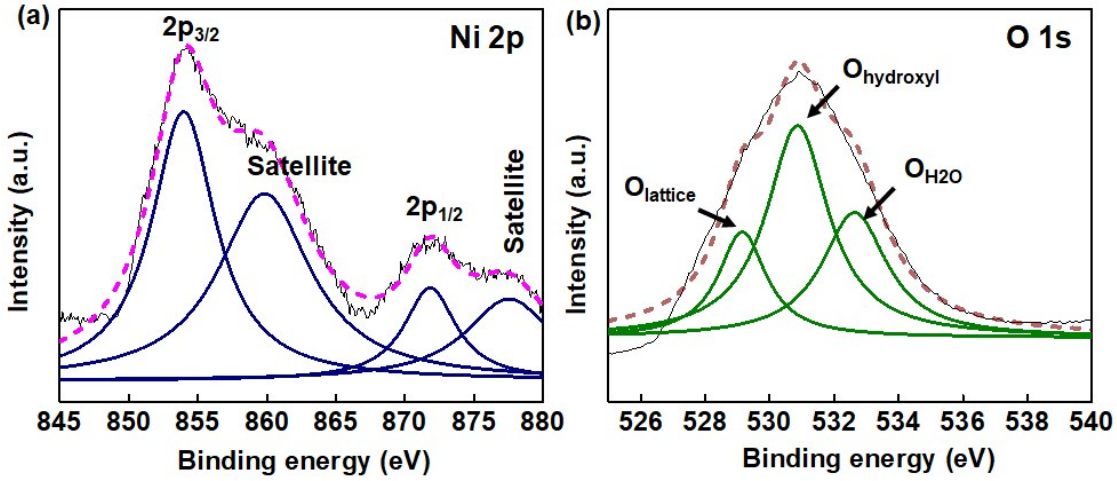

Fig. S7. XPS spectra recorded for spent NiO sample (a) Ni 2p and (b) O 1s.

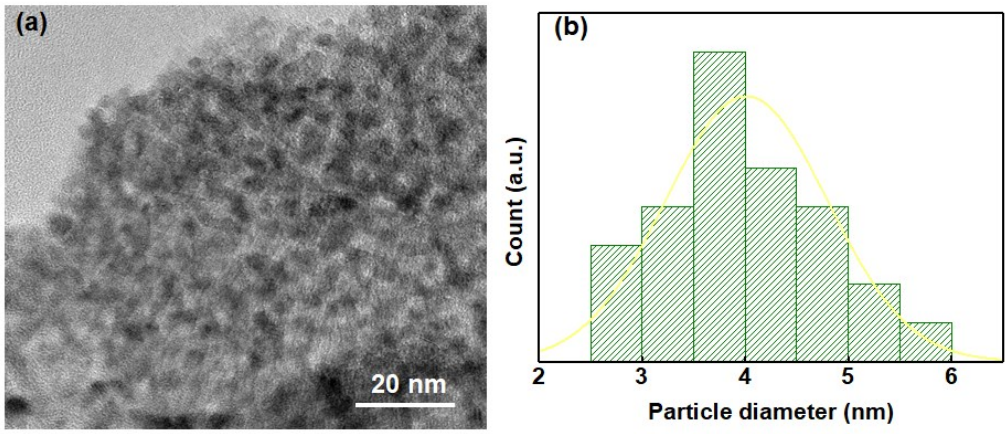

Fig. S8. (a) TEM image and (b) Particle size distribution curve for spent NiO sample.

References

[1] Y. Wang, M. Craven, X. Yu, J. Ding, P. Bryant, J. Huang, X. Tu, Plasma-enhanced catalytic synthesis of ammonia over a Ni/Al_2O_3 catalyst at near-room temperature: insights into the importance of the catalyst surface on the reaction mechanism, ACS catal. 9 (2019) 10780-10793.

[2] P. Chawdhury, Y. Wang, D. Ray, S. Mathieu, N. Wang, J. Harding, F. Bin, X. Tu, C. Subrahmanyam, A promising plasma-catalytic approach towards single-step methane conversion to oxygenates at room temperature, *Appl. Catal. B: Environ.* 284 (2020) 119735.