

Supplementary Information

The Interplay of Kinetics and Thermodynamics in the Catalytic Steam Methane Reforming
over Ni/MgO-SiO₂

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- I. The reversibility of the water-gas shift reaction was accounted for by using the equilibrium relation.

$$K_4 = \frac{k_{4+}}{k_{4-}} = \frac{K_S}{K_2} \quad \text{Eq. S1}$$

The rate expression of the methane steam reaction is not altered.

$$r_3 = \frac{k_3 K_1 K_2 z C_{tot} P_{CH_4} P_{H_2O}}{(1 + K_1 P_{CH_4} + K_2 P_{H_2O})^2} = \frac{k'_3 K_1 K_2 P_{CH_4} P_{H_2O}}{(1 + K_1 P_{CH_4} + K_2 P_{H_2O})^2} \quad \text{Eq. S2}$$

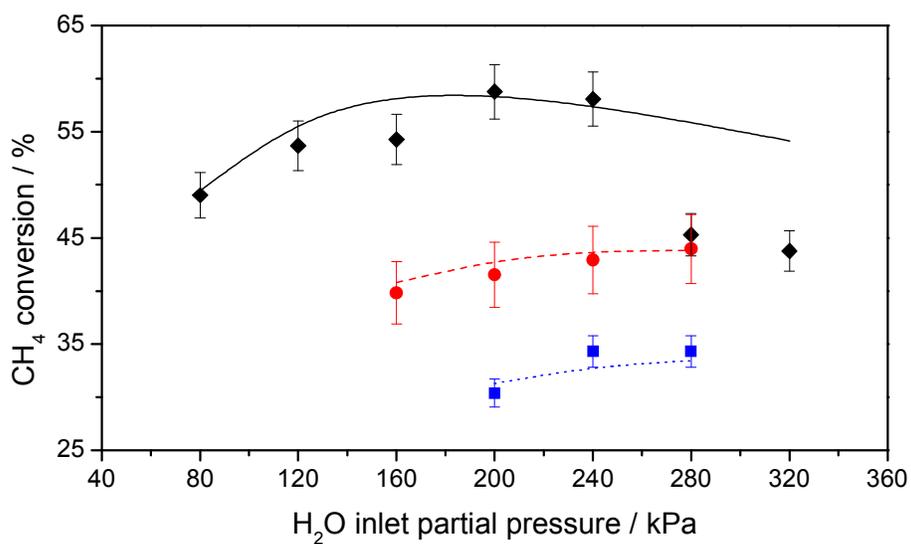
The rate expression for the water-gas shift reaction is altered by addition of the back-reaction term.

$$r_4 = \frac{k_{4+} K_2 C_{tot} \left(P_{CO} P_{H_2O} - \frac{P_{CO_2} P_{H_2}}{K_S} \right)}{1 + K_1 P_{CH_4} + K_2 P_{H_2O}} = \frac{k'_{4+} K_2 \left(P_{CO} P_{H_2O} - \frac{P_{CO_2} P_{H_2}}{K_S} \right)}{1 + K_1 P_{CH_4} + K_2 P_{H_2O}} \quad \text{Eq. S3}$$

In order to solve the plug flow reactor model, , the rate expressions are substituted in the net rate of formation R_i for each component (Eq. 22-26).

The results are presented in the following pages, as comparisons of the simple model presented in the main text and the simple model with the reverse water-gas shift incorporated. As will be seen, there is little difference between the models.

Simple model



Simple model with reverse water-gas shift.

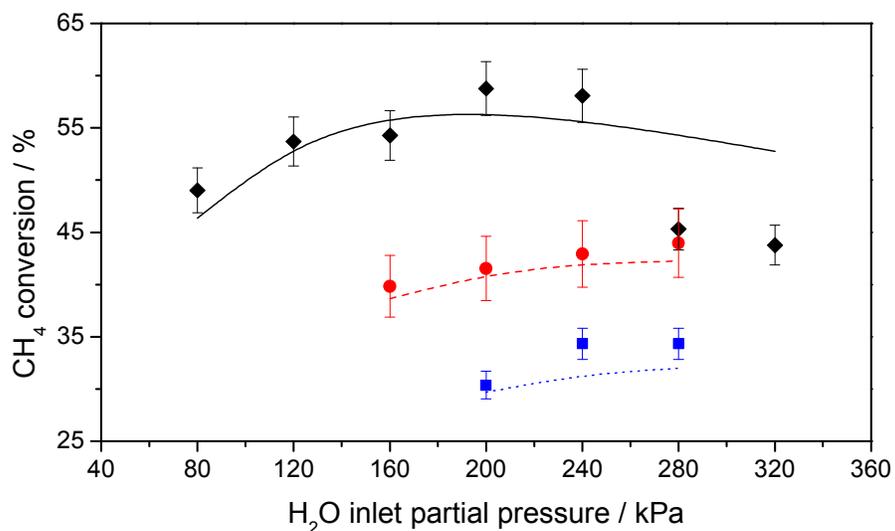


Fig. S1. CH₄ conversion as a function of the H₂O inlet pressure at a total pressure of 0.40 MPa and 923 K. Points: experimentally observed, lines: calculated by solving the set of Eqs. 8 with the net rates of formation given by Eqs. 22 to 26. The rate and equilibrium coefficients are estimated by a weighted regression and are shown in Table 2. ♦, full line, black - 40 kPa CH₄ inlet partial pressure ($p_{\text{CH}_4}^0$) or a space time of 3.36 kg s mol⁻¹, ●, dashed line, red - 80 kPa $p_{\text{CH}_4}^0$ or 1.68 kg s mol⁻¹, ■, dotted line, blue - 120 kPa $p_{\text{CH}_4}^0$ or 1.12 kg s mol⁻¹.

Simple model.

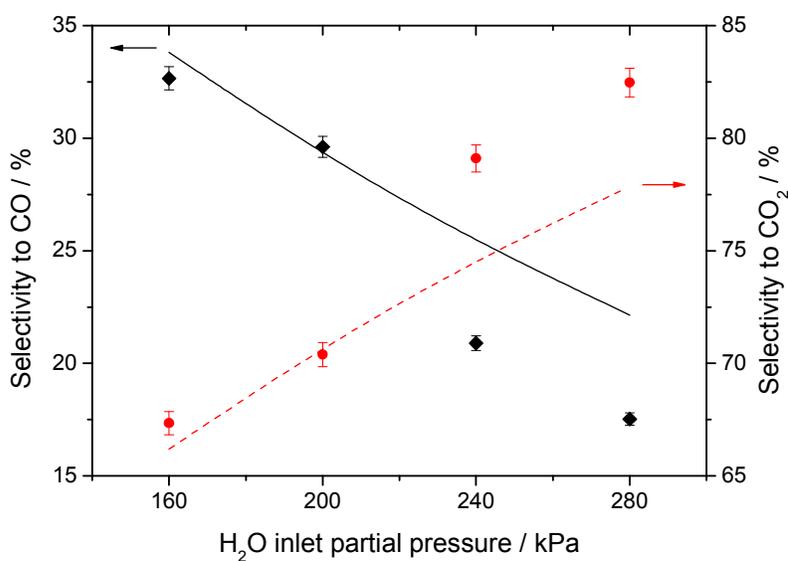
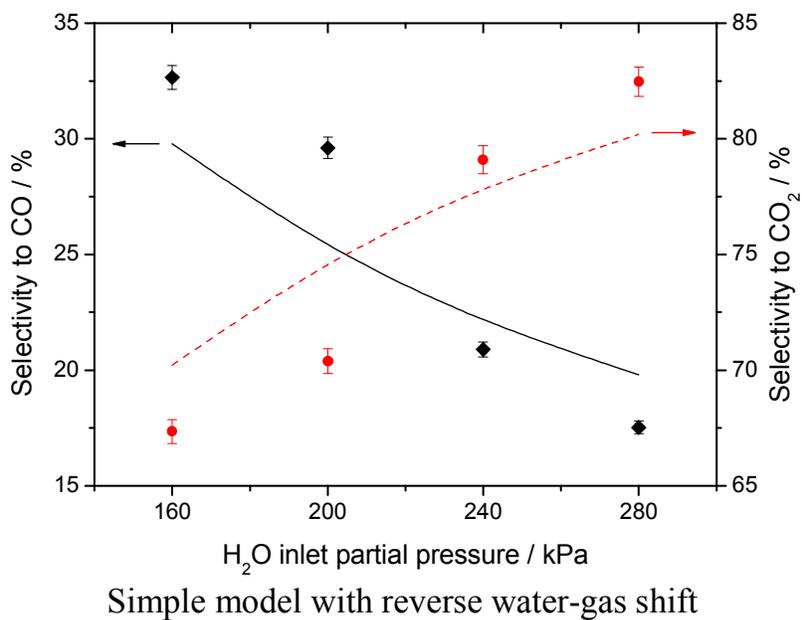
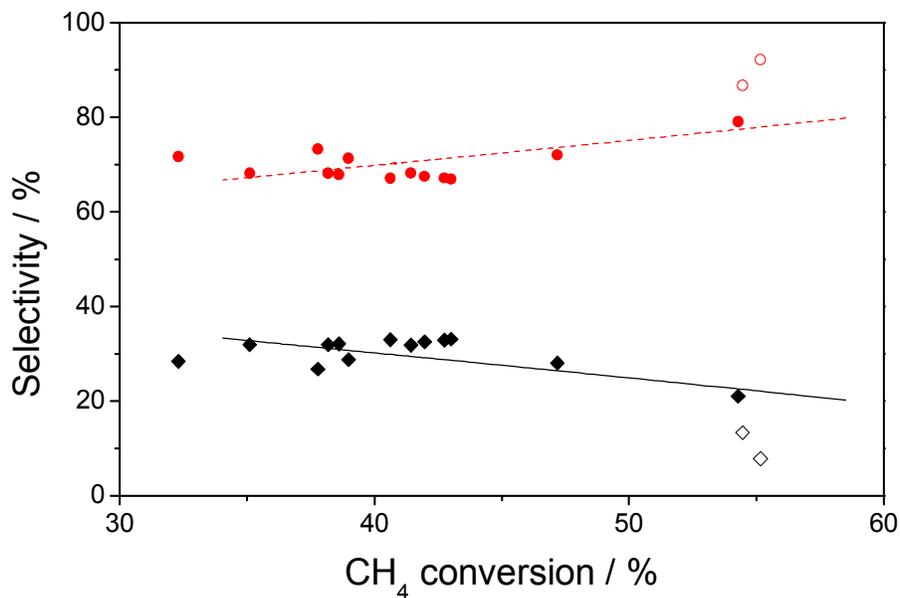


Fig. S2. Selectivity to CO and CO₂ as a function of the inlet partial pressure of H₂O at a total pressure of 0.4 MPa, a temperature of 923 K, a space time of 1.44 kg s mol⁻¹ and conversions between 40 % and 44 %. Points: experimentally observed, lines: calculated by solving the set of Eqs. 8 with the net rates of formation given by Eqs. 22 to 26. The rate and equilibrium coefficients are estimated by a weighted regression and are shown in Table 2. ♦, full line, black - selectivity to CO, ●, dashed line, red - selectivity to CO₂.



Simple model with reverse water-gas shift

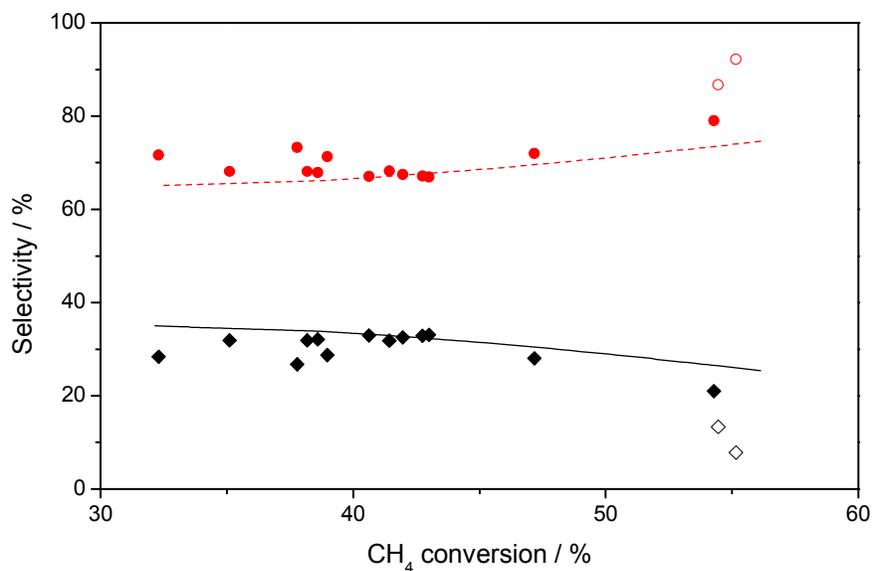


Fig. S3. Selectivity to CO and CO₂ as a function of the conversion at a total pressure of 0.40 MPa, a temperature of 923 K, a catalyst mass of 0.1 g, a H₂O inlet partial pressure of 160 kPa and a CH₄ inlet partial pressure between 20 and 100 kPa. Points: experimentally observed, lines: calculated by solving the set of Eqs. 8 with the net rates of formation given by Eqs. 22 to 26. The rate and equilibrium coefficients are estimated by a weighted regression and are shown in Table 2. ♦, full line, black - selectivity to CO, ●, dashed line, red - selectivity to CO₂.

II) Calculation of lack of heat transfer limitations

Mears Criterion

$$\left| \frac{-\Delta H r d}{h T} \cdot \frac{E}{R T} \right| < 0.15$$

ΔH : Heat of the reaction [J/mol] r : reaction rate [mol/s m³]

d : distance between tubes [m] h : heat transfer coefficient [J/m² K s]

T : temperature [K] E : activation energy [J/mol]

R : gas constant [J/mol K]

$\Delta H = -2.04 \times 10^5$ J/mol (reaction heat of SMR)

$r = 5.77 \times 10^{-3}$ mol/s m³ (catalyst bed) or 0.879 mol/s m³ (catalyst particle)

$d = (ID_{\text{quartz}} - OD_{\text{alumina}})/2 = 2.5 \times 10^{-3}$ m

$h = 770$ J/m² K s (calculation is described later)

$T = 923$ K

$E = 1.5 \times 10^5$ J/mol

As the mean value of following reported values

Xu-Froment(1989)¹ 240 kJ/mol

Yang(2015): 134 kJ/mol (ref. 18 of MS)

Numaguchi(1988)² 107 kJ/mol

Saito(2015)³ 99.1 kJ/mol

Hughes(2001)⁴ 209 kJ/mol

$R = 8.31$ J/mol K

$$\left| \frac{-\Delta H r d}{h T} \cdot \frac{E}{R T} \right| = \frac{2.04 \cdot 5.77 \cdot 2.5}{770 \cdot 923} \cdot \frac{1.5}{8.31 \cdot 923} \times 10^4 = 8.1 \times 10^{-5}$$

The criterion is calculated to be 8.1×10^{-5} , which is much lower than 0.15 thus the heat transfer can be ignored.

Details of calculations:

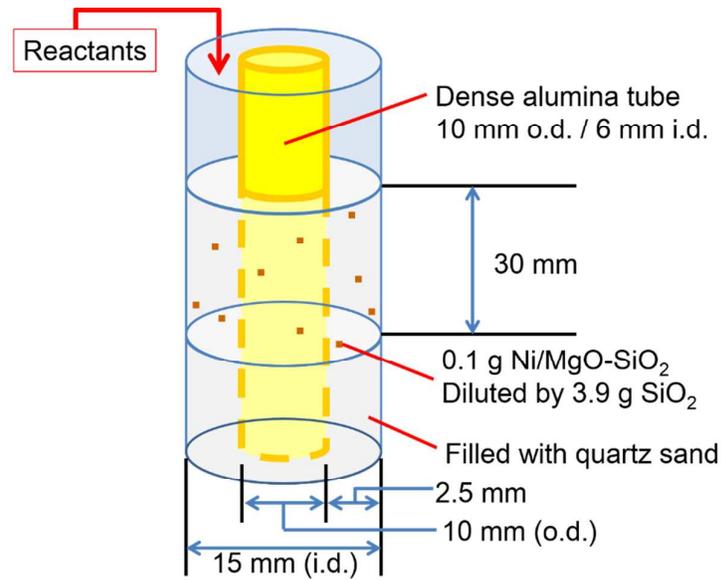


Fig. 1 Reactor used in the steam methane reforming studies

CH₄ consumption rate 1.69×10^{-5} mol / s

Catalyst weight 0.0001 kg

Catalyst bed volume 2.95×10^{-6} m³

Catalyst density 5200 kg/m³

Total Pressure 0.40 MPa

Profile of flow(outlet flow)

Pressure: 0.4 MPa, Temperature: 923 K,

Total mole flow: 309 μmol/s (452 Ncm³/min)

F_{CH₄}: 11.8 μmol/s F_{H₂}: 68.7 μmol/s F_{CO₂}: 13.5 μmol/s

F_{CO}: 3.32 μmol/s F_{H₂O}: 102 μmol/s F_{N₂}: 109 μmol/s

Calculation of h

$$h = J_h C_{pf} G_f (Pr_f)^{-2/3} = \frac{18.1 \mu_f}{\rho_f u d} C_{pf} G_f \left(\frac{k_{tf}}{\mu_f C_{pf}} \right)^{2/3}$$

μ_f : viscosity of flow [Kg/m s]

ρ_f : density of flow [kg/m³]

u : linear velocity [m/s]

d : specific length

C_{pf} : specific heat of flow [J/kg K]

G_f : mass velocity [kg/m² s]

$$\mu_f = 3.14 \times 10^{-5} \text{ Kg / m s}$$

$$\rho_f = 0.0191 [\text{kg/mol}] / (8.31 [\text{J / K mol}] \times 923 [\text{K}] / 4 \times 10^5 [\text{Pa}]) = 1.00 \text{ kg / m}^3$$

$$u = 452 [\text{Ncm}^3/\text{min}] / 60 [\text{s/min}] / ((0.75^2 - 0.5^2) \pi [\text{cm}^2]) / 100 [\text{cm/m}] / (0.4/0.1) [\text{Ncm}^3/\text{cm}^3] \\ = 0.019 \text{ m / s}$$

$$d = 0.0025 \text{ m}$$

$$C_{pf} = 1917 \text{ J / kg K}$$

$$G_f = u \times \rho_f = 0.019 [\text{m/s}] \times 1.00 [\text{kg/m}^3] = 0.019 \text{ kg / m}^2 \text{ s}$$

$$h = 18.1 \times 3.14 \times 10^{-5} / (1.00 \times 0.019 \times 0.0025) \times 1917 \times 0.019 \times \\ (0.141 / (3.14 \times 10^{-5} \times 1917))^{2/3} = 770 \text{ J / m}^2 \text{ s K}$$

Gas properties are shown in Table A2. The values of k at 650 °C was calculated as

$$k(\text{total}, 650^\circ\text{C}) = k(\text{total}, 100^\circ\text{C}) \times [k(\text{air}, 100^\circ\text{C})/k(\text{air}, 650^\circ\text{C})]$$

and C_p at 650°C was calculated in the same manner. The values of $k(\text{air}, 650^\circ\text{C})$ and $C_p(\text{air}, 650^\circ\text{C})$ was obtained from Fig. S4a and S4b respectively.

Table S1. of gas properties

	$k(100^\circ\text{C})$ [J / m s K] ⁵	$C_p(100^\circ\text{C})$ [J / kg K] ⁶	M [kg / mol]	$C_p'(100^\circ\text{C})$ [J / mol K]	$\mu(600^\circ\text{C})$ [kg / m s] ⁷
CH ₄	0.0500	2449	0.016	39.2	2.53 x 10 ⁻⁵
H ₂	0.214	14486	0.002	29.0	1.84 x 10 ⁻⁵
CO ₂	0.0222	921	0.044	40.5	3.74 x 10 ⁻⁵
CO	0.0305	1047	0.028	29.3	3.86 x 10 ⁻⁵
H ₂ O	0.0241	2098	0.018	37.8	3.26 x 10 ⁻⁵
N ₂	0.0313	1043	0.028	29.2	3.82 x 10 ⁻⁵
Total	0.0699	1717	0.0191	32.7	3.14 x 10 ⁻⁵
Total(650°C)	0.141	1917	-	36.7	-

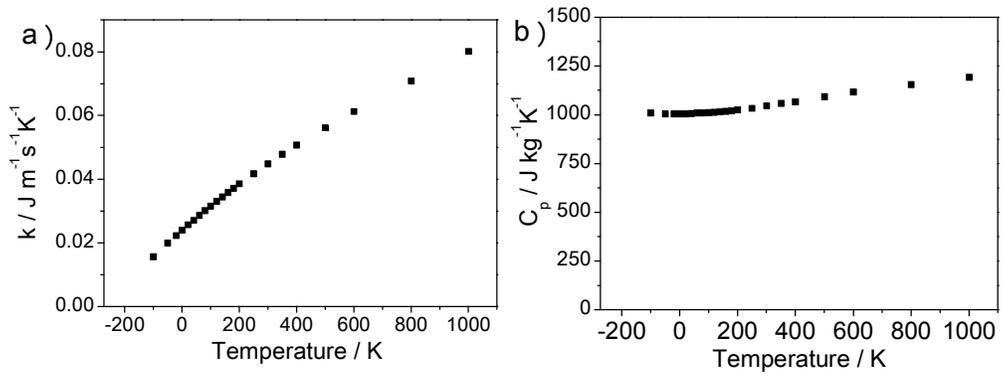


Fig. S4. a) The temperature dependency of thermal conductivity of air⁵
b) The temperature dependency of specific heat of air⁶

¹ Xu, J.; Froment, G.F. Methane steam reforming, methanation and water-gas shift: I. intrinsic kinetics. *AIChE J.* **1989**, 35, 88.

² Numaguchi, T.; Kikuchi, K. Intrinsic kinetics and design simulation in a complex reaction network: steam-methane reforming. *Chem. Eng. Sci.* **1988**, 43, 2295.

³ Saito, M.; Kojima, J.; Iwai, H.; Yoshida, H. The limiting process in steam methane reforming with gas diffusion into a porous catalytic wall in a flow reactor. *Int. J. Hydrogen Energy* **2015**, 40, 8844.

⁴ Hou, K.; Hughes, R. The kinetics of methane steam reforming over a Ni/ α -Al₂O₃ catalyst. *Chem. Eng. J.* **2001**, 82, 311.

⁵ <http://wikitech.info/1471>

⁶ <http://www.hakko.co.jp/qa/qakit/html/h01040.htm>

⁷ http://www.engineeringtoolbox.com/gases-absolute-dynamic-viscosity-d_1888.html