

Supplementary Information for:

The Consequences of Surface Heterogeneity of Cobalt Nanoparticles on the Kinetics of CO Methanation.

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S.1. Particle size distribution of cobalt clusters for each catalyst

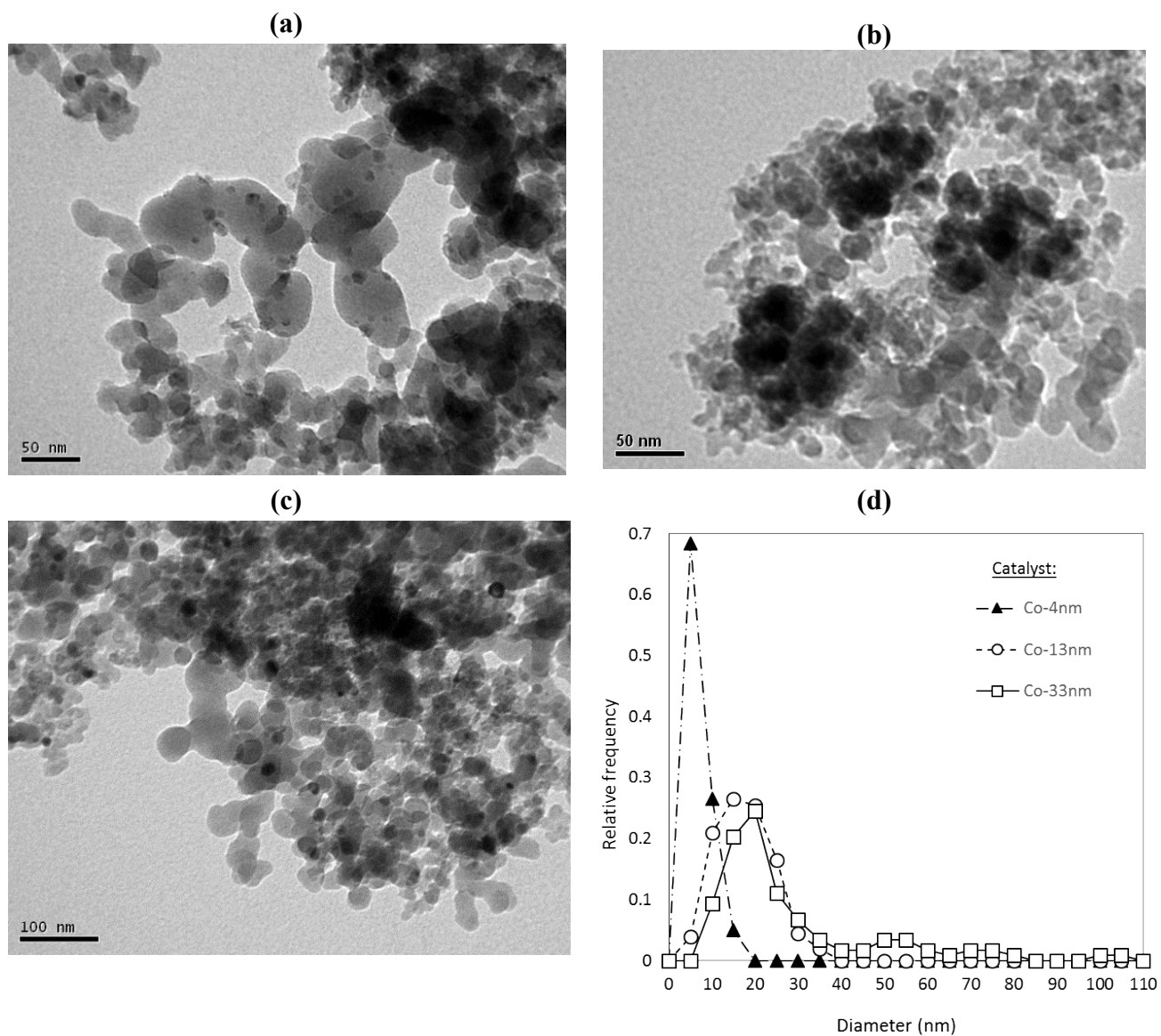


Figure S₁. TEM micrographs of catalysts: (a) Co-4nm, (b) Co-13nm, (c) Co-33nm; (d) distribution of Co particle size for Co-4nm, Co-13nm and Co-33nm catalysts.

S.2. Operando-FTIR measurements for CO saturation on Co-4 nm.

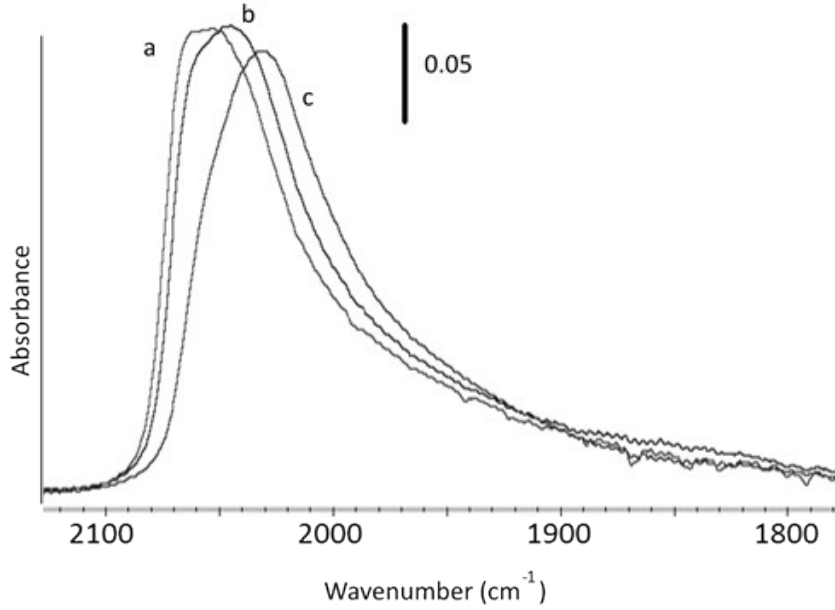


Figure S₂: In-situ FTIR signal for the linearly adsorbed CO on Co-4nm catalyst. Effect of temperature at 3kPaCO-18kPaH₂ (a) 120°C, (b) 150°C, (c) 200°C

S.3. Temkin's model for non-dissociative adsorption:

The mathematical formalism of the Temkin's model for the adsorption of a gas on an intrinsic non uniform surface can be developed applying the Integral Equation approach.

If a continuous distribution of N sites with different properties it assumed, the coverage of a specie adsorbed in a heterogeneous surface can be calculated as:

$$\theta_{total} = \int \frac{K(Q_{CO}) P_{CO}}{1 + K(Q_{CO}) P_{CO}} \times \frac{dN}{N} \quad (S.1)$$

The distribution of dN/N depends in the characteristics of the surface. The Temkin's model assumes that the distribution of the sites can be correlated with the heat of adsorption of the adsorbed species as it follows:

$$\frac{dN}{N} = \frac{dQ_{CO}}{\Delta Q_{CO}} \quad (S.2)$$

Considering, $\Delta Q_{CO} = Q_0 - Q_1$ and $\int_{Q_1}^{Q_0} \frac{dQ_{CO}}{\Delta Q_{CO}} = 1$, where Q_0 and Q_1 are the heats of adsorption of CO at low and high coverage, respectively.

As it had been considered in previous studies [1-4], it can be assumed that the adsorbed species are immobile. Therefore, the adsorption coefficient is provided by the statistical thermodynamics assuming the loss of three degrees of translation:

$$K(\theta) = \frac{h^3}{(2\pi m)^{3/2}} \frac{1}{(kT)^{5/2}} \exp\left(\frac{Q(\theta)}{RT}\right) \quad (\text{S.3})$$

For a non-dissociative adsorption, the generalized expression of the Temkin's model is:

$$\theta_{total} = \int_{Q_1}^{Q_0} \frac{K(Q_{CO}) P_{CO}}{1 + K(Q_{CO}) P_{CO}} \times \frac{dQ_{CO}}{\Delta Q_{CO}} \quad (\text{S.4})$$

The integration can be achieved using an auxiliary variable $V = K(Q_{CO}) P_{CO}$, thus:

$$dQ_{CO} = \frac{RT}{V} dV \quad (\text{S.5})$$

with R the ideal gas constant and T the temperature. Finally, the generalized expression of the Temkin's model is:

$$\theta_{total} = \int_{K(Q_1)P_{CO}}^{K(Q_0)P_{CO}} \frac{RT}{1+V} \times \frac{dV}{\Delta Q_{CO}} = \frac{RT}{\Delta Q} \ln\left(\frac{1 + K(Q_0)P_{CO}}{1 + K(Q_1)P_{CO}}\right) \quad (\text{S.6})$$

S.4. Effect of cobalt particle size on the CO consumption

The effect of cobalt particle size on the CO consumption turnover rate at 250, 280 and 300°C is shown below:

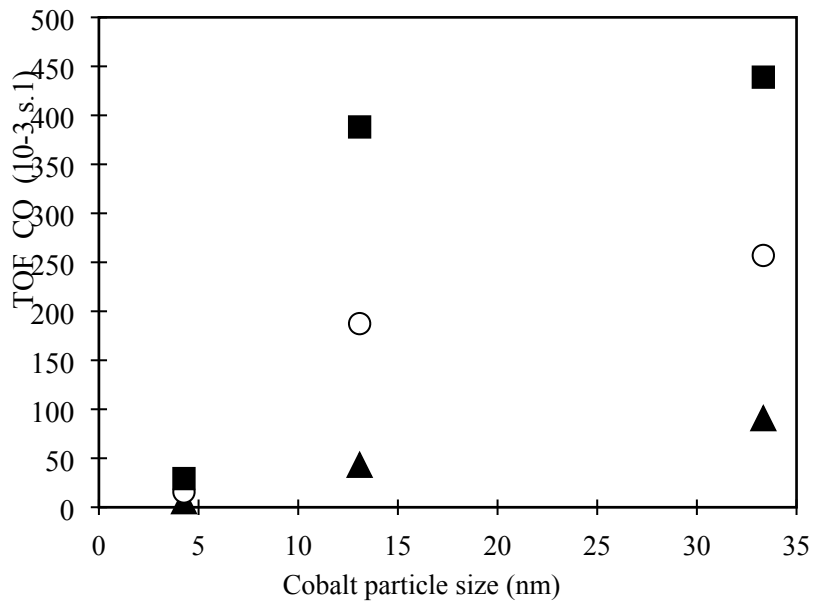


Figure S3: Turnover frequency reaction rate of CO hydrogenation as a function of the cobalt particle size at 1kPa CO-18kPa H₂ (□): 250°C, (○): 280°C and (■): 300°C.

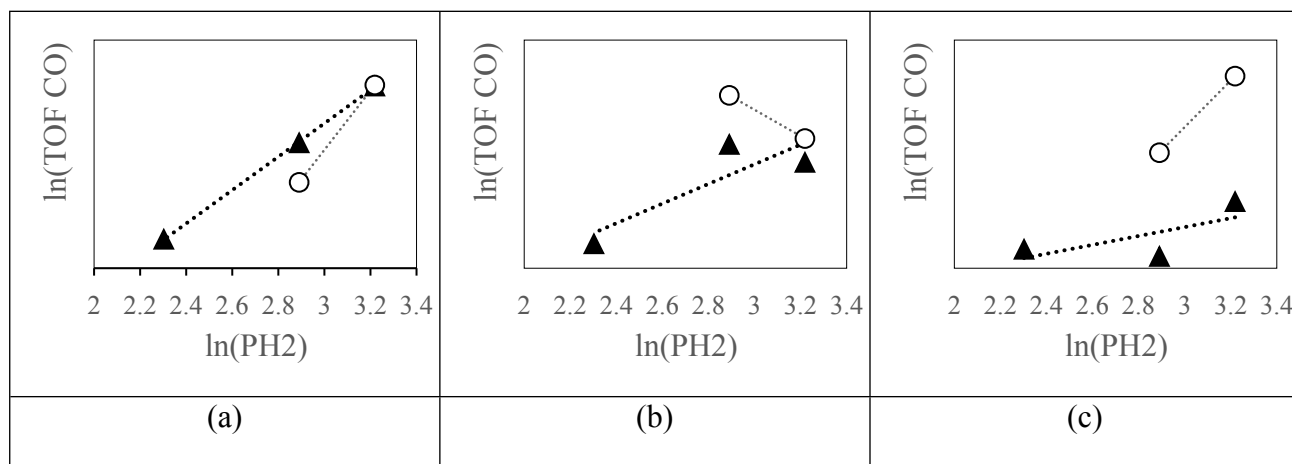


Figure S4: Effect of H₂ pressure at (□) 1kPa CO and (○) 2kPa CO on the TOF CO for (a) Co-4nm, (b) Co-13nm, (c) Co-33nm.

S.5. Experimental measurement of CO coverage at reaction conditions

In order to estimate the CO coverage on supported metallic cobalt catalysts at reaction conditions, the Adsorption Equilibrium Infrared Spectroscopy (AEIR) analytical method was applied using the equation S.7 in the FTIR measurements:

$$\theta_{CO}(T, p_{CO}) = \frac{A(T, P_{CO})}{A_M} \quad (S.7)$$

For the Co-33nm catalyst, the area under the peak of the adsorbed CO ($A(T, P_{CO})$) was measured at 250°C and 2kPa CO-18kPa H₂ (similar to reaction conditions). The A_M , i.e., the area of the adsorbed CO band (in absorbance mode) at full CO coverage was estimated from the infrared band at saturation conditions: 150°C y 2kPaCO-18kPa H₂. The coverage calculated was $\theta_{CO} = 0.7 ML$ based on the areas shown in the figure below.

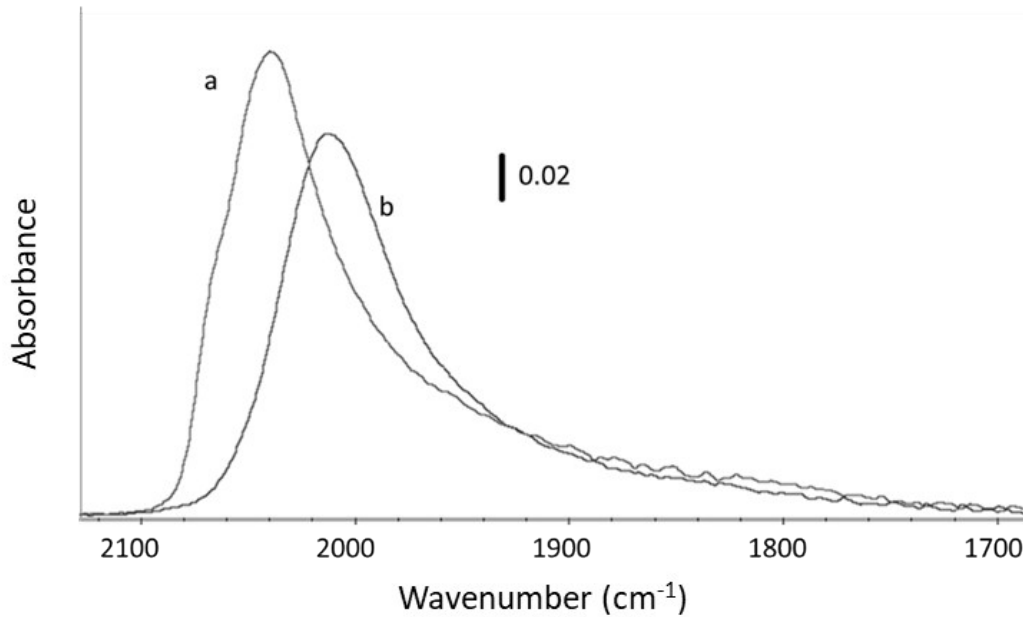


Figure S₅: Adsorbed CO band for Co-33nm catalyst at (a): CO saturation conditions, i.e. 2kPa CO-18kPa H₂ and 150°C, (b): 2kPa CO-18kPa H₂ and 250°C.

S.6. Langmuir kinetic model - first H-addition as the KRS

The figure below shows a parity plot for the CO consumption turnover rate adjusted to the Langmuir's kinetic model-first H-addition as the KRS.

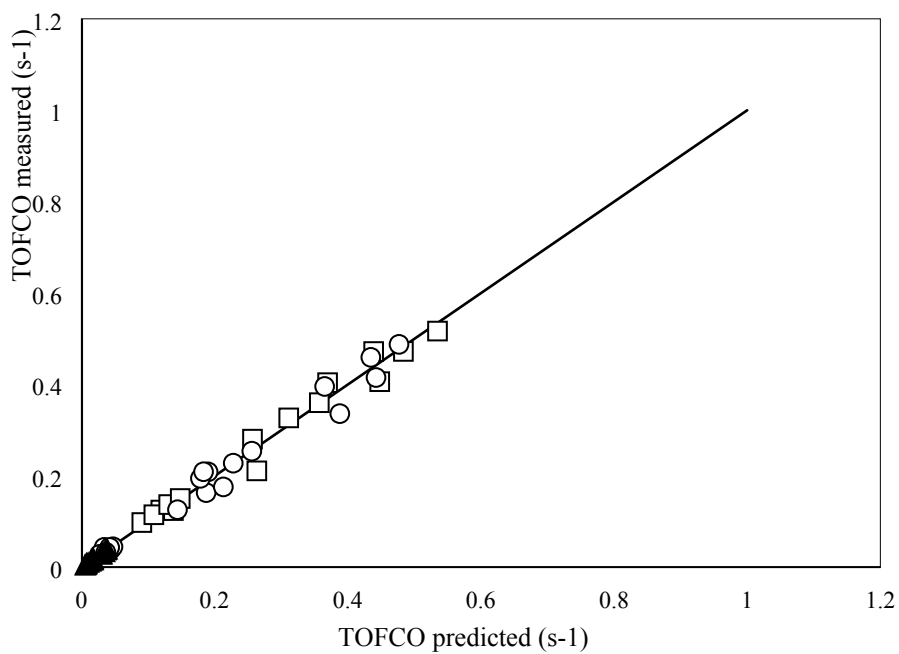


Figure S₆: Measured and predicted turnover rates by Langmuir's model (Eq. 6) for CO+H₂ reaction at 250-300°C on Co-4nm (■), Co-13nm (○), Co-33nm (□).

S.7. Temkin kinetic model - second H-addition as the KRS

The kinetic data was also fitted to a Temkin's model derived from the mechanism in which the first H* addition (step 3) is quasi-equilibrated and the second H* addition (step 4) is the KRS. This implies, the following kinetic model:

$$TOF_{CO} = \frac{\alpha P_{H_2}^{(RT)} (P_{CO}(K_{CO}^0 - K_{CO}^1))}{\Delta Q_{CO} (1 + K_{CO}^0 P_{CO})(1 + K_{CO}^1 P_{CO})} \quad (S.8)$$

The kinetic data of the cobalt catalysts were fitted to the equation S.8, getting the following parameters:

Table S₁: Parameters obtained from the fitting of kinetic data by Temkin's model (Equation S.8) at 250, 280 y 300°C, 1-2 kPa CO, 10-30 kPa H₂.

Parameter	Co-4nm	Co-13nm	Co-33nm
$\alpha(250^\circ C)$ [s ⁻¹ Pa ^{-0.5}]	5.44E-06	1.04E-05	1.91E-05
$\alpha(280^\circ C)$ [s ⁻¹ Pa ^{-0.5}]	9.61E-06	4.23E-05	8.15E-05
$\alpha(300^\circ C)$ [s ⁻¹ Pa ^{-0.5}]	1.71E-05	1.04E-04	3.14E-04
Q_0 [kJ·mol ⁻¹]	141	106	93.0
Q_1 [kJ·mol ⁻¹]	87	88	92.9
R ²	0.92	0.88	0.80
$E_\alpha = E_4 - Q_{H_2}$ [kJ mol ⁻¹]	56	114	137

For Co-33nm, the adjustment gives Q_{CO}(0)=Q_{CO}(1)=93 kJ/mol, which is inconsistently with the FTIR analysis, where a surface heterogeneity was found(Q_{CO}(0)>Q_{CO}(1)).

References

- [1] Couble, J. and D. Bianchi, *Heats of adsorption of linearly adsorbed CO species on Co²⁺ and Co⁰ sites of reduced Co/Al₂O₃ catalysts in relationship with the CO/H₂ reaction*. Applied Catalysis A: General, 2012. **445-446**: p. 1-13.
- [2] Couble, J. and D. Bianchi, *Experimental microkinetic approach of the CO/H₂ reaction on Pt/Al₂O₃ using the Temkin formalism. 2. Coverages of the adsorbed CO and hydrogen species during the reaction and rate of the CH₄ production*. Journal of Catalysis, 2017. **352**: p. 686-698.
- [3] Couble, J. and D. Bianchi, *Experimental microkinetic approach of the CO/H₂ reaction on Pt/Al₂O₃ using the Temkin formalism. 1. Competitive chemisorption between adsorbed CO and hydrogen species in the absence of reaction*. Journal of Catalysis, 2017. **352**: p. 672-685.

- [4] Derrouiche, S. and D. Bianchi, *Heats of adsorption of the linear and bridged CO species on a Ni/Al₂O₃ catalyst by using the AEIR method*. Applied Catalysis A: General, 2006. **313**(2): p. 208-217.