

Supporting Information

Kinetic and *in-situ* FTIR study of CO methanation on a Rh/Al₂O₃ catalyst.

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S1. Effect of CO pressure on forward turnover formation rate of CH₄.

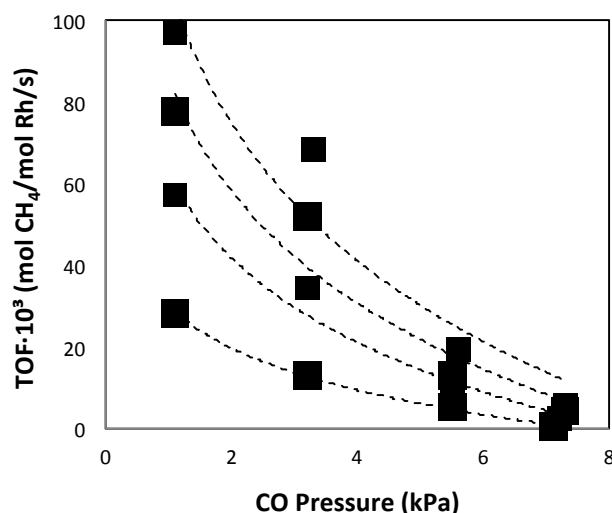


Figure S1. Forward turnover formation rate of CH₄ on Rh/Al₂O₃ as a function of CO pressures at 300°C. P_{H₂} (0 – 22.5 kPa), P_{H₂}: (◆) 5.8 kPa, (●) 11.0 kPa, (◻) 16.0 kPa, (◼) 21.5 kPa. Space velocity: 4 – 10 cm³·s⁻¹·g_{cat}⁻¹.

S2. Derivation for Langmuir-Hinshelwood rate expressions.

The symbols \rightleftharpoons , \rightarrow and \rightleftharpoons represent the quasi-equilibrated, irreversible and reversible steps, respectively.

The CO and H₂ adsorptions have been assumed as quasi-equilibrated steps Scheme 1, steps 1 and 2), therefore the CO* and H* are calculated by Equations S1 and S2, where θ_* represents the fractional concentration of vacancies.

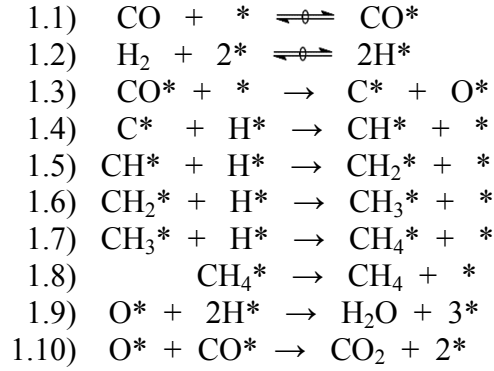
$$\theta_{CO^*} = K_{CO} \cdot P_{CO} \cdot \theta_* \quad (\text{Eq.S1})$$

$$\theta_{H^*} = K_{H_2}^{0.5} \cdot P_{H_2}^{0.5} \cdot \theta_* \quad (\text{Eq.S2})$$

K_{H_2} and K_{CO} represent the equilibrium constants for the molecular CO adsorption and the dissociative H_2 adsorption, respectively.

S.2.1. Unassisted C-O bond dissociation mechanism.

Scheme 1



Since the reaction rates for the steps 1.3 and 1.8 are equal at steady state condition, the methane formation rate can be calculated as:

$$r_{CH_4} = k_{1.3} \cdot \theta_{CO^*} \cdot \theta_* \quad (\text{Eq.S3})$$

For a site balance with vacancy, H^* and CO^* as MASI,

$$\theta_* = \frac{1}{(1 + K_{H_2}^{0.5} P_{H_2}^{0.5} + K_{CO} P_{CO})}$$

(Eq.S4)

Substituting Eqs.S1, S2 and S4 into Eq.S3 leads to Eq.5 in the manuscript.

$$r_{CH_4} = \frac{k P_{CO}}{(1 + K_{H_2}^{0.5} P_{H_2}^{0.5} + K_{CO} P_{CO})^2} \quad (5)$$

For a site balance with vacancy and CO^* as MASI,

$$\theta_* = \frac{1}{(1 + K_{CO} P_{CO})}$$

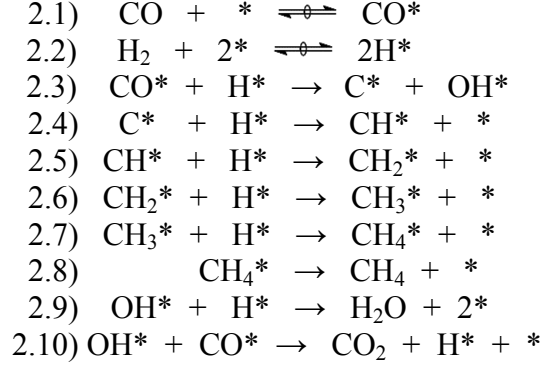
(Eq.S5)

Substituting Eqs.S1, S2 and S5 into Eq.S3 leads to Eq.6 in the manuscript.

$$r_{CH_4} = \frac{kP_{CO}}{(1 + K_{CO}P_{CO})^2} \quad (6)$$

S.2.2. C-O bond dissociates after first H* addition.

Scheme 2.



At steady state conditions Eq.S6 determines the methane formation rate:

$$r_{CH_4} = k_{2.3} \cdot \theta_{CO^*} \cdot \theta_{H^*} \quad (\text{Eq.S6})$$

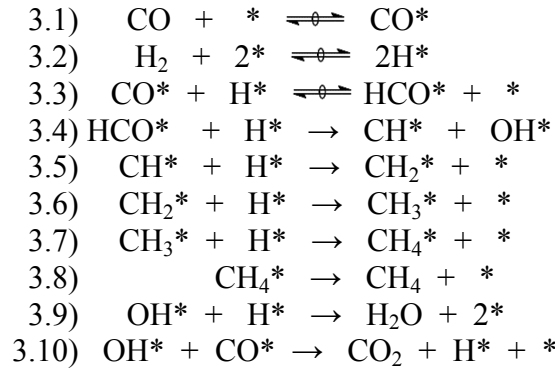
In-situ FTIR measurements are consistent with the site balance represented by Eq.S5;

Therefore, substituting Eqs.S1, S2 and S5 into Eq.S6 leads to Eq.7 in the manuscript.

$$r_{CH_4} = \frac{k_{2.3} K_{CO} K_{H_2}^{0.5} P_{CO} P_{H_2}^{0.5}}{(1 + K_{CO} P_{CO})^2} = \frac{\alpha_2 \cdot P_{CO} P_{H_2}^{0.5}}{(1 + K_{CO} P_{CO})^2} \quad (7)$$

S.2.3. C-O bond dissociates after the second H* addition.

Scheme 3.



At steady state conditions Eq.S7 represents the methane formation rate:

$$r_{CH_4} = k_{3.4} \cdot \theta_{HCO^*} \cdot \theta_{H^*} \quad (\text{Eq.S7})$$

Substituting Eqs.S1, S2 and S5 into Eq.S7 leads to Eq.8 in the manuscript.

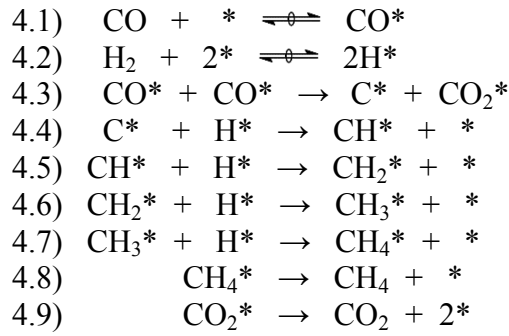
$$r_{CH_4} = \frac{k_{3.4} K_{HCO} K_{CO} K_{H_2} P_{CO} P_{H_2}}{(1 + K_{CO} P_{CO})^2} = \frac{\alpha_3 \cdot P_{CO} P_{H_2}}{(1 + K_{CO} P_{CO})^2} \quad (8)$$

K_{HCO} represents the equilibrium constants for the surface reaction of HCO* formation.

S.2.4. The CO disproportionation mechanism.

This could be considered as a particular case of the direct (unassisted) CO dissociation mechanism (Scheme 1), in which the reaction rate is determined by the combination of two CO* species to form C* and CO₂.

Scheme 4.



At steady state conditions, the methane formation rate is defined by the rate of C* formation in the disproportionation step (4.3):

$$r_{CH_4} = k_{4.3} \cdot \theta_{CO^*}^2 \quad (\text{Eq.S8})$$

Substituting Eqs.S1 and S5 into Eq.S8 leads to Eq.S9.

$$r_{CH_4} = \frac{k_{4.3} \cdot P_{CO}^2}{(1 + K_{CO} P_{CO})^2} \quad (\text{Eq.S9})$$

This kinetic model does not properly represent the kinetic data reported in the manuscript because neither contain the positive effect of H₂ pressure on reaction rate nor is consistent with the negative effect of CO pressure on methane formation rate.