**Supporting information for:**

**Synthesis of Na2WO4-MnxOy supported on SiO2 or La2O3 as fiber catalysts by electrospinning for oxidative coupling of methane**

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**Table S1.** Mn-Na2WO4/SiO2 based catalysts in OCM reaction.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **No.** | **Catalyst** | **Reaction temperature (˚C)** | **C2+ yield****(%)** | **C2+ selectivity****(%)** | **CH4 conversion****(%)** | **Ref.** |
| 1 | Mn-Na2WO4/SiO2 | 800 | 23.9 | 64.9 | 36.8 | (Jiang et al., 1993) |
| 2 | Mn/Na2WO4/SiO2 | 800 | 26.4 | 80.0 | 33.0 | (Palermo et al., 1998) |
| 3 | Na2WO4/La–Mn/SiO2 | 800 | 25.6 | 55.9 | 45.8 | (Jingjing Wu, 2007) |
| 4 | La/Na2WO4/Mn/SiO2 | 800 | 19.8 | 47.6 | 41.7 | (Jingjing Wu, 2007) |
| 5 | Na2WO4/La/Mn/SiO2 | 800 | 22.1 | 51.7 | 42.8 | (Jingjing Wu, 2007) |
| 6 | Na2WO4/Mn/La/SiO2 | 800 | 22.6 | 52.2 | 43.3 | (Jingjing Wu, 2007) |
| 7 | Mn/Na2WO4/SiO2 | 775 | 16.0 | 80.0 | 20 | (Malekzadeh et al., 2001) |
| 8 | Mn-Na2WO4/SiO2 | 850 | 17.0 | 75 | 22 | (Ji et al., 2002) |
| 9 | Na2WO4/Mn/SiO2 | 850 | 17.2 | 54.0 | 32.0 | (Ji et al., 2003) |
| 10 | Na2WO4/Mn/SiO2 | 800 | 11.2 | 27.4 | 41.0 | (Wu et al., 2007) |
| 11 | La/Na2WO4/Mn/SiO2 | 800 | 10.6 | 25.4 | 41.7 | (Wu et al., 2007) |
| 12 | Na-W-Mn/SiO2 | 850 | 29 | 69 | 42 | (Chua et al., 2008) |
| 13 | W-Na-Mn/SiO2 | 775 | 18.3 | 39.6 | 46.1 | (Mahmoodi et al., 2010) |
| 14 | Na-W-Mn/SiO2 | 800 | 19.1 | 63.2 | 30.2 | (Lee et al., 2013) |
| 15 | Mn-Na2WO4/SiO2 | 800 | 18.5 | 73.3 | 28.5 | (Elkins and Hagelin-Weaver, 2015) |
| 16 | Mn-Na2WO4/SiO2 | 750 | 5.2 | 63.4 | 8.2 | (Hiyoshi and Ikeda, 2015) |

**Table S1.** (Continue)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **No.** | **Catalyst** | **Reaction temperature (˚C)** | **C2+ yield****(%)** | **C2+ selectivity****(%)** | **CH4 conversion****(%)** | **Ref.** |
| 17 | MnxOy-Na2WO4/SiO2 (grade 923) | 750 | 1.3 | 63.6 | 2.0 | (Yildiz et al., 2016) |
| 18 | Na2WO4/Mn/SiO2 (silica gel) | 770 | 16.9 | 50.8 | 33.4 | (Yildiz et al., 2016) |
| 19 | Na2WO4/Mn/SiO2 | 800 | 2.5 | 67.6 | 3.2 | (Fleischer et al., 2016) |
| 20 | Na2WO4-Mn/SiO2 | 800 | 19.6 | 66.4 | 29.5 | (Fleischer et al., 2016) |
| 21 | Na2WO4/Mn/SiO2 (silica gel) | 800 | 17.1 | 51.0 | 33.5 | (Fleischer et al., 2016) |
| 22 | Na2WO4/Mn/SiO2 (fumed silica) | 800 | 16.5 | 52.7 | 33.3 | (Fleischer et al., 2016) |
| 23 | Mn/Na2WO4/SiO2 | 725 | 16.0 | 64.0 | 25.0 | (Uzunoglu et al., 2017) |
| 24 | Mn-Na-W/SiO2 | 750 | 16.0 | 64.0 | 25.0 | (Hayek et al., 2017) |
| 25 | La-Na2WO4/SiO2 | 800 | 10.9 | 24.0 | 33.5 | (Gu et al., 2018) |
| 26 | MnxOy-Na2WO4/SiO2  | 750 | 4.5 | 61.3 | 7.4 | (Gu et al., 2018) |
| 27 | Na2WO4-Mn/SiO2 | 800 | 20.0 | 67.0 | 30.0 | (Gu et al., 2018) |
| 28 | MnOx-Na2WO4/SiO2 | 770 | 12.4 | 70.4 | 17.6 | (Hayek et al., 2019) |
| 29 | Mn-Na2WO4/SiO2 | 825 | 24.2 | 78.0 | 31.0 | (Godini et al., 2014) |
| 30 | Mn-Na2WO4/SiO2 | 750 | 14.0 | 78.0 | 18.0 | (Liang et al., 2018) |

**Table S2.** La2O3-based catalysts in OCM reaction.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **No.** | **Catalyst** | **Reaction temperature (˚C)** | **C2+ yield****(%)** | **C2+ selectivity****(%)** | **CH4 conversion****(%)** | **Ref.** |
| 1 | La2O3 | 850 | 10.7 | 85.3 | 12.5 | (V.R Choudhary, 1999) |
| 2 | La2O3–Nd2O3 | 850 | 11.2 | 85.8 | 13.1 | (V.R Choudhary, 1999) |
| 3 | La2O3–Sm2O3 | 850 | 10.0 | 87.6 | 11.4 | (V.R Choudhary, 1999) |
| 4 | La2O3–Gd2O3 | 850 | 8.2 | 85.9 | 9.5 | (V.R Choudhary, 1999) |
| 5 | La2O3–Er2O3 | 850 | 5.6 | 79.3 | 7.1 | (V.R Choudhary, 1999) |
| 6 | La2O3–Yb2O3 | 850 | 8.0 | 83.0 | 9.6 | (V.R Choudhary, 1999) |
| 7 | Mg-La2O3 | 800 | 13.9 | 51.8 | 26.1 | (Vasant R. Choudhary et al., 1998) |
| 8 | Ca-La2O3 | 800 | 13.3 | 51.8 | 25.6 | (Vasant R. Choudhary et al., 1998) |
| 9 | Sr-La2O3 | 800 | 16.2 | 60.7 | 26.7 | (Vasant R. Choudhary et al., 1998) |
| 10 | Ba-La2O3 | 800 | 13.2 | 57.2 | 23.5 | (Vasant R. Choudhary et al., 1998) |
| 11 | La2O3 | 750 | 11.6 | 59.1 | 19.6 | (DeBoy and Hicks, 1988) |
| 12 | Li/ La2O3 | 800 | 16.4 | 75.9 | 21.6 | (DeBoy and Hicks, 1988) |
| 13 | Na/ La2O3 | 800 | 13.8 | 69.2 | 20.0 | (DeBoy and Hicks, 1988) |

**Table S2.** (Continue)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **No.** | **Catalyst** | **Reaction temperature (˚C)** | **C2+ yield****(%)** | **C2+ selectivity****(%)** | **CH4 conversion****(%)** | **Ref.** |
| 14 | K/ La2O3 | 800 | 13.2 | 64.0 | 20.6 | (DeBoy and Hicks, 1988) |
| 15 | Mg/ La2O3 | 750 | 13.5 | 65.4 | 20.7 | (DeBoy and Hicks, 1988) |
| 16 | Ca/ La2O3 | 750 | 12.5 | 64.3 | 19.4 | (DeBoy and Hicks, 1988) |
| 17 | Na-LaMnO3 | 825 | 19.2 | 60.0 | 32.0 | (Shican Jiang, 2021) |
| 18 | Sr0.8La0.2TiO3 | 800 | 11.0 | 37.1 | 29.6 | (Seoyeon Lim, 2019) |
| 19 | BaCO3/LaOF | 800 | 16.4 | 45.3 | 36.1 | (C.T. Au, 1997) |
| 20 | LaLiO2 | 700 | 17.8 | 39.8 | 44.8 | (Masami Yamamura, 1995) |
| 21 | SrF2/ La2O3 | 700 | 19.6 | 57.3 | 34.2 | (Wei Zheng Weng, 1998) |
| 22 | BaO/ La2O3 | 800 | 12.0 | 47.5 | 25.3 | (Wei Zheng Weng, 1998) |
| 23 | BaF2/ La2O3 | 800 | 14.2 | 53.8 | 26.4 | (Wei Zheng Weng, 1998) |
| 24 | LaOF | 800 | 9.8 | 39.2 | 24.9 | (Wei Zheng Weng, 1998) |
| 25 | BaF2/ LaOF | 800 | 18.7 | 60.2 | 31.0 | (Wei Zheng Weng, 1998) |
| 26 | LiMg7La0.1 | 700 | 23.5 | 97.8 | 23.0 | (Bi Yingli, 1988) |
| 27 | Li4-6LaTi | 750 | 14.2 | 75.0 | 19.0 | (Gerald S. Lane, 1989) |
| 28 | (LiLa)0.9(MgSr)0.1 | 700 | 16.2 | 58.0 | 28.0 | (A. Kiennemann, 1990) |
| 29 | La2Zr2O7 | 750 | 15.1 | 65.6 | 23.0 | (Xiuzhong Fang, 2019) |

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**Figure S1.** TGA of each catalyst. Test condition: 30 to 900 ºC at a heating rate of 10 ºC min-1 in 50 mL min-1 N2 gas.



(b)

(a)

**Figure S2.** Example GC chromatograms of NWMSi-F: (a) normal scale, (b) large scale . Reaction conditions: 50 mg catalysts under 35 mL min-1, feed gas ratio of CH4:O2:N2 of 3:1:4 and reactor temperature = 700 ºC.

Carbon balance check

$$n\_{2}mol CO$$

$$n\_{3}mol CO\_{2}$$

$$n\_{4}mol C\_{2}H\_{4}$$

$$n\_{5}mol C\_{2}H\_{6}$$

$$n\_{6}mol C\_{3}H\_{6}$$

$$n\_{7}mol C\_{3}H\_{8}$$

$$n\_{8}mol n-C\_{4}H\_{10}$$

$$n\_{9}mol isoC\_{4}H\_{10}$$

$$n\_{10}mol isoCH\_{4}$$

$$n\_{1}mol CH\_{4} $$

$$n\_{11}mol O\_{2}$$

$$n\_{12}mol N\_{2}$$

Reactor

35 mL/min

**Figure S3.** Flowchart of oxidative coupling of methane reaction

**Table S3.** An example of the carbon balance for the performance of NWMSi-F catalyst that is shown in Figure 8.

|  |  |  |  |
| --- | --- | --- | --- |
| Time(hr) | CH4-input(x10-5mol) | Sum of carbon productsa + CH4-out ($×$10-5mol) | CH4 balance errorb (%) |
| 1 | 2.510 | 2.445 | 2.6 |
| 2 | 2.510 | 2.492 | 0.7 |
| 3 | 2.510 | 2.472 | 1.5 |
| 4 | 2.510 | 2.420 | 3.6 |
| 5 | 2.510 | 2.465 | 1.8 |
| 6 | 2.510 | 2.507 | 0.1 |
| 7 | 2.510 | 2.487 | 0.9 |
| 8 | 2.510 | 2.507 | 0.1 |
| 9 | 2.510 | 2.510 | 0.0 |
| 10 | 2.510 | 2.502 | 0.3 |
| 11 | 2.510 | 2.500 | 0.4 |
| 12 | 2.510 | 2.435 | 3.0 |
| 13 | 2.510 | 2.487 | 0.9 |
| 14 | 2.510 | 2.492 | 0.7 |
| 15 | 2.510 | 2.497 | 0.5 |
| 16 | 2.510 | 2.477 | 1.3 |
| 17 | 2.510 | 2.485 | 1.0 |
| 18 | 2.510 | 2.452 | 2.3 |
| 19 | 2.510 | 2.487 | 0.9 |
| 20 | 2.510 | 2.485 | 1.0 |
| 21 | 2.510 | 2.485 | 1.0 |
| 22 | 2.510 | 2.492 | 0.7 |
| 23 | 2.510 | 2.497 | 0.5 |
| 24 | 2.510 | 2.507 | 0.1 |

aSum of carbon producs= $2\left(n\_{C\_{2}H\_{4}}+ n\_{C\_{2}H\_{6}}\right)+3\left(n\_{C\_{3}H\_{6}}+ n\_{C\_{3}H\_{8}}\right)+4\left(n\_{C\_{4}H\_{10}}\right)+ n\_{CO}+ n\_{CO\_{2}}$

b$CH\_{4} balance error (\%) = \left[n\_{CH\_{4} in }- \left(Sum of carbon products+ n\_{CH\_{4} out}\right)\right] × 100/ n\_{CH\_{4} in}$

**Table S4.** The characteristic XRD values of crystalline phases from the results in Figures 1 and 9.

|  |  |  |  |
| --- | --- | --- | --- |
| **Crystalline structure** | **Symbol** | **2θ (degree)** | **ICDD No.** |
| Na2WO4 | ⬧ | 16.8, 27.6, 48.8, 57.0 | 01-074-2369 |
| Mn2O3 | ⏶ | 32.9, 38.3, 55.3 | 00-002-0896 |
| $α$-cristobalite | ⦁ | 22.0, 28.5, 31.4, 36.2,42.8, 44.8, 47.0, 48.7, 54.2, 57.2 | 00-001-0438 |
| $α$-tridymite | ■ | 21.8, 30.2, 48.7 | 00-003-0227 |
| La2O3 | 🟊 | 26.1, 29.1, 30.0, 39.5, 46.0, 52.8, 53.4, 55.4, 55.9, 62.2, 72.1, 75.2, 79.1 | 01-073-2141 |
| La(MnO3) | ⦁ | 22.3, 32.3, 58.4, 72.1, 75.5, 79.0 | 01-089-0027 |

**Table S4.** (Continue)

|  |  |  |  |
| --- | --- | --- | --- |
| **Crystalline structure** | **Symbol** | **2θ (degree)** | **ICDD No.** |
| La(OH)3 | ■ | 33.9, 42.5, 56.4 | 00-006-0585 |





**Figure S4**. Pore size distribution profiles: (a) Si, (b) NWMSi, (c) La, and (d) NWMLa.

**Table S5.** OCM reaction results for the different catalysts. Reaction condition: 50 mg catalysts under 35 mL min-1 and feed gas ratio of CH4:O2:N2 of 3:1:4.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Temperature (ºC) | Olefin selectivity(%) | C2+selectivity (%) | Olefin/paraffin (mol/mol) | CH4conversion (%) | Yield (%) |
| **Olefin** | **C2+** |
| Si-P | 450 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 500 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 550 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 600 | 6.6 ± 0.3 | 6.6± 0.3 | 0.0 | 0.3 ± 0.0 | 0.0  | 0.0 |
| 650 | 0.7 ±0.0 | 9.7 ± 0.5 | 0.1 ± 0.0 | 1.1 ± 0.1 | 0.0  | 0.1 ± 0.0 |
| 700 | 4.3 ± 0.2 | 16.1 ± 0.8 | 0.4 ± 0.0 | 4.1 ± 0.2 | 0.2 ± 0.0 | 0.7 ± 0.0 |
| 750 | 16.7 ± 0.8 | 27.6 ± 1.4 | 1.6 ± 0.1 | 9.7 ± 0.5 | 1.6 ± 0.1 | 2.7 ± 0.1 |
|  |  |  |  |  |  |  |

**Table S5.** (Continued)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Temperature (ºC) | Olefin selectivity(%) | C2+selectivity (%) | Olefin/paraffin (mol/mol) | CH4conversion (%) | Yield (%) |
| **Olefin** | **C2+** |
| Si-F | 450 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 500 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 550 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 600 | 0.0 | 1.5 ± 0.1 | 0.0 | 0.7 ± 0.0 | 0.0 | 0.0 |
| 650 | 0.7 ± 0.0 | 6.5 ± 0.3  | 0.1 ± 0.0 | 3.2 ± 0.2 | 0.0 | 0.2 ± 0.0 |
| 700 | 5.8 ± 0.3 | 14.5 ± 0.7 | 0.7 ± 0.0 | 8.2 ± 0.4 | 0.5 ± 0.0 | 1.2 ± 0.1 |
| 750 | 21.1 ± 1.1 | 32.8 ± 1.6 | 1.8 ± 0.1 | 12.2 ± 0.6 | 2.6 ± 0.1 | 4.0 ± 0.2 |

**Table S5.** (Continued)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Temperature (ºC) | Olefin selectivity(%) | C2+selectivity (%) | Olefin/paraffin (mol/mol) | CH4conversion (%) | Yield (%) |
| **Olefin** | **C2+** |
| NWMSi-P | 450 | 0.0 | 0.0  | 0.0 | 0.0 | 0.0 | 0.0  |
| 500 | 0.0 | 0.0  | 0.0 | 0.0  | 0.0 | 0.0  |
| 550 | 0.0 | 0.0  | 0.0 | 0.0  | 0.0 | 0.0  |
| 600 | 0.1 ± 0.0 | 6.5 ± 0.3 | 0.0 | 0.6 ± 0.0 | 0.0 | 0.1 ± 0.0 |
| 650 | 7.2 ± 0.4 | 24.6 ± 1.2 | 0.5 ± 0.7 | 8.9 ± 0.4 | 0.7 ± 0.0 | 2.1 ± 0.1 |
| 700 | 39.3 ± 2.0 | 54.5 ± 2.7 | 2.8 ± 0.4 | 31.7 ± 1.6 | 12.5 ± 0.6 | 17.3 ± 0.9 |
| 750 | 44.3 ± 2.2 | 53.0 ± 2.7 | 6.1 ± 1.2 | 33.8 ± 1.7 | 15.0 ± 0.8 | 17.9 ± 0.9 |

**Table S5.** (Continued)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Temperature (ºC) | Olefin selectivity(%) | C2+selectivity (%) | Olefin/paraffin (mol/mol) | CH4conversion (%) | Yield (%) |
| **Olefin** | **C2+** |
| NWMSi-F | 450 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 500 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 550 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 600 | 1.3 ± 0.1 | 15.3 ± 0.7 | 0.1 ± 0.2 | 1.7 ± 0.1 | 0.02 ± 0.0 | 0.3 ± 0.0 |
| 650 | 25.4 ± 1.2 | 50.3 ± 2.5 | 1.1 ± 0.2 | 15.1 ± 0.8 | 4.0 ± 0.2 | 7.6 ± 0.4 |
| 700 | 43.9 ± 2.2 | 60.1 ± 3.0 | 3.0 ± 0.2 | 34.0 ± 1.7 | 14.9 ± 0.7 | 20.4 ± 1.0 |
| 750 | 47.6 ± 2.4 | 56.6 ± 2.8 | 6.4 ± 0.8 | 32.2 ± 1.6 | 15.3 ± 0.8 | 18.2 ± 0.9 |

**Table S5.** (Continued)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Temperature (ºC) | Olefin selectivity(%) | C2+selectivity (%) | Olefin/paraffin (mol/mol) | CH4conversion (%) | Yield (%) |
| **Olefin** | **C2+** |
| La-P | 450 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 500 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 550 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 600 | 3.6 ± 0.2 | 21.2 ± 1.1 | 0.0 | 5.7 ± 0.3 | 0.2 ± 0.0 | 1.2 ± 0.1 |
| 650 | 21.2 ± 1.1 | 40.7 ± 2.0 | 1.1 ± 0.2 | 22.0 ± 1.1 | 4.8 ± 0.3 | 9.0 ± 0.4 |
| 700 | 26.0 ± 1.3 | 40.8 ± 2.0 | 0.8 ± 0.0 | 25.7 ± 1.3 | 6.7 ± 0.3 | 10.5 ± 0.5 |
| 750 | 26.0 ± 1.3 | 33.6 ± 1.7 | 3.7 ± 0.7 | 26.8 ± 1.3 | 7.0 ± 0.4 | 9.0 ± 0.4 |

**Table S5.** (Continued)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Temperature (ºC) | Olefin selectivity(%) | C2+selectivity (%) | Olefin/paraffin (mol/mol) | CH4conversion (%) | Yield (%) |
| **Olefin** | **C2+** |
| La-F | 450 | 0.0 | 0.0  | 0.0 | 1.9 ± 0.1 | 0.0 | 0.0  |
| 500 | 0.0 | 0.0  | 0.0 | 5.3 ± 0.3 | 0.0 | 0.0 |
| 550 | 0.8 ± 0.0 | 4.6 ± 0.2 | 0.2 ± 0.1 | 12.7 ± 0.6 | 0.1 ± 0.01 | 0.6 ± 0.0 |
| 600 | 15.9 ± 0.8 | 33.3 ± 1.7 | 0.9 ± 0.1 | 25.3 ± 1.3 | 4.0 ± 0.2 | 8.5 ± 0.4 |
| 650 | 17.8 ± 0.9 | 34.4 ± 1.7 | 1.1 ± 0.0 | 26.7 ± 1.3 | 4.7 ± 0.2 | 9.2 ± 0.5 |
| 700 | 17.5 ± 0.9 | 32.4 ± 1.6 | 1.2 ± 0.0 | 26.9 ± 1.3 | 4.7 ± 0.1 | 8.7 ± 0.4 |
| 750 | 16.8 ± 0.8 | 26.3 ± 1.3 | 1.8 ± 0.1 | 25.8 ± 1.3 | 4.3 ± 0.2 | 6.8 ± 0.3 |

**Table S5.** (Continued)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Temperature (ºC) | Olefin selectivity(%) | C2+selectivity (%) | Olefin/paraffin (mol/mol) | CH4conversion (%) | Yield (%) |
| **Olefin** | **C2+** |
| NWMLa-P | 450 | 0.0 | 0.0 | 0.0 | 0.6 ± 0.0 | 0.0 | 0.0 |
| 500 | 5.6 ± 0.3 | 14.0 ± 0.7 | 0.3 ± 0.03 | 17.4 ± 0.9 | 1.2 ± 0.1 | 2.6 ± 0.1 |
| 550 | 5.8 ± 0.3 | 18.1 ± 0.9 | 0.1 ± 0.1 | 20.4 ± 1.0 | 1.4 ± 0.1 | 4.1 ± 0.2 |
| 600 | 8.0 ± 0.4 | 23.7 ± 1.2 | 0.5 ± 0.1 | 21.6 ± 1.1 | 1.9 ± 0.1 | 5.5 ± 0.3 |
| 650 | 11.6 ± 0.6 | 34.5 ± 1.7 | 0.7 ± 0.0 | 24.3 ± 1.2 | 2.7 ± 0.1 | 8.4 ± 0.4 |
| 700 | 20.5 ± 1.5  | 36.3 ± 1.8 | 1.4 ± 0.7 | 23.4 ± 1.2 | 4.8 ± 0.2 | 8.5 ± 0.4 |
| 750 | 25.1 ± 1.3 | 33.1 ± 1.7 | 4.2 ± 0.2 | 24.4 ± 1.2 | 6.3 ± 0.3 | 8.2 ± 0.4 |

**Table S5.** (Continued)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Temperature (ºC) | Olefin selectivity(%) | C2+selectivity (%) | Olefin/paraffin (mol/mol) | CH4conversion (%) | Yield (%) |
| **Olefin** | **C2+** |
| NWMLa-F | 450 | 0.0 | 0.0 | 0.0 | 0.3 ± 0.01 | 0.0 | 0.0 |
| 500 | 3.1 ± 0.2 | 20.0 ± 0.1 | 0.2 ± 0.0 | 23.5 ± 1.2 | 0.7 ± 0.0 | 4.7 ± 0.2 |
| 550 | 6.4 ± 0.3 | 22.8 ± 1.1 | 0.4 ± 0.0 | 28.2 ± 1.4 | 1.8 ± 0.1 | 6.4 ± 0.3 |
| 600 | 13.2 ± 0.7 | 32.7 ± 1.6 | 0.7 ± 0.3 | 26.1 ± 1.3 | 3.4 ± 0.2 | 8.5 ± 0.4 |
| 650 | 16.1 ± 0.8 | 38.9 ± 1.9 | 0.7 ± 0.1 | 24.1 ± 1.2 | 4.0 ± 0.2 | 9.6 ± 0.5 |
| 700 | 17.5 ± 0.9 | 32.4 ± 1.6 | 1.2 ± 0.3 | 26.9 ± 1.3 | 4.7 ± 0.2 | 8.7 ± 0.4 |
| 750 | 16.2 ± 0.8 | 24.9 ± 1.2 | 1.9 ± 0.5 | 26.6 ± 1.3 | 4.3 ± 0.2 | 6.6 ± 0.3 |

**Table S6.** Quantification results of XPS O 1s spectra of the Si-based and La-based catalysts.

|  |  |
| --- | --- |
| Catalyst | O 1s binding energy (eV) / Percentage fraction |
| O2- | Mn—O | OH-, $CO\_{3}^{2-}$ | Si—O | $$O\_{2}^{-}$$ | Na—O—W |
| Si-F | 531.3/1.9 | - | - | 533.3/95.5 | 535.0/2.5 | - |
| NWMSi-F | 531.3/11.2 | 529.7/1.5 | - | 532.8/68.8 | 533.8/13.7 | 534.7/5.0 |
| La-F | 529.2/9.3 | - | 531.6/74.0 | - | 533.0/16.7 | - |
| NWMLa-F | 529.0/8.1 | 529.4/17.6 | 531.4/39.9 | - | 532.2/29.8 | 534.1/4.6 |

**Table S7.** Relative peak area for XPS O 1s spectra of the Si-based and La-based catalysts.

|  |  |
| --- | --- |
| Catalyst | Relative peak area (a.u.) |
| O2- | Mn—O | OH-, $CO\_{3}^{2-}$ | Si—O | $$O\_{2}^{-}$$ | Na—O—W |
| Si-F | 656.9 | - | - | 32,380.6 | 854.0 | - |
| NWMSi-F | 3,957.9 | 538.2 | - | 24,260.8 | 4,751.9 | 1,778.8 |
| La-F | 1,301.3 | - | 10,404.0 | - | 2,347.6 | - |
| NWMLa-F | 1,250.6 | 2,731.3 | 6,183.8 | - | 4,607.5 | 711.4 |



**Figure S5.** XPS spectra of (a) Na 1s, (b) W 4f, and (c) Mn 2p regions obtained from NWMSi-F and NWMLa-F catalysts.

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