Supplementary Information

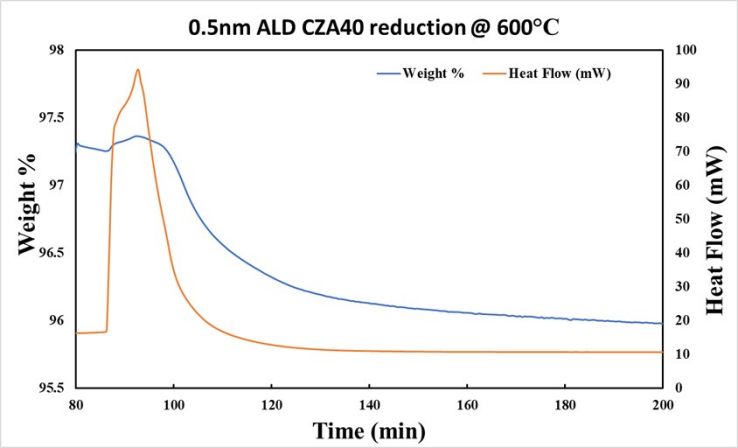

Figure S.1. *Reduction profile of 0.5nm ALD CZA40 (a Ni/Ce/Al_2O_3 catalyst from previous work), 5% H_2/N_2, prior to DRM screening in DSC/TGA. Final curves of wt% and heat flow show essentially complete reduction.*

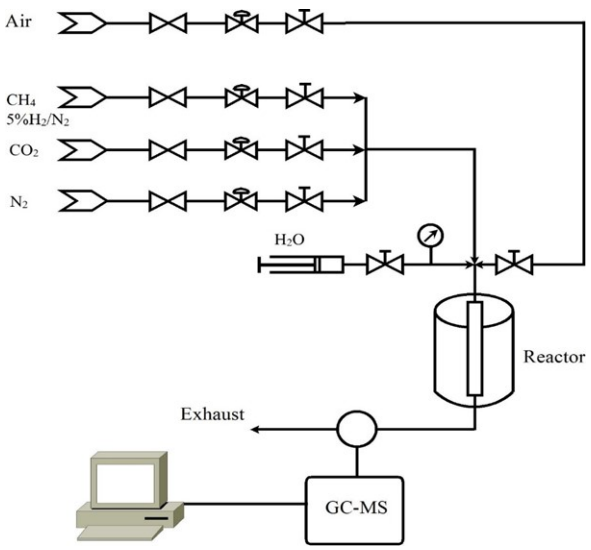

Figure S.2. *Schematic of the reactor system for DRM.[2] GC parameters in Table S1. Reprinted from ref. 1 with permission from author Changyi Jiang.*

Analytical (GC) details

The gas samples from the reactor were analyzed by an Agilent 6890N GC/MS. Three 1/8" molecular sieve packed columns, a Wasson K1 (6 ft), K2 (7 ft), and K2S (2 ft) in series were used to separate hydrogen from the rest of the gaseous mixture, with the H_2 analyzed by a thermal conductivity detector. A 1 mL sample was injected using N_2 as the carrier gas at 30 psig. Another 1 mL sample was injected into a 0.53 mm, 50 m capillary column (Wasson KC080) to separate N_2, CO, CO_2, CH_4 and water, also analyzed by a thermal conductivity detector. Helium was the carrier gas, controlled by electronic flow controller. A third sample was injected (as needed) to a 100 m, 0.25 mm Wasson KC066 column which separated all components and interfaced to the MSD, which was used for confirmation component identities. Helium was the carrier gas, controlled by electronic flow controller. The oven program and TCD details are provided below. GC calibration factors and retention times are presented in Table S1.

Front Inlet – Split; 120°C; P: 4.5 psi; column flow 0.5 mL/min; total flow: 7.8 mL/min; split ratio = 10:1; split flow = 4.8 mL/min

Back Inlet – Split; 120°C; P: 7.4 psi; column flow 5.4 mL/min; total flow: 79 mL/min; split ratio = 13.1:1; split flow=70.4 mL/min 78

Front Detector – TCD; 200°C; 16.5 mL/min ref. flow; 11 mL/min makeup flow; Gas = He

Back Detector – TCD; 200°C; 20 mL/min ref. flow; 3 mL/min makeup flow; Gas = N2; Negative polarity

GC Oven Program – Initial Temp = 30 °C; Initial time = 7 min; Rate1 = 10 °C/min to 100 °C; 5 min hold; Rate2 = 10 °C/min to 130 °C; 16 min hold; Post Temp = 30 °C;

Post Time = 15 min; Total run time = 38 min

Packed Column Auxiliary Oven Temperature Program – Initial Temp = 50 °C; Initial time = 5 min; Rate1 = 10 °C/min to 120 °C, hold 11 min; Rate2 = 10 °C/min to 50°C; Chase heater – 100 °C; Injector (GSVs) oven – 200 °C

Rate/Conversion Calculations from TGA/DSC Data

Aspen HYSIS® was used to compute the heat of reaction at a given conversion. The % conversion in DRM was varied until the computed heat flow matched the measured heat flow from the DSC. We simulated the combined DRM/RWGS reactions in HYSIS as well. The neglect of the effects of RWGS on the DSC heat flux is justified both by its relative thermoneutrality, and the knowledge that RWGS rates are always less than DRM rates,[1] which was also verified experimentally. For example, the calculated endothermic heat of reaction for DRM is 7.2-7.5 times that of RWGS over 650-800 °C.[2] Therefore since the RWGS reaction is at least three times slower than the DRM rate (based on observed H_2/CO ratios), the error in the computed DRM conversion by neglecting the RWGS in this calculation from the DSC data is <5%. The conversions so obtained were therefore in the differential range, which allows for direct computation of the rate from the differential reactor equation.

Table S.1. GC Calibration Factors and Retention Times[1]

Component	GC Factor Mol (μmol)/area (MM)	Retention Time (min)
CO	0.46	3.6
CO_2	0.44	8.9
N_2	0.37	3.5
CH_4	0.69	4.3
H_2O	0.55	21.3
H_2	0.082	2.8[1]

[1]For the packed columns.

Table S.2. N_2 Physisorption and Ni Contents[1]

Catalyst	Surface Area (m2/g)	Pore Volume (cm3/g)	Ni wt%	Ni:Ga molar ratio
Ni/Al_2O_3	180	0.53	4.0	N/A
Ni0.4/Ga0.13/Al	140	0.38	6.0	3
Ni0.27/Ga0.27/Al	130	0.33	6.0	1
Ni0.13/Ga0.40/Al	120	0.26	6.0	0.33
Ni/Ga_2O_3	63	0.18	4.0	0.07
Ni0.5/Ce/Zr	200	0.31	4.0	N/A
Ni0.3/Co0.3/Ce3/La	125	0.81	3.0	N/A
Ni0.088/Mg4/Al	170	0.29	2.0	N/A

[1]The wt%'s on the catalysts prepared by incipient wetness (all Ni-Ga except Ni/Ga_2O_3) are exact and not from ICP. The others are from ICP of the filtrate, which showed 1 ppm Ni or less.

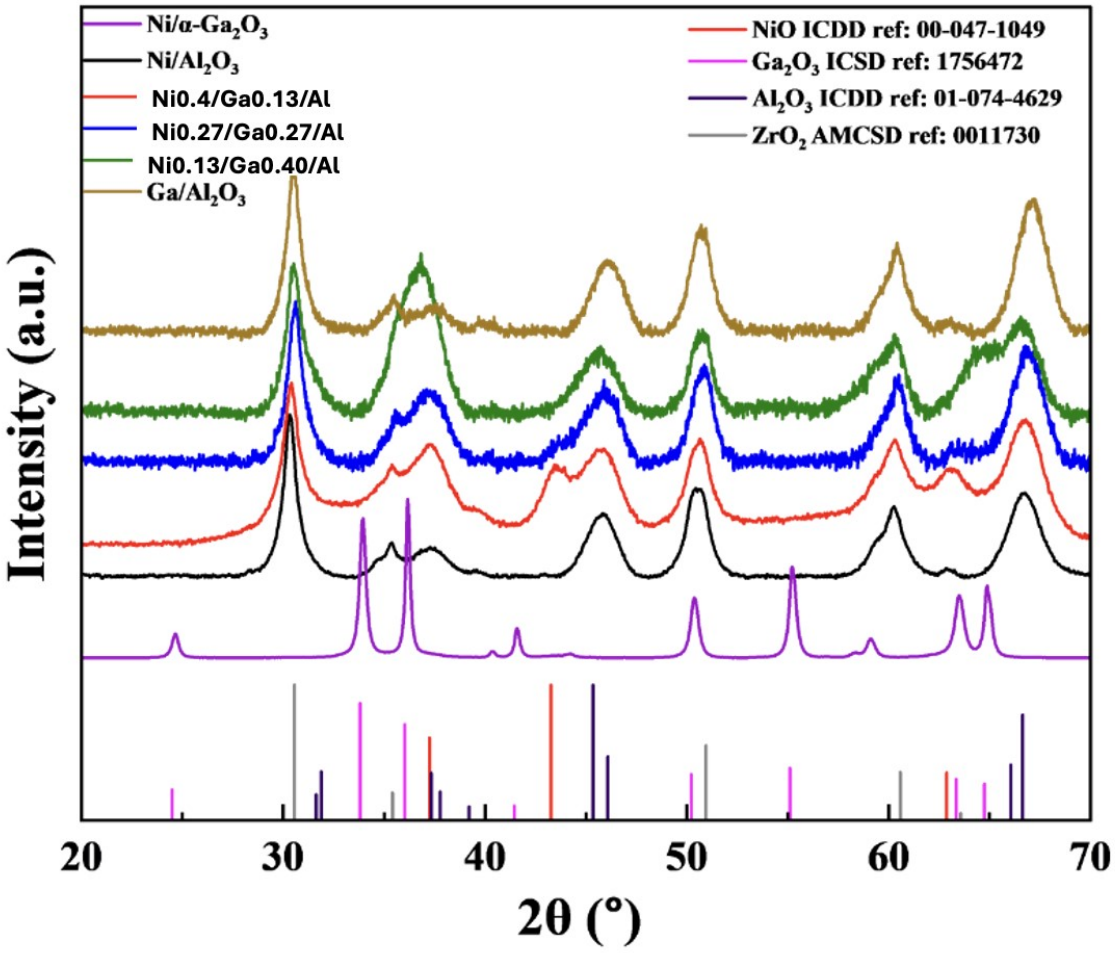

Figure S.3. *XRD of fresh Ni-Ga catalysts.*

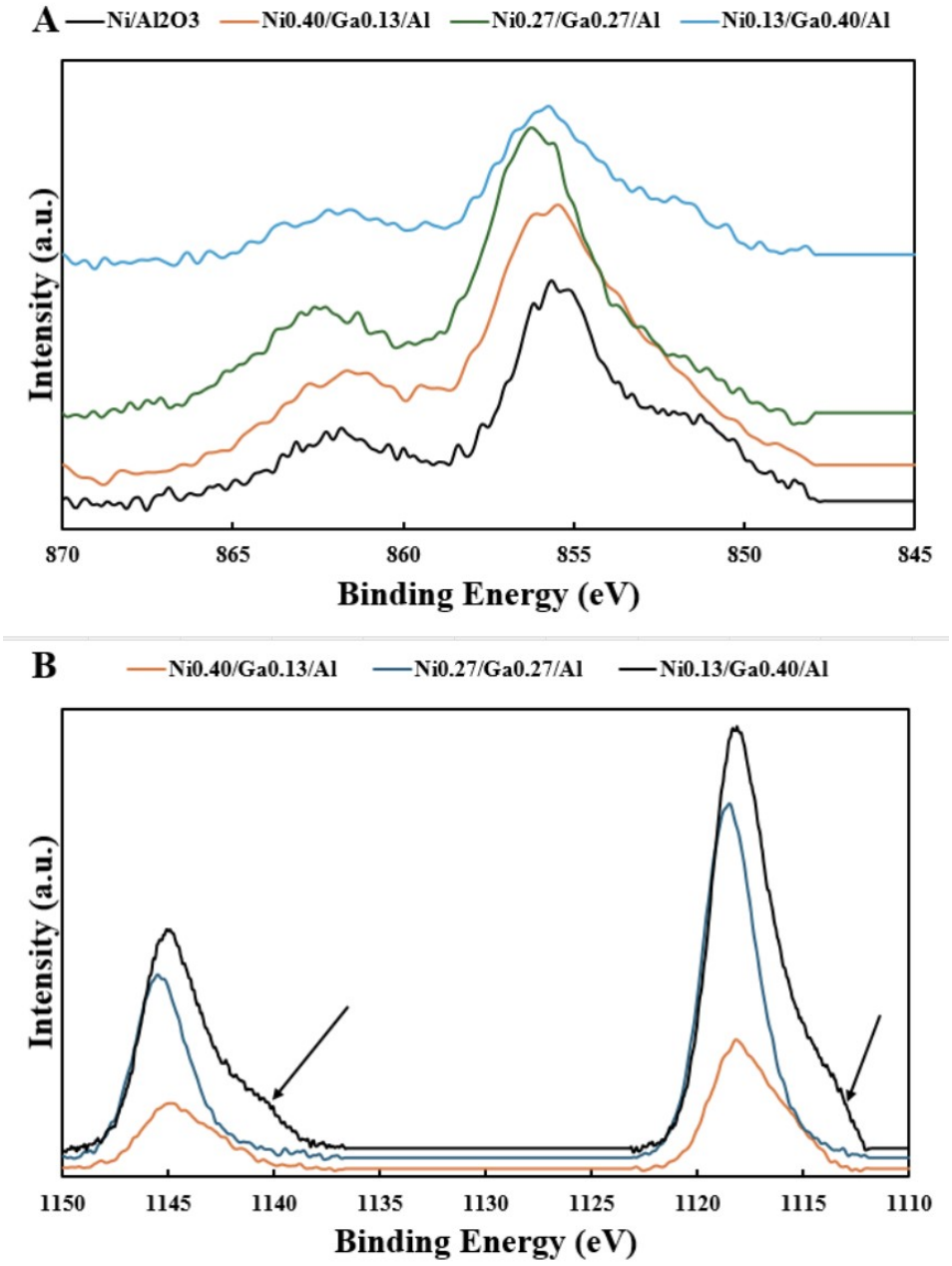

Figure S.4 *(a.) Ni 2p XPS spectra (b.) Ga 2p XPS spectra of Ni-Ga/Al_2O_3 series of catalyts. Arrows indicate Ga shoulder peaks at lower binding energy.*

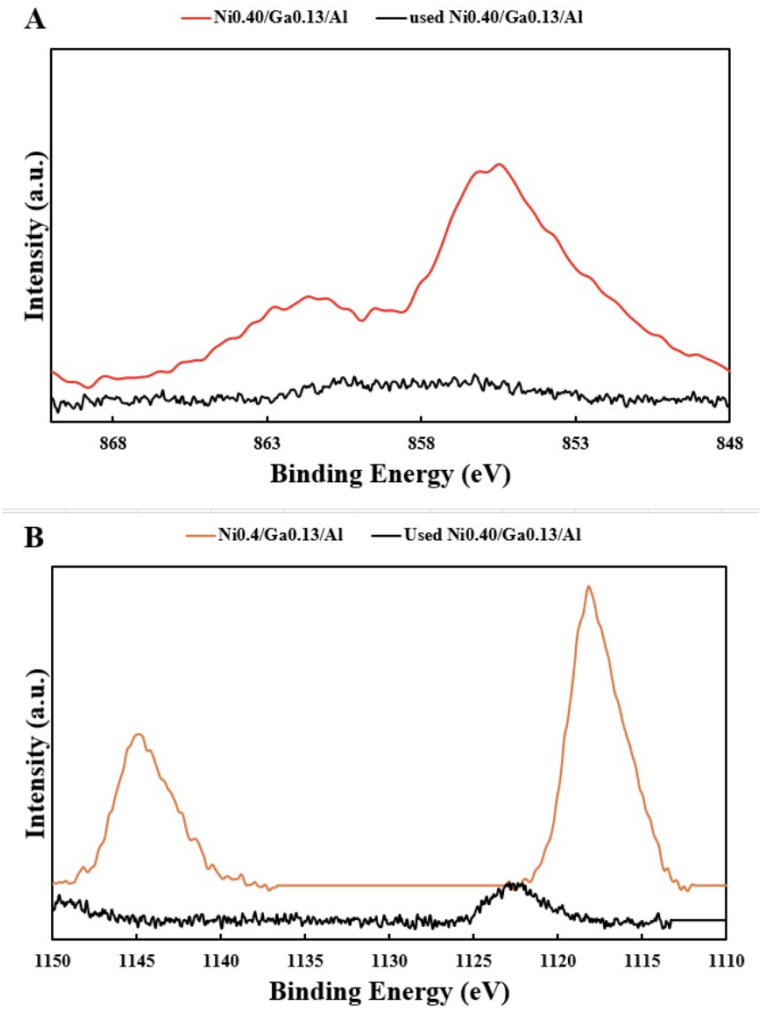

Figure S.5 *(a.) Ni 2p XPS and (b.) Ga 2p XPS spectra, comparing fresh and used (in DRM) Ni0.4/Ga0.13/Al catalysts.*

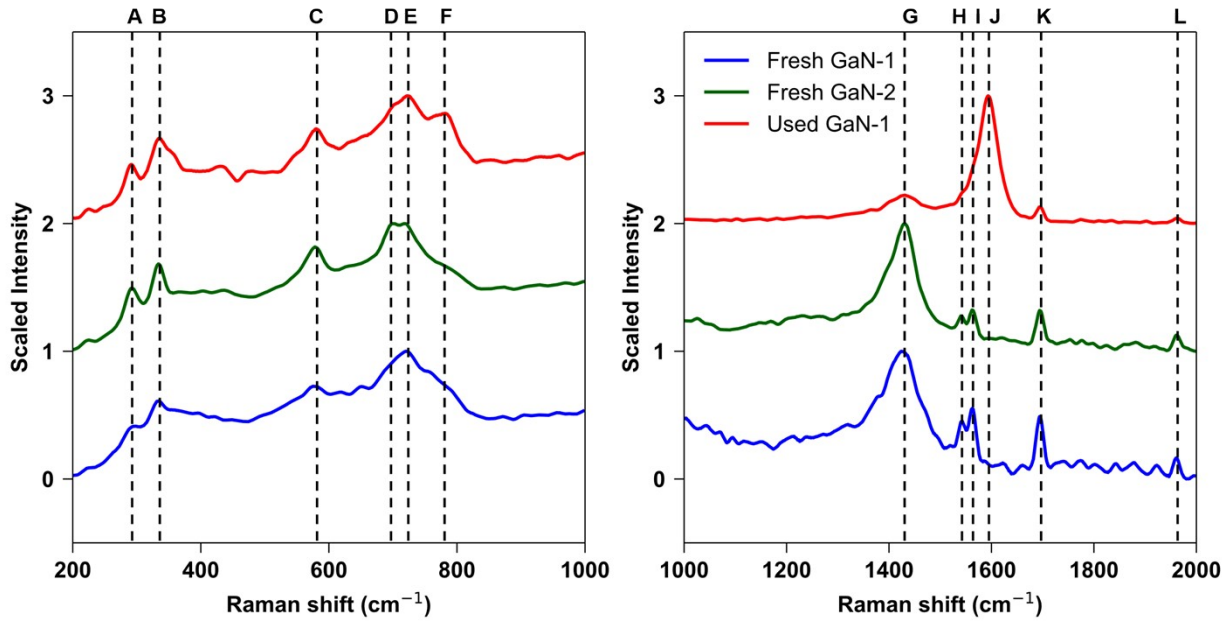

Figure S.6. *(Left) UV Raman spectra of the oxide region for fresh and used (in DRM) Ni–Ga/Al$_2$O$_3$ catalysts; (Right) Same but for the carbon region.*

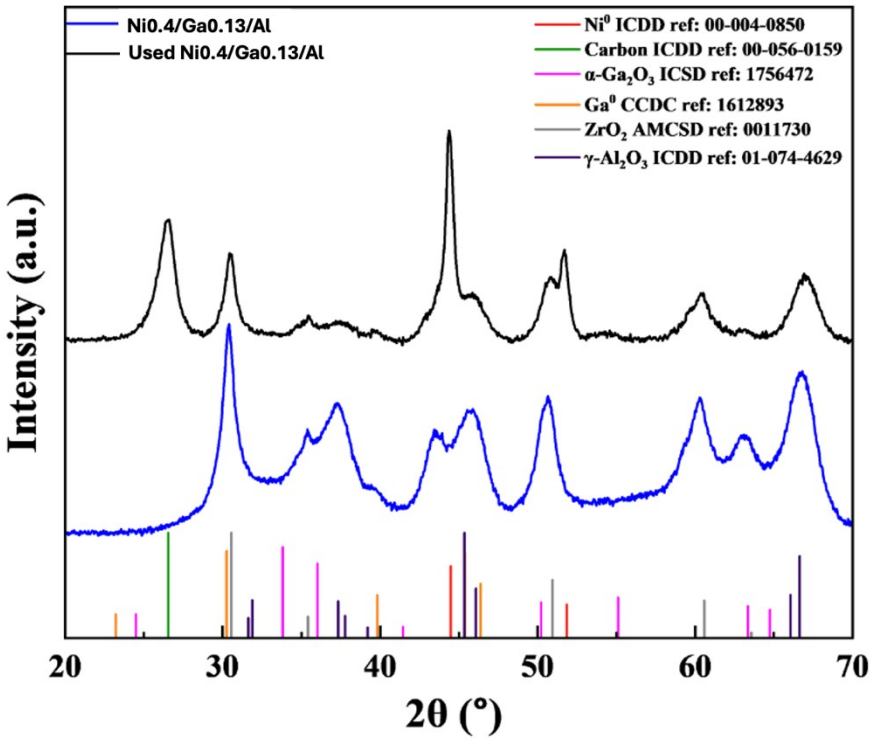

Figure S.7. *XRD of fresh and used (in DRM) Ni0.4/Ga0.13/Al.*

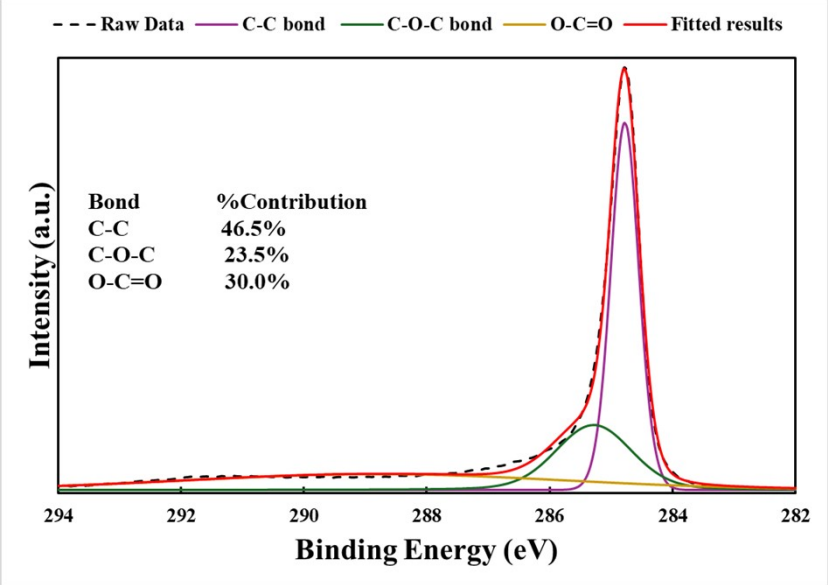

Figure S.8. *Carbon 1s XPS of used (in DRM) Ni0.4/Ga0.13/Al.*

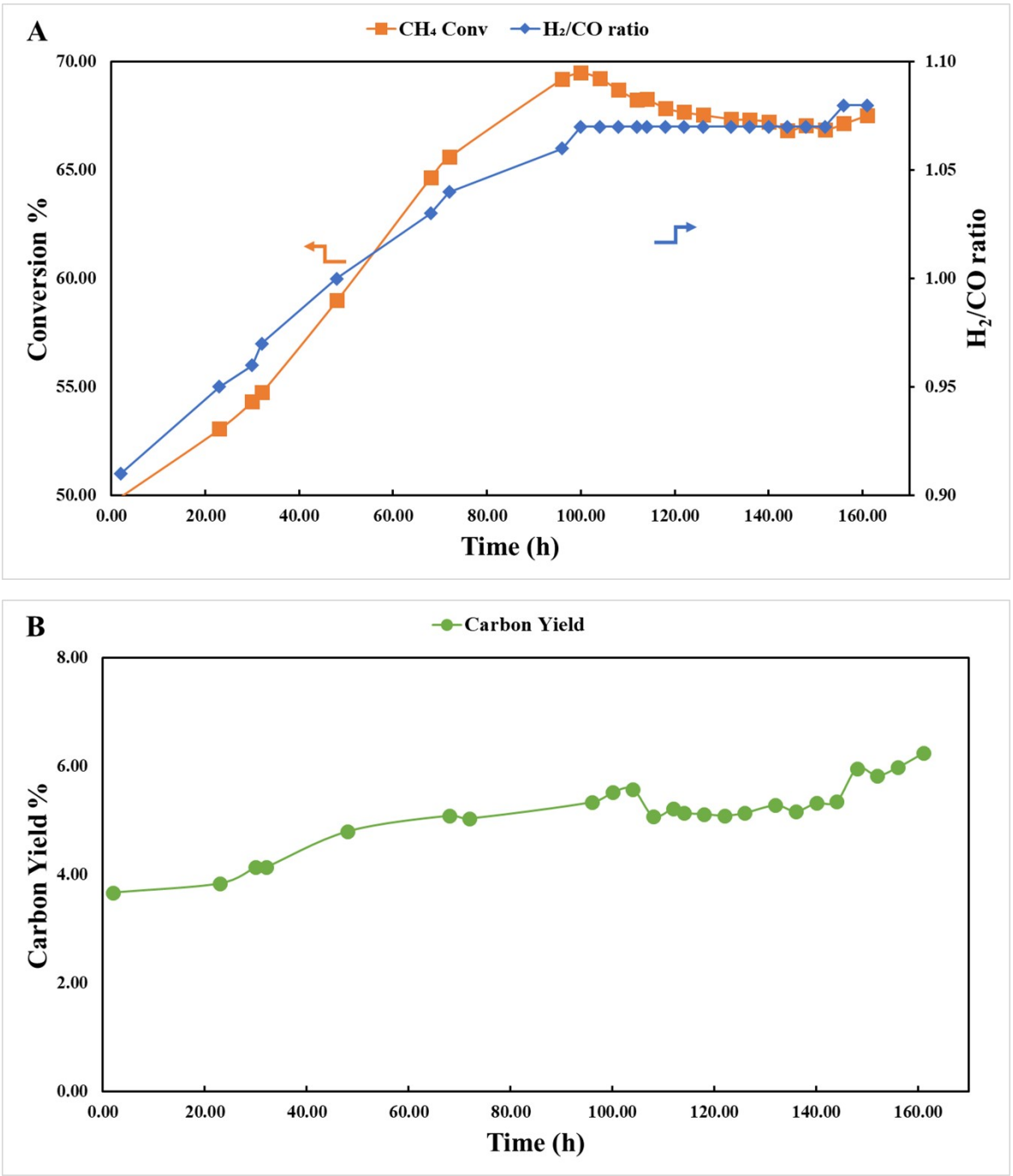

Figure S.9. *High conversion DRM reaction of Ni0.4/Ga0.13/Al:* ***a.)*** *activity/selectivity data and* ***b.)*** *carbon yield. Conditions: 700°C, 1:1 CH_4:CO_2 in feed, 1.2 bar total pressure, 37800 GHSV. Maximum CH_4 conversion: 70%, maximum H_2/CO: 1.05.*

Table S.3. Catalyst performance metrics of DRM kinetics experiments at 700°C.[1]

Catalyst	Feed Conditions	Feed Partial Pressure (bar)	DRM Rate (mmol/mgcat * h)	Coking Rate (mg/mgcat * h)
Ni0.5/Ce3/Zr	1.2:1 CO_2:CH_4	0.23 CH_4 : 0.27 CO_2	0.25	4.7E-04
	1:1 CO_2:CH_4	0.26 CH_4 : 0.26 CO_2	0.27	1.7E-03
	1:1 CO_2:CH_4	0.26 CH_4 : 0.26 CO_2	0.28	-1.3-03
	1:1 CO_2:CH_4	0.26 CH_4 : 0.26 CO_2	0.30	-2.4E-04
	1:1 CO_2:CH_4	0.14 CH_4 : 0.14 CO_2	0.14	1.6E-03
	1.2:1 CO_2:CH_4	0.23 CH_4 : 0.27 CO_2	0.25	-1.1E-03
	1.2:1 CO_2:CH_4	0.23 CH_4 : 0.27 CO_2	0.29	-1.30E-03
	1.4:1 CO_2:CH_4	0.20 CH_4 : 0.28 CO_2	0.24	-1.4E-03
	1.6:1 CO_2:CH_4	0.18 CH_4 : 0.29 CO_2	0.26	7.7E-04
	1.6:1 CO_2:CH_4	0.18 CH_4 : 0.29 CO_2	0.27	-1.3E-04
	2 :1 CO_2:CH_4	0.15 CH_4 : 0.3 CO_2	0.21	-1.5E-03
	1.2 :1 CO_2:CH_4	0.25 CH_4 : 0.26 CO_2	0.29	-1.5E-03
	1.4 :1 CO_2:CH_4	0.24 CH_4 : 0.27 CO_2	0.33	-1.5E-03
	1:1 CO_2:CH_4	0.26 CH_4 : 0.26 CO_2	0.28	-1.0E-03
	5% CO	0.26 CH_4 : 0.26 CO_2 : 0.03 CO	0.19	-7.3E-04
	10% CO	0.25 CH_4 : 0.25 CO_2 : 0.06 CO	0.18	-8.6E-04
	15% CO	0.24 CH_4 : 0.24 CO_2 : 0.08 CO	0.18	-2.0E-03
	20% CO	0.23 CH_4 : 0.23 CO_2 : 0.12 CO	0.17	-1.1E-03
	1:1 CO_2:CH_4	0.26 CH_4 : 0.26 CO_2	0.28	-1.3E-03
	1.2% water	0.26 CH_4 : 0.25 CO_2:0.012 H_2O	0.32	-1.2E-03
	4.2% water	0.25 CH_4 : 0.25 CO_2:0.042 H_2O	0.33	-1.8E-03
	14% water	0.23 CH_4 : 0.23 CO_2:0.14 H_2O	0.39	8.85E-04
Ni0.088/Mg4/Al	1:1 CO_2:CH_4	0.26 CH_4 : 0.26 CO_2	0.21	7.2E-03
	1.2:1 CO_2:CH_4	0.23 CH_4 : 0.27 CO_2	0.20	1.2E-03
	1:1 CO_2:CH_4	0.26 CH_4 : 0.26 CO_2	0.23	1.7E-03
Ni/Al_2O_3	1:1 CO_2:CH_4	0.26 CH_4 : 0.26 CO_2	0.19	-6.2E-04
	1.2:1 CO_2:CH_4	0.23 CH_4 : 0.27 CO_2	0.18	-5.7E-04
	1.4:1 CO_2:CH_4	0.20 CH_4 : 0.28 CO_2	0.17	-5.9E-04
	1.6:1 CO_2:CH_4	0.18 CH_4 : 0.29 CO_2	0.17	-6.3E-04
Ni0.4/Ga0.13/Al	1:1 CO_2:CH_4	0.26 CH_4 : 0.26 CO_2	0.45	2.7E-01
	1.2:1 CO_2:CH_4	0.23 CH_4 : 0.27 CO_2	0.42	4.5E-02
	1:1 CO_2:CH_4	0.26 CH_4 : 0.26 CO_2	0.41	5.5E-02
	2:1 CO_2:CH_4	0.15 CH_4 : 0.30 CO_2	0.37	5.0E-03
	1:1 CO_2:CH_4	0.26 CH_4 : 0.26 CO_2	0.41	2.9E-02

[1]Total pressure 1.01 bar. Balance is N_2.

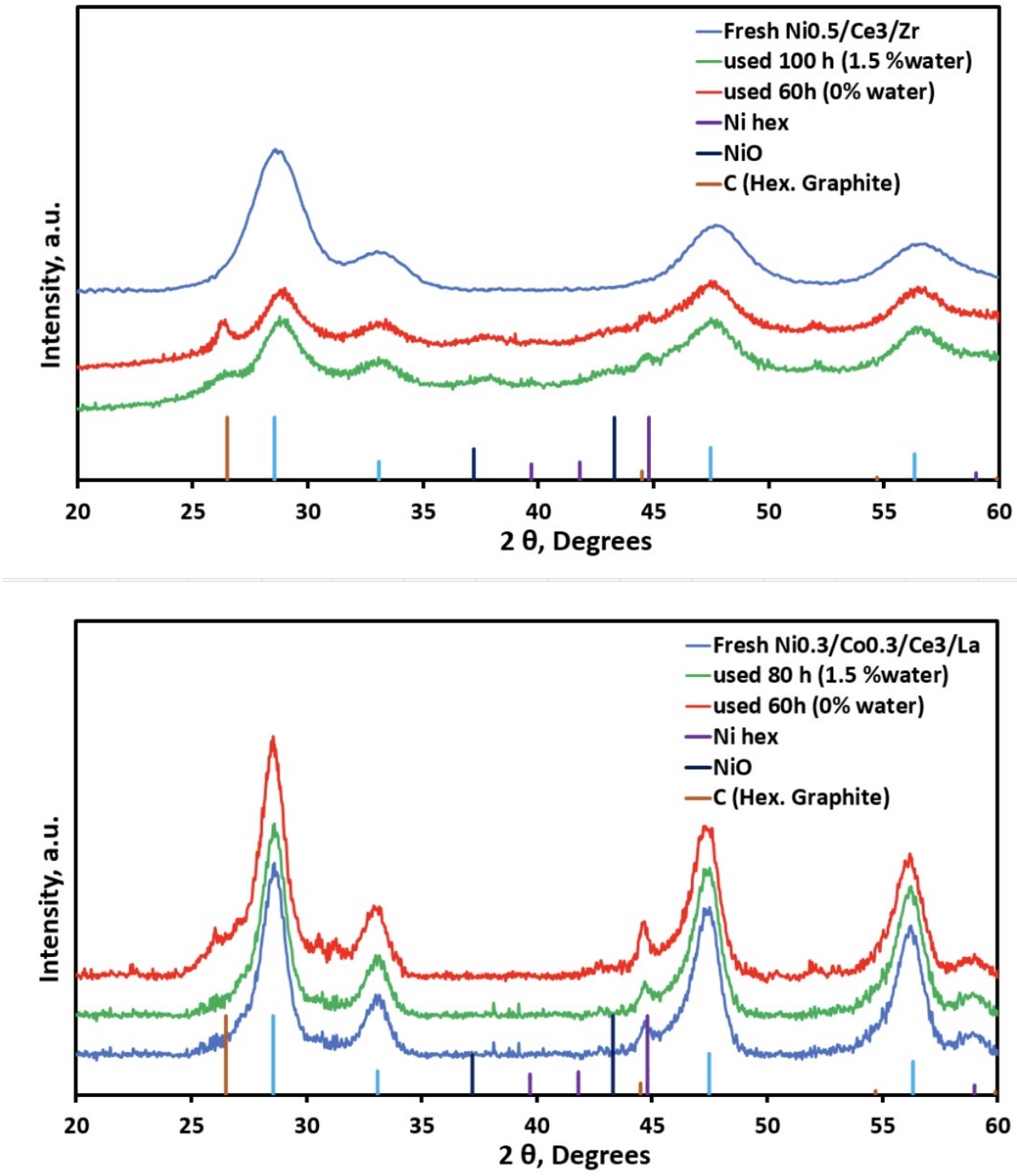

Figure S.10. *XRD of fresh and used Ni0.5/Ce3/Zr and Ni0.3/Co0.3/Ce3/La catalysts*

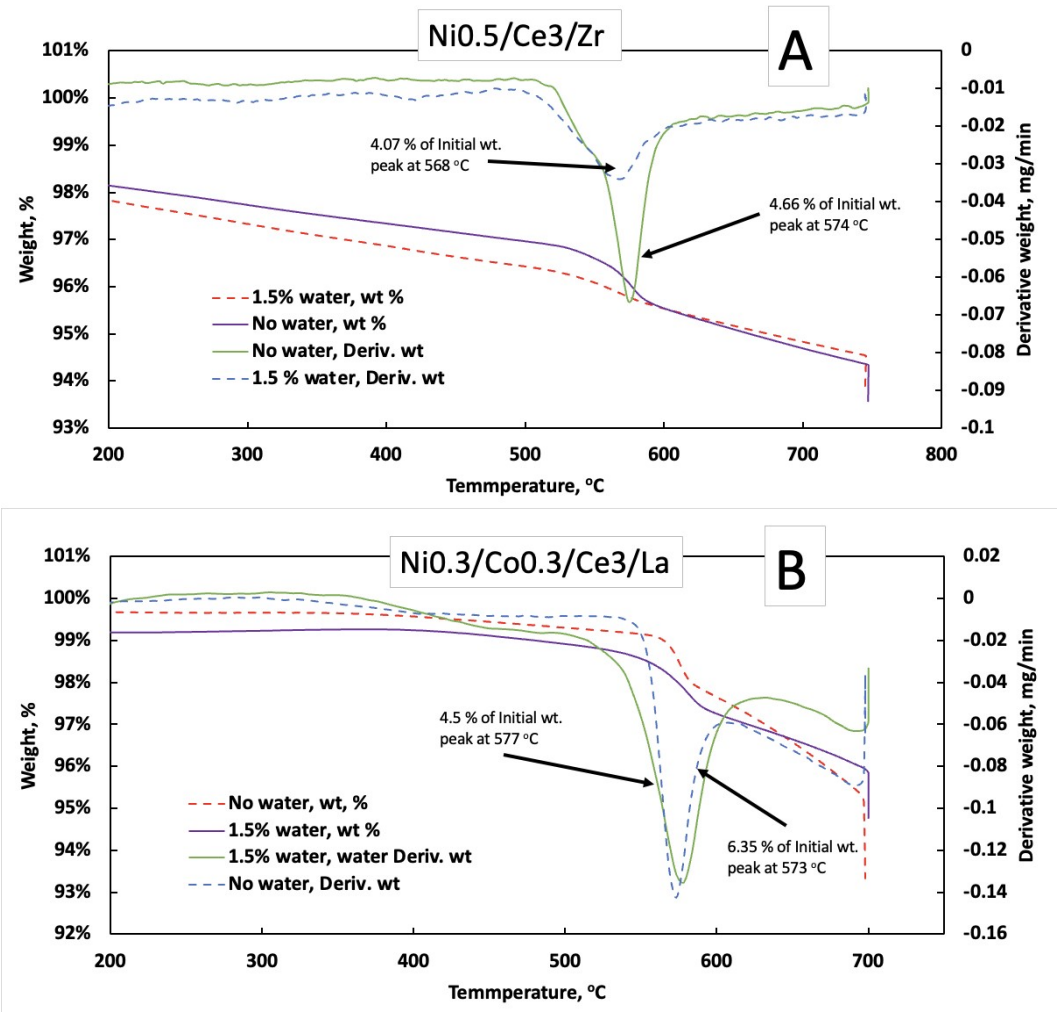

Figure S.11. *TPO of used Ni0.5/Ce3/Zr and Ni0.3/Co0.3/Ce3/La catalysts*

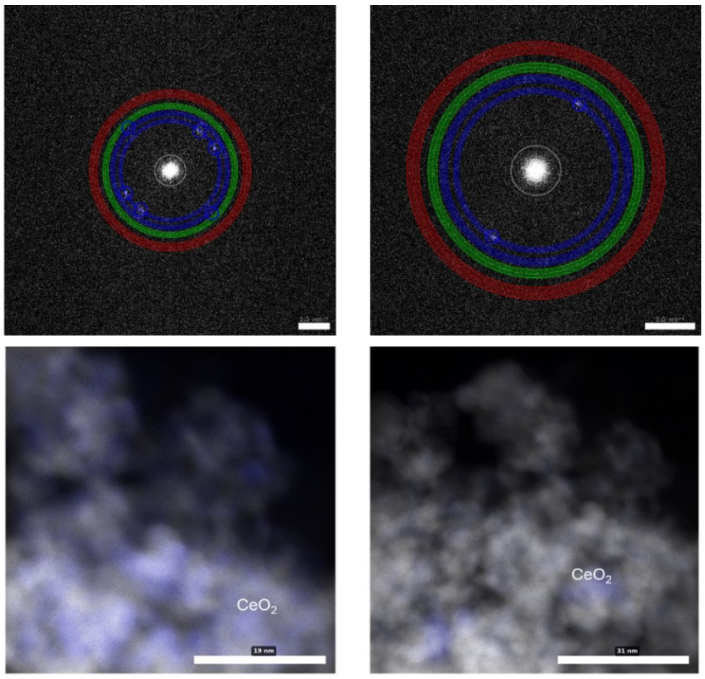

Figure S.12. *FFT-based phase mapping of Ni0.5/Ce3/Zr catalyst after 60 h DRM at 700 ℃, GHSV 60000* mL/g_{cat}•h*, dry feed. Top panels: FFT patterns showing CeO_2 (111, 200) reflections (blue), 2.0 nm^{-1} scale bar. Bottom panels: real-space phase maps highlighting CeO_2 domains (blue), 19 (L) and 31 (R) nm scale bars.*

Weisz Moduli calculation details

The Weisz Modulus can be expressed as:

$$W_m = \frac{r_{vobs} L^2}{C_A D_e} = \eta\, \phi^2$$

Where r_{vbos} is the observed reaction rate per unit particle volume, L the characteristic diffusion dimension, for spherical particles one-third the particle radius, C_A concentration of the limiting reactant in the bulk fluid and D_e its effective diffusivity in the catalyst particle. η is the effectiveness factor and ϕ is the Thiele modulus.

Particle Sieving determined the weight-average spherical diameter (d_p) for each catalyst. For spheres, $L = d_p/3$. C_A was obtained using the ideal gas law. The effective diffusivity was approximated using the "random pore" model as follows:

$$D_e \sim \frac{\varepsilon^2}{\left(\frac{1}{DK_j} + \frac{1}{Dj_m}\right)}$$

Where ε is the void fraction in the catalyst bed, roughly 0.4. Dj_m is the bulk diffusivity of reactant j in a mixture. At 700°C the D_{jm} of CH_4 and CO_2 were approximated using Aspen as 1.5 cm^2/s. DK_j is the Knudson diffusivity in cm^2/s, calculated as follows:

$$DK_j = 9700(r)_{avg}\sqrt{\frac{T}{MW_j}}$$

where $(r)_{avg}$ is the average pore radius of the catalyst. This was approximated for any catalyst that didn't have a full pore size distribution using BET analysis. The approximation for r_{avg} is 2*PV/SA, where PV is the pore volume and SA is the surface area of the catalyst. T is the temperature in K. and MW is the g/mol molecular weight of the reactant.

η was calculated as follows: $\eta = \frac{\tanh \phi}{\phi}$

Therefore: $W_m = \phi \tanh \phi$

MATLAB Program to Simulate High Conversion Reactor

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%% these are the operating conditions                                 %%%
%%% only change these parameters - nothing else                         %%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% set to 1 for isothermal operation, 0 for nonisothermal
isothermal = 1;
% feed conditions
T0 = 700;    % inlet temperature, C
FA0 = 6.13/2;  % molar feed rate of CH4, mmol/min
FB0 = 6.13/2;  % molar feed rate of CO2, mmol/min
FC0 = 0.001;  % molar feed rate of CO,  mmol/min
FD0 = 0; % molar feed rate of H2, mmol/min
FE0 = 0.001; % molar feed rate of water, mmol/min
% reactor parameters
Ptot = 1.1;  % total pressure, bar
W   = 250;   % total weight of catalyst in the reactor, mg
UA = 0.1;    % heat transfer coefficient, J/min-mg-K
Tw = 700;    % wall temperature, C
% kinetic parameters
% x1 (y(1)) is molar flow extent for DRM
% x2 (y(2)) is molar flow extent for RWGS
% y(3) is total mixture enthalpy
% y(4) is reactor T
Tref = 700;  % reference temperture for kinetics, C
Ea = 250;    % activation energy for DRM, kJ/mol
k1 = 1.4e-02; % rate coefficient for DRM at Tref, mmol/min-mgbar^1.1
mA = 0.6; mB = 0.7; mC = -0.1; % rxn orders for CH4, CO2, and CO
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%\\

% convert temperatures to K
T0 = T0+273;
Tw = Tw+273;
Tref = Tref+273;

% molar feed rates of all 5 components, mmol/min
% [CH4 CO2 CO H2 H2O]
F0 = [FA0 FB0 FC0 FD0 FE0];

model.F0 = F0;
model.Ptot = Ptot;
model.UA = UA;
model.Tw = Tw;
model.isothermal = isothermal;
model.Tref = Tref;
model.Ea = Ea;
model.k1 = k1;
model.m = [mA mB mC];

% put odefun in the correct format for ode15i
odefun = @(t,y,yp) reactor_ode(y,yp,model);
% initial conditions
```

```
% we have to specify one initial condition for each differential equation
% since we have two differential equations (for x1 and Hdot) we need to
% specify two initial conditions (x1 and T)
% specify y0(1) = 0 (initial x1) and y0(4) = T0 (initial T)
% the other components of y0 and yp0 are set by decic, but we still have to
% pass guess values (so we use guess values of zero)
% y0_fix and yp0_fix tell decic which components of y0 and yp0 are held
% fixed and which are varied to satisfy odefun(t,y0,yp0) = 0
y0  = [0; 0; 0; T0]; y0_fix  = [1; 0; 0; 1];
yp0 = [0; 0; 0; 0];  yp0_fix = [0; 0; 0; 0];
[y0,yp0] = decic(odefun, 0, y0, y0_fix, yp0, yp0_fix);

% solve ODE
% ode15i requires the first argument to be a function odefun(t,y,yp)
% here, we define @(t,y,yp) odefun(y,yp,F0) as an anonymous function
sol = ode15i(odefun, [0,W], y0, yp0);

% plot conversion, selectivity, and T vs. fractional bed length (z)
clf
hold on
xlabel('fractional bed length')
yyaxis left % plot on the left y-axis
ylabel('conversion / selectivity')
% extent of reaction (DRM), mmol/min
x1 = @(z) deval(sol,W*z,1).';
% extent of reaction (RWGS), mmol/min
x2 = @(z) deval(sol,W*z,2).';
% temperature, K
T = @(z) deval(sol,W*z,4).';
warning off MATLAB:fplot:NotVectorized
% plot CH4 conversion = x1/FA0
fplot(@(z) x1(z)/FA0, [0 1])
% plot H2 selectivity = (2*x1 - x2)/(2*x1)
fplot(@(z) (2*x1(z)-x2(z))/(2*x1(z)), [0 1])
ylim([0,1])
yyaxis right % plot on the right y-axis
ylabel('Temperature [C]')
% plot temperature in C
fplot(@(z) T(z)-273, [0 1])
if isothermal
    ylim([T0-50, T0+50]-273)
end
hold off
legend({'CH4 conversion','H2 selectivity','T'},'location','south')
```

```
function f = reactor_ode(y, yp, model)

isothermal = model.isothermal;
```

```
F0 = model.F0;
Ptot = model.Ptot;
UA = model.UA;
Tw = model.Tw;
Ea = model.Ea;
k1 = model.k1;
Tref = model.Tref;
m = model.m;
mA = m(1); mB = m(2); mC = m(3);

R = 8.314e-3;   % gas constant, kJ/mol-K

% stoichimetric coefficients nu_ij
% row is rxn, col is species
% rxn 1 (DRM):  CH4 + CO2 <=> 2 CO + 2 H2
% rxn 2 (RWGS): CO2 + H2 <=> CO + H2O
nu = [-1 -1 2 2 0; 0 -1 1 -1 1];

A1 = k1/exp(-Ea/(R*Tref)); % pre-exponential factor for DRM, mmol/min-mg

% extract dependent variables from y
x = y(1:2);  % [x1,x2], mmol/min
Hdot = y(3); % J/min
T = y(4);    % K

% compute molar flow rates of all 5 species from the extent of rxn
F = F0 + x.'*nu; % F is a row vector, mmol/min
% compute partial pressures of all 5 species, bar
P = Ptot * F/sum(F);
% compute enthalpy, J/mmol
[h,g] = thermo(T);
% compute the free energy
DeltaG = nu*g.';
% compute the equilibrium constant of the two reactions
K = exp(-DeltaG/(R*T));
% rate of DRM, mmol/min-mg (dx1/dW)
% K(1) = 38.2
% K(2) = 1.71
r1 = A1*exp(-Ea/(R*T))*P(1)^mA*P(2)^mB*P(3)^mC* (1 - (P(3)^1.9*P(4)^2)/(K(1)*P(1)^-
0.4*P(2)^-0.3) );
% equilibrium constraint for RWGS
g2 = K(2)*P(2)*P(4) - P(3)*P(5);

% qdot: rate of heat flow through reactor walls, J/min-mg (dHdot/dW)
% gT:   constraint relating enthalpy to temperature, J/min
if isothermal
    qdot = 0;
    gT = F0*h.' - Hdot;
else
    qdot = UA*(Tw-T);
    gT = F*h.' - Hdot;
end

% compute F(y,yp)
% for differential equations: F(y,yp) = fp(y) - yp
```

```
% for algebraic equations:    F(y,yp) = g(y)
f = [r1-yp(1); g2; qdot-yp(3); gT];

end



% compute molar enthalpies of components at temperature T
% in units of kJ/mol or J/mmol

function [h,g,s] = thermo(T)

x = T/1000;

A = [ -0.703029       24.99735     25.56759     33.066178     30.092    ];
B = [108.4773  55.18696      6.09613    -11.363417      6.832514 ];
C = [-42.52157       -33.69137      4.054656    11.432816      6.793435 ];
D = [  5.862788        7.948387    -2.671301    -2.772874     -2.53448  ];
E = [  0.678565       -0.136638     0.131021    -0.158558      0.082139 ];
F = [-76.84376      -403.6075    -118.0089      -9.980797   -250.881    ];
G = [158.7163228.2431     227.3665     172.707974   223.3967 ];

h = A*x + B*x^2/2 + C*x^3/3 + D*x^4/4 - E/x + F;
s = A*log(x) + B*x + C *x^2/2 + D*x^3/3 - E/(2*x^2) + G;
g = h - x*s;

end
```

(1) Jiang, C.; Akkullu, M. R.; Li, B.; Davila, J. C.; Janik, M. J.; Dooley, K. M. Rapid screening of ternary rare-earth – Transition metal catalysts for dry reforming of methane and characterization of final structures. *Journal of Catalysis* **2019**, *377*, 332-342. DOI: https://doi.org/10.1016/j.jcat.2019.07.020.
(2) *All equlibrium calculations performed using Aspen, HYSYS REQUIL subprogram*; 2019.