Supporting Information

Co-production of Hydrogen and Methanol from Methane by Chemical Looping Reforming

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Supporting text

Figure S1. Thermodynamic analysis of methane POx/CO_2-splitting reactions and selected redox materials.

Figure S2. Experimental setup of performance testing.

Figure S3. XRD patterns of SF-C (a) and SF-M (b) samples.

Figure S4. SEM images of SF-CM sample: as-prepared (a), SF-CM CH_4-reduced (b), H_2O-regenerated (c). Reaction conditions: $m_{\mathrm{SF\text{-}CM}}$=2 g; T=900 °C, F_{ox}=200 STP mL/min (5 vol.% methane), F_{re}=194.5 STP mL/min (2.31 vol.% steam), P=1 atm.

Figure S5. Iron size distribution of the10th reduced SF-CM sample.

Figure S6. Flow diagram of MeH_2 scheme.

Figure S7. Flow diagram of MeOH scheme.

Figure S8. Influence of the price of methanol (a), natural gas (b), hydrogen (c) and electricity (d) on net income of MeH_2 and MeOH schemes.

Figure S9. The Grand Composite Curve of MeH_2 (a) and MeOH (b) schemes.

Supporting text

In methane POx step, methane conversion, syngas and coke selectivity were calculated as follows,

$$n_{CH4,i} = t_{ox} F_{CH4,i} \tag{S1}$$

$$n_{CH4,o} = \int_0^{t_{ox}} F_{CH4,o} dt \tag{S2}$$

$$n_{H2,ox} = \int_0^{t_{ox}} F_{H2,ox} dt \tag{S3}$$

$$n_{CO,ox} = \int_0^{t_{ox}} F_{CO,ox} dt \tag{S4}$$

$$n_{CO2,ox} = \int_0^{t_{ox}} F_{CO2,ox} dt \tag{S5}$$

$$n_{ox} = n_{CO,ox} + 4 \times n_{CO2,ox} \tag{S6}$$

$$X_{CH4}(\%) = 100\% \times \frac{n_{CH4,i} - n_{CH4,o}}{n_{CH4,i}} \tag{S7}$$

$$X_{CH4,ins}(\%) = 100\% \times \frac{F_{CH4,i} - F_{CH4,o}}{F_{CH4,i}} \tag{S8}$$

$$S_{Syn}(\%) = 100\% \times \frac{n_{CO,ox} + n_{H2,ox}}{3(n_{CH4,i} - n_{CH4,o})} \tag{S9}$$

$$S_{coke}(\%) = 100\% \times \frac{n_{coke}}{n_{CH4,i} - n_{CH4,o}} \tag{S10}$$

where $n_{H2,ox}$, $n_{CO,ox}$, $n_{CO2,ox}$, n_{coke} and n_{ox} are the total mole numbers of H_2, CO, CO_2, coke produced, and oxygen transferred, respectively. $n_{CH4,i}$ and $n_{CH4,o}$ are total mole numbers of input and output methane, respectively. $F_{CH4,o}$, $F_{H2,ox}$, $F_{CO,ox}$ and $F_{CO2,ox}$ are the molar flowrates of output CH_4, H_2, CO, and CO_2, respectively. $F_{CH4,i}$ is the molar flowrate of input methane. t_{ox} is the period of POx step. X_{CH4} is methane conversion,

$X_{CH4,ins}$ is the instantaneous methane conversion. S_{syn} and S_{coke} are syngas selectivity and coke selectivity, respectively.

In water splitting step, water conversion and hydrogen purity were calculated as follows,

$$n_{H2O} = \int_0^{t_{re}} F_{Ar} \frac{c_{H2O}}{1-c_{H2O}} dt \tag{S1}$$

$$n_{H2,re} = \int_0^{t_{re}} F_{H2,re} dt \tag{S12}$$

$$n_{CO,re} = \int_0^{t_{re}} F_{CO,re} dt \tag{S13}$$

$$n_{CO2,re} = \int_0^{t_{re}} F_{CO2,re} dt \tag{S14}$$

$$n_{coke} = n_{CO,re} + n_{CO2,re} \tag{S15}$$

$$X_{H2O}(\%) = 100\% \times \frac{n_{H2,re}}{n_{H2O}} \tag{S16}$$

$$P_{H2}(\%) = 100\% \times \frac{n_{H2,re}}{n_{H2,re}+n_{CO,re}+n_{CO2,re}} \tag{S17}$$

where n_{H2O} is the total mole number of water fed to the reactor. c_{H2O} is the concentration of steam in the feed. $n_{H2,re}$, $n_{CO,re}$, and $n_{CO2,re}$ are the total mole numbers of H_2, CO, and CO_2 produced, respectively. F_{Ar} is the molar flowrate of argon. $F_{H2,re}$, $F_{CO,re}$, and $F_{CO2,re}$ represent the molar flowrates of output H_2, CO and CO_2, respectively. t_{re} is the period of water splitting step. X_{H2O} represents H_2O to H_2 conversion. P_{H2} is the purity of hydrogen product.

The system exergy efficiency was calculated as follows,

$$E_{ex,ch,i} = F_i E_{ex,ch,s,i} \tag{S18}$$

$$E_{ex,ph,i} = F_i(H_i - H_{0,i} - T_0(S_i - S_{0,i})) \tag{S19}$$

$$E_{ex,W,j} = W_j \tag{S20}$$

$$E_{ex} = \sum E_{ex,ch,i} + \sum E_{ex,ph,i} + \sum E_{ex,W,j} + \sum E_{ex,q,k} \tag{S21}$$

$$E_{ex,q,k} = Q_k(1 - \frac{T_0}{T_k}) \tag{S22}$$

$$\eta_{ex,s} = \frac{E_{ex,out}}{E_{ex,in}} \tag{S23}$$

where $E_{ex,ch,i}$ is chemical exergy of each stream[1]. $E_{ex,ph,i}$ is the physical exergy of each stream. $E_{ex,W,j}$ is work exergy of each work input. $E_{ex,q,k}$ is heat exergy of each heat input. *i*, *j*, *k* represents the components of the stream, work, and heat. F_i is the flowrate of component i in the stream. H_i and S_i are the enthalpy and entropy of component i in the stream. T_0 is the environmental temperature, and $S_{0,i}$ is the entropy of compound i at T_0. T_k is the temperature of heat flow *k*, and Q_k is the heat into or out of the system of heat flow *k*. E_{ex} represents the exergy of the system which includes chemical exergy and physical exergy of the stream, work exergy and heat exergy. $E_{ex,out}$ and $E_{ex,in}$ are the total output and input exergy of the system, respectively. $\eta_{ex,s}$ is the exergy efficiency.

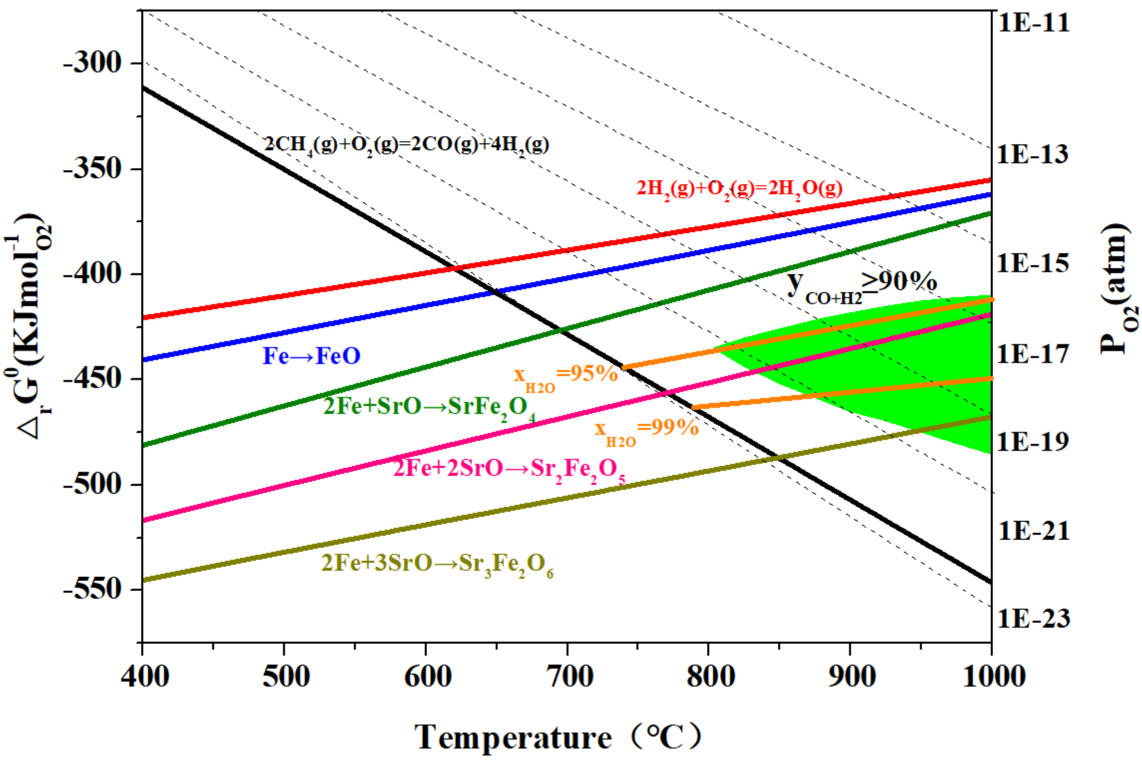

Figure S1. Thermodynamic analysis of methane POx/CO_2-splitting reactions and selected redox materials.

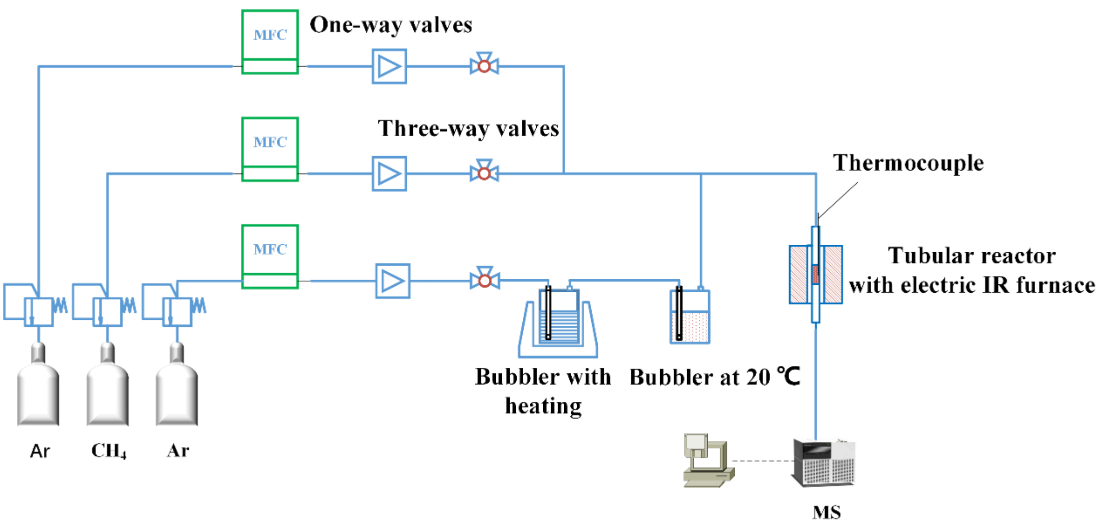

Figure S2. Experimental setup of performance testing.

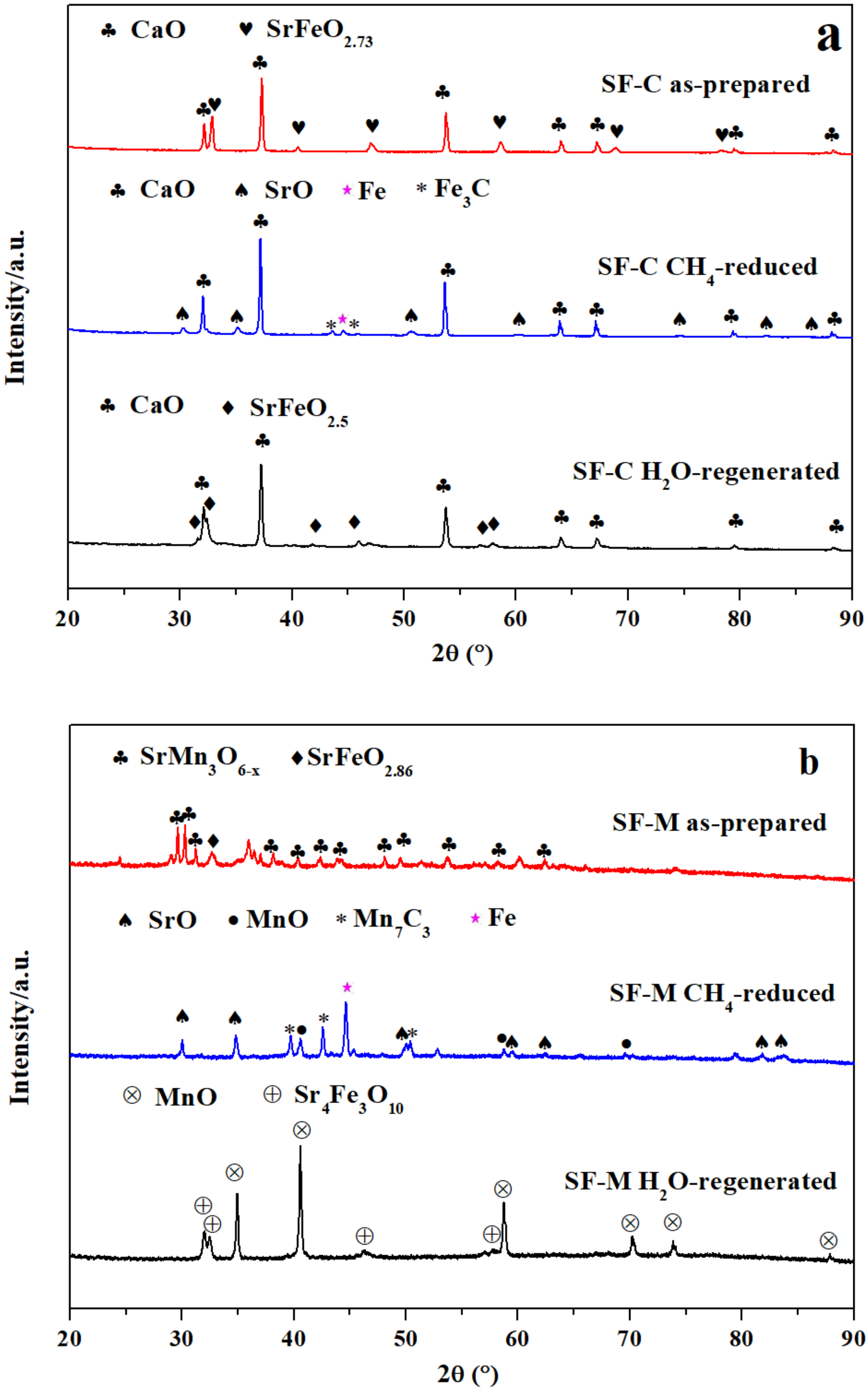

Figure S3. XRD patterns of SF-C (a) and SF-M (b) samples.

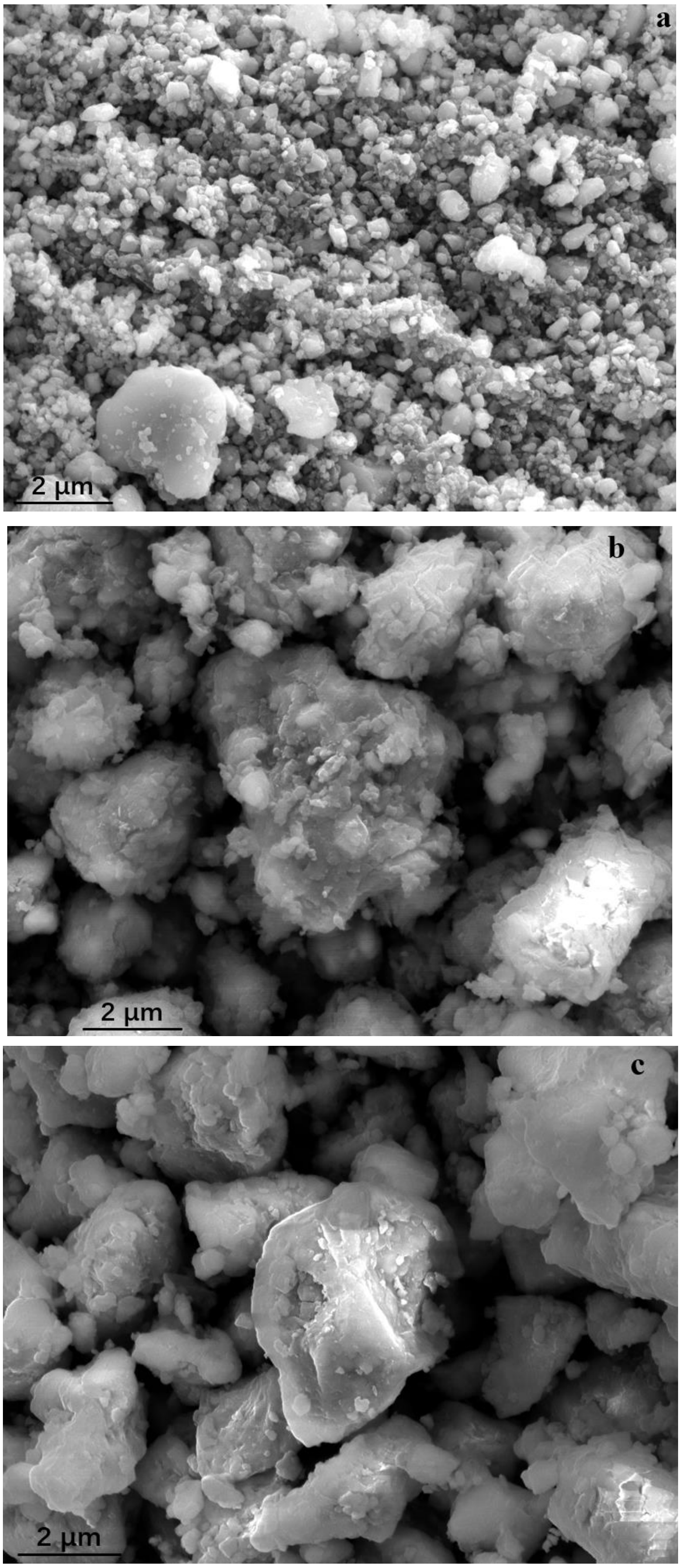

Figure S4. SEM images of SF-CM sample: as-prepared (a), SF-CM CH_4-reduced (b), H_2O-regenerated (c). Reaction conditions: $m_{SF\text{-}CM}$=2 g; T=900 °C, F_{ox}=200 STP mL/min (5 vol.% methane), F_{re}=194.5 STP mL/min (2.31 vol.% steam), P=1 atm.

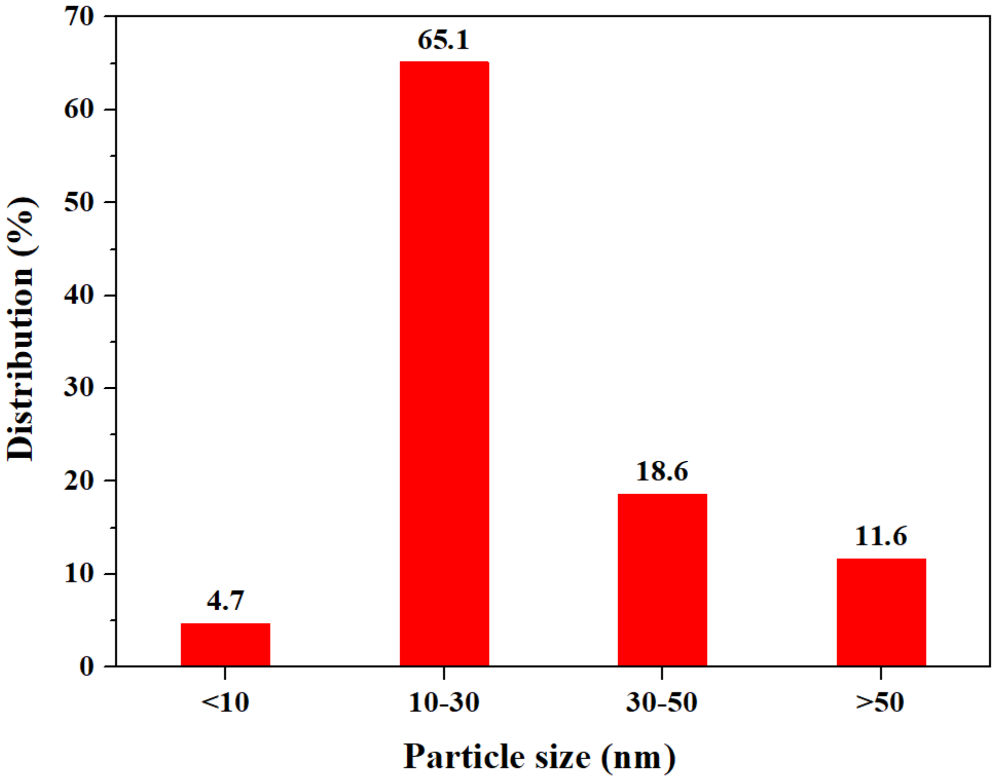

Figure S5. Iron size distribution of the 10^{th} reduced SF-CM sample.

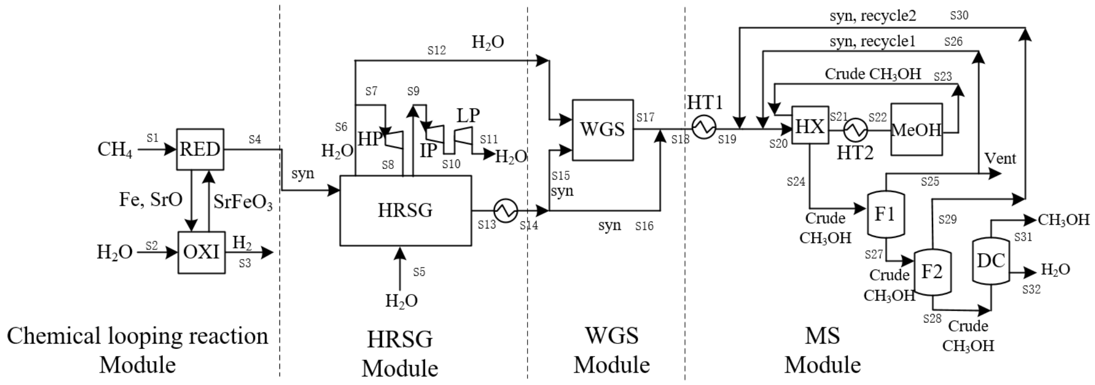

Figure S6. Flow diagram of MeH_2 scheme. RED: Reducer, OXI: Oxidizer, WGS: Water Gas Shift Reactor, HRSG: Recovery Steam Generator, HP: High Pressure Cylinder, IP: Intermediate Pressure Cylinder, LP: Low Pressure Cylinder, HX: Heat Exchanger, MeOH: Methanol Synthesis Reactor, F1: Flash Tank1, F2: Flash Tank 2, HT1: Heater 1, HT2: Heater 2, DC: Distillation Column, syn: syngas.

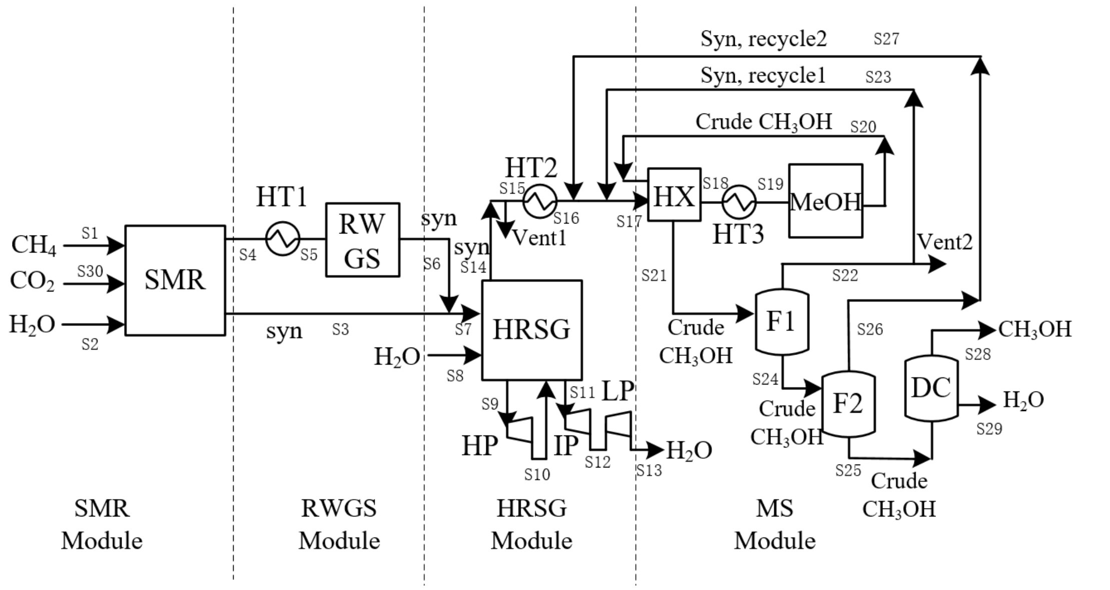

Figure S7. Flow diagram of MeOH scheme. SMR: Steam Methane Reforming Reactor, RWGS: Reverse Water Gas Shift Reactor, HRSG: Recovery Steam Generator, HP: High Pressure Cylinder, IP: Intermediate Pressure Cylinder, LP: Low Pressure Cylinder, HX: Heat Exchanger, MeOH: Methanol Synthesis Reactor, F1: Flash Tank1, F2: Flash Tank 2, HT1: Heater 1, HT2: Heater 2, DC: Distillation Column, syn: syngas.

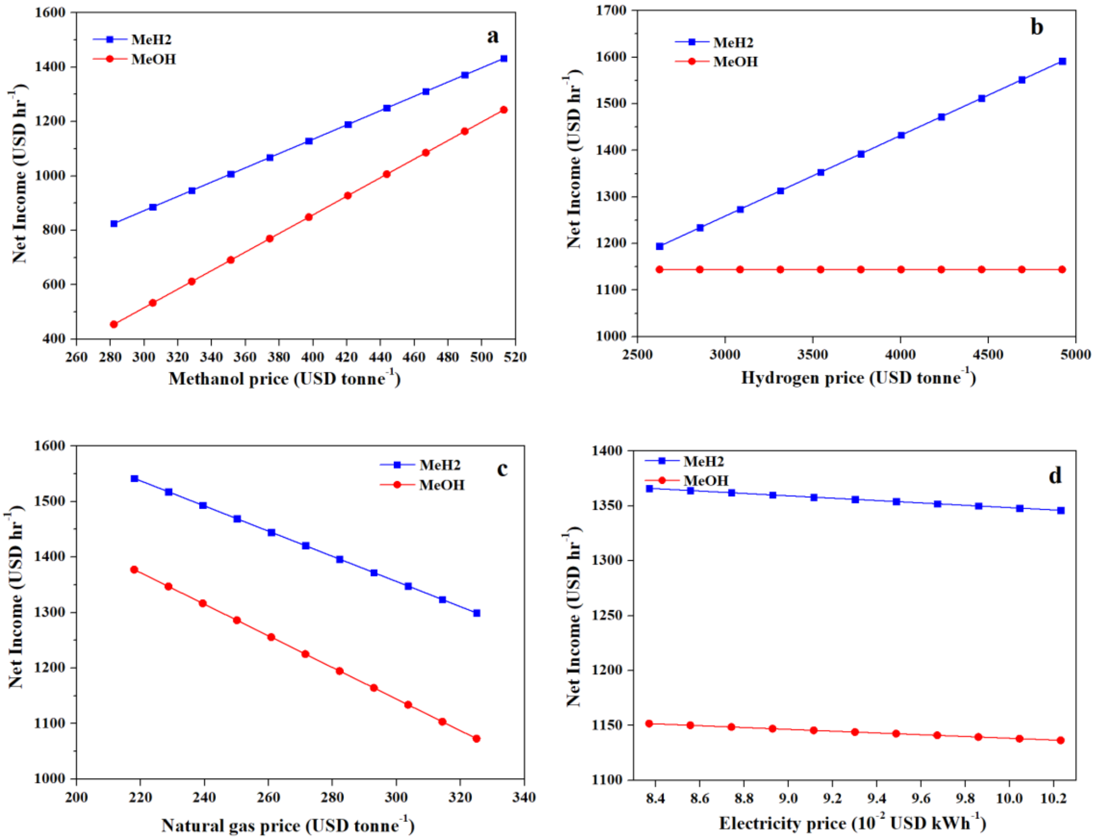

Figure S8. The effect of methanol (a), hydrogen (b), natural gas (c), and electricity (d) price on the net income of solar-driven processes.

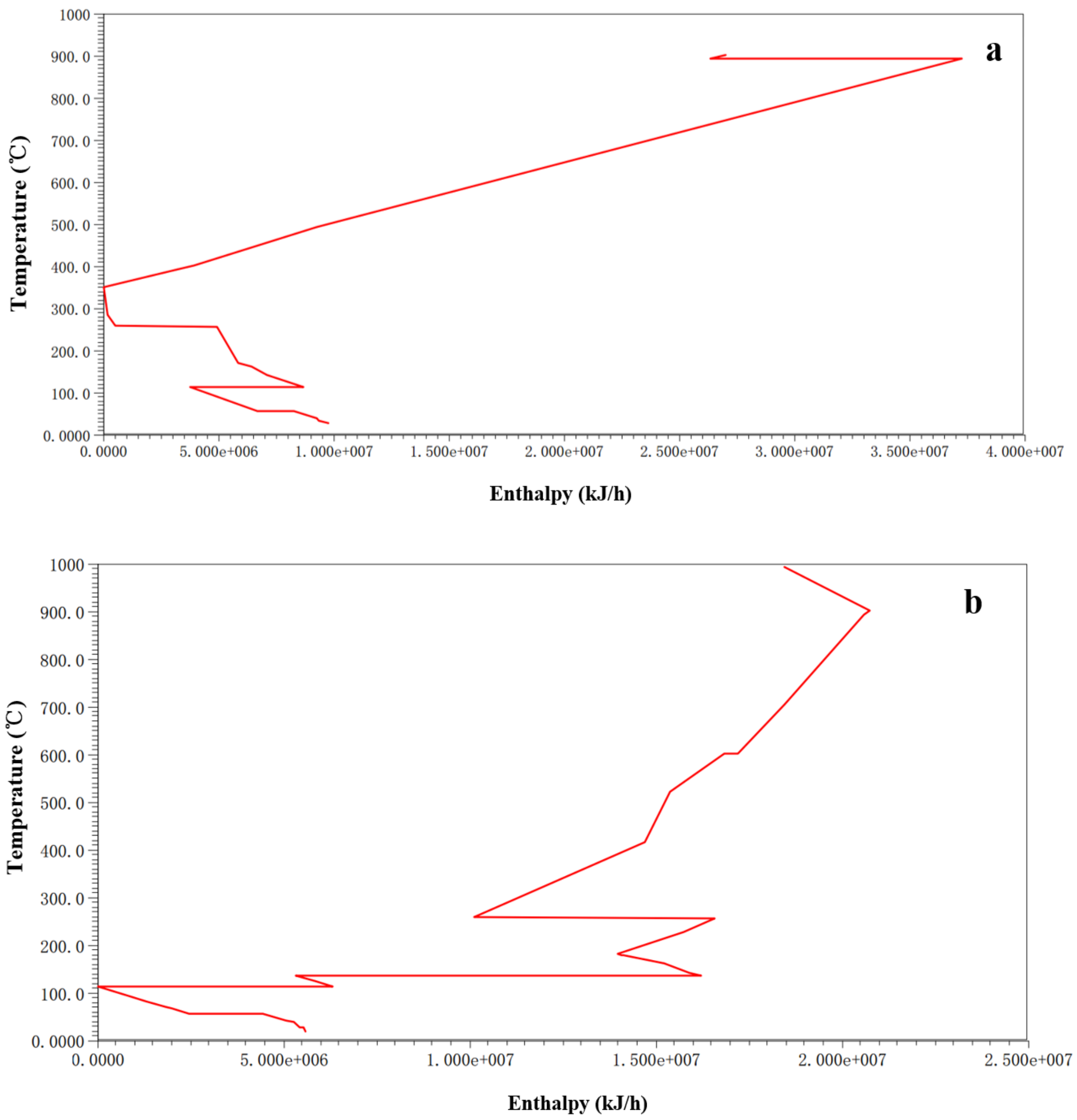

Figure S9. The Grand Composite Curve of MeH_2 (a) and MeOH (b) scheme.

Table S1. Bulk composition of as-prepared of SF-CM sample.

Element	Measured molar ratio*	Calculated molar ratio
Sr	1.05	1.00
Fe	1.00(Ref.)	1.00(Ref.)
Ca	4.55†	3.52
Mn	3.02	3.52

*ICP-MS measurement

†Measurement uncertainty is large

Table S2. Stream table of MeH_2 scheme.

	S1	S2	S3	S4	S12	S15	S22	S31
	To RED	To OXI	H_2 product	To HRSG	To WGS	To WGS	To MeOH	CH_3OH product
Mole Flow (kmol/s)								
CO	0	0	0	0.0235125	0	0.0058781	0.0282932	3.64E-08
CO_2	0	0	0	0.0002375	0	5.938E-05	0.0278314	0.000281
H_2	0	0	0.0239679	0.0475	0	0.011875	0.1652062	2.309E-07
H_2O	0	0.02421	0.0002421	0	0.0230555	0	0.0004455	5.025E-08
N_2	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0
CH_4	0.025	0	0	0.00125	0	0.0003125	0.0313874	2.82E-06
MeOH	0	0	0	0	0	0	0.0011001	0.0228131
Mole Fraction								
CO	0	0	0	0.3243103	0	0.3243103	0.1112751	1.576E-06
CO_2	0	0	0	0.0032759	0	0.0032759	0.1094589	0.0121672
H_2	0	0	0.99	0.6551724	0	0.6551724	0.649743	9.995E-06
H_2O	0	1	0.01	0	1	0	0.001752	2.176E-06
N_2	0	0	0	0	0	0	0	0
O_2	0	0	0	0	0	0	0	0
CH_4	1	0	0	0.0172413	0	0.0172413	0.1234443	0.0001221
MeOH	0	0	0	0	0	0	0.0043268	0.987697
Total Flow (kmol/s)	0.025	0.02421	0.02421	0.0725	0.0230555	0.018125	0.2542639	0.0230973
Temperature K	621.1232	407.5489	1173.15	1173.15	773.15	673.15	433.15	337.1491
Pressure (Pa)	2000000	300000	2026500	2000000	12400000	2000000	10000000	100000

Table S3. Stream table of MeOH scheme.

	S1	S2	S5	S7	S19	S28	S30
	To SMR	To SMR	To RWGS	To HRSG	To MeOH	CH3OH product	To SMR
Mole Flow (kmol/s)							
CO	0	0	0.0060543	0.0230113	0.0353606	4.864E-08	0
CO_2	0	0	0.0033297	0.0082688	0.0413914	0.0003358	0.0088869
H_2	0	0	0.0208174	0.0665613	0.0728989	1.525E-08	0
H_2O	0	0.075	0.0151184	0.0532249	0.0006507	7.412E-08	0
N_2	0	0	0	0	0	0	0
O_2	0	0	4.7E-20	1.097E-19	0	0	0
CH_4	0.025	0	0.000782	0.0026068	0.0879386	7.404E-06	0
CH_3OH	0	0	3.641E-09	1.214E-08	0.0018711	0.0296318	0
Mole Fraction							
CO	0	0	0.1313246	0.1497419	0.1472678	1.623E-06	0
CO_2	0	0	0.0722247	0.0538074	0.1723841	0.011204	1
H_2	0	0	0.451553	0.4331357	0.3036048	5.087E-07	0
H_2O	0	1	0.3279343	0.3463516	0.0027101	2.473E-06	0
N_2	0	0	0	0	0	0	0
O_2	0	0	1.02E-18	7.137E-19	0	0	0
CH_4	1	0	0.0169633	0.0169633	0.3662407	0.000247	0
CH_3OH	0	0	7.897E-08	7.897E-08	0.0077925	0.9885443	0
Total Flow (kmol/s)	0.025	0.075	0.0461019	0.1536732	0.2401115	0.0299752	0.0088869
Temperature (K)	349.6994	498.15	873.15	1085.938	433.15	337.1704	404.101
Pressure (Pa)	2533130	300000	200000	200000	10000000	100000	300000

Table S4. The price of the feedstock, products and electricity.

Items	Price
Hydrogen	3,560 USD/tonne
Methanol	484 USD/tonne
Natural gas	300 USD/tonne
Electricity	0.093 USD/kWh

Table S5. Energy requirements of MeH_2 and MeOH scheme.

	MeH_2 (MW)	MeOH (MW)
SMR	N/A	8.60
RED	10.74	N/A
OXI	-3.05	N/A
RWGS	N/A	0.10
WGS	-0.29	N/A
MeOH	-1.23	-1.80

Reference

(1) Peters, J. F.; Petrakopoulou, F.; Dufour, J. Exergetic Analysis of a Fast Pyrolysis Process for Bio-Oil Production. *Fuel Process. Technol.* **2014**, *119*, 245–255.