

Supporting Information

Thermokinetic and Spectroscopic Mapping of Carbon Monoxide Adsorption on Highly Dispersed Pt/ γ -Al₂O₃

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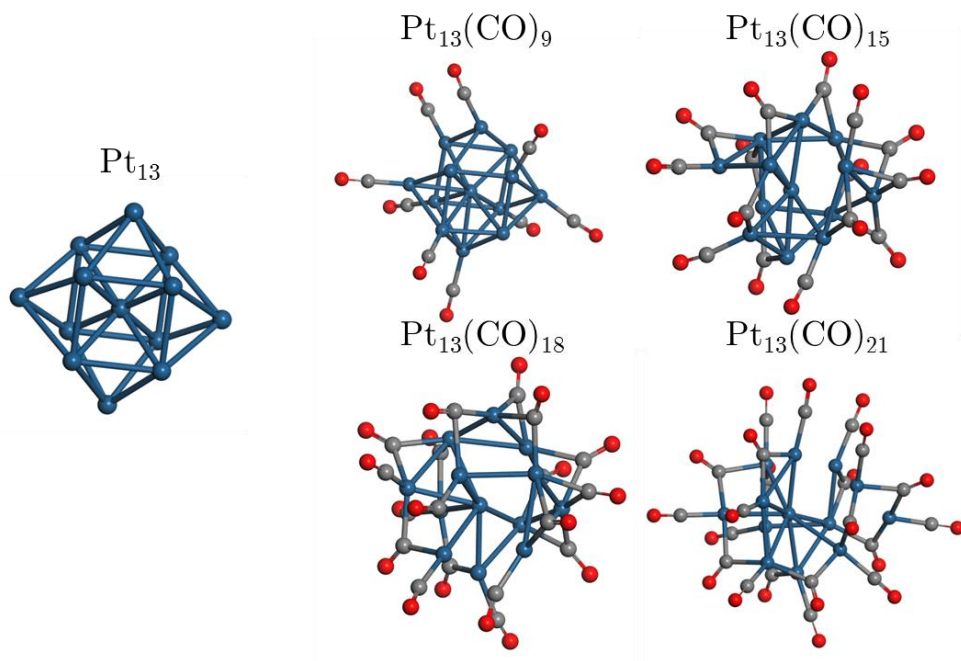


Figure S1. Illustrations of the non-supported Pt₁₃(CO)_m structures.

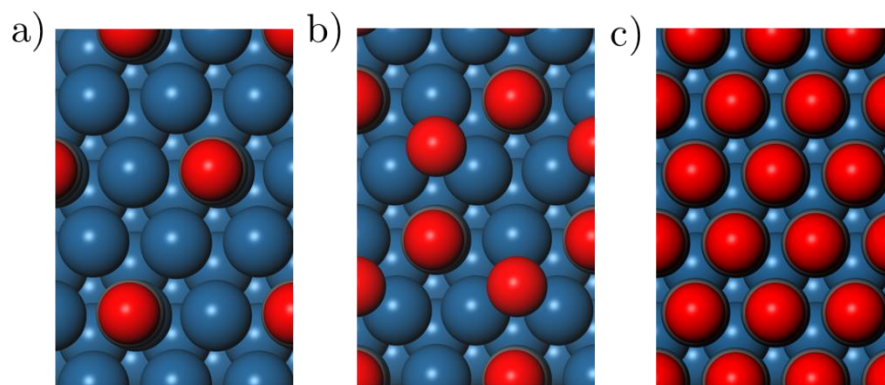


Figure S2. Illustrations of a) Pt(111)(CO)_{0.25ML}, b) Pt(111)O_{0.25ML}(CO)_{0.25ML} and c) Pt(111)(CO)_{1ML}.

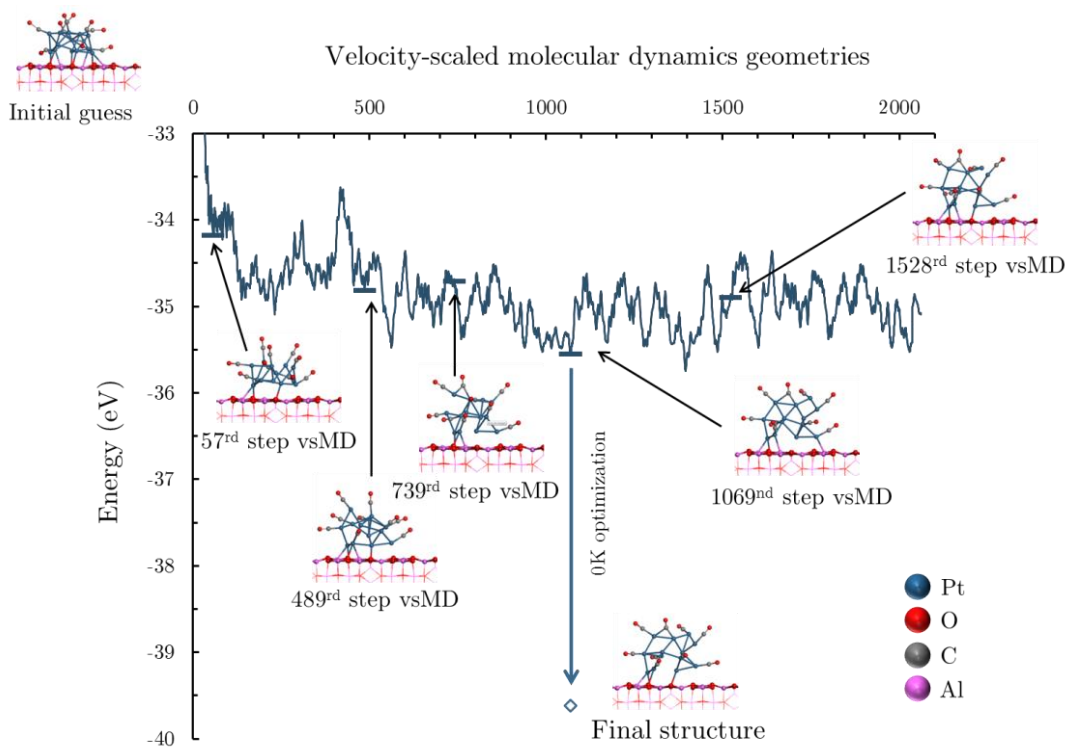


Figure S3. Illustration of the velocity-scaled molecular dynamics of $\text{Pt}_{13}(\text{CO})_9$. The structures describe the evolution of the morphology along chosen points of the MD (instantaneous, non-quenched geometries).

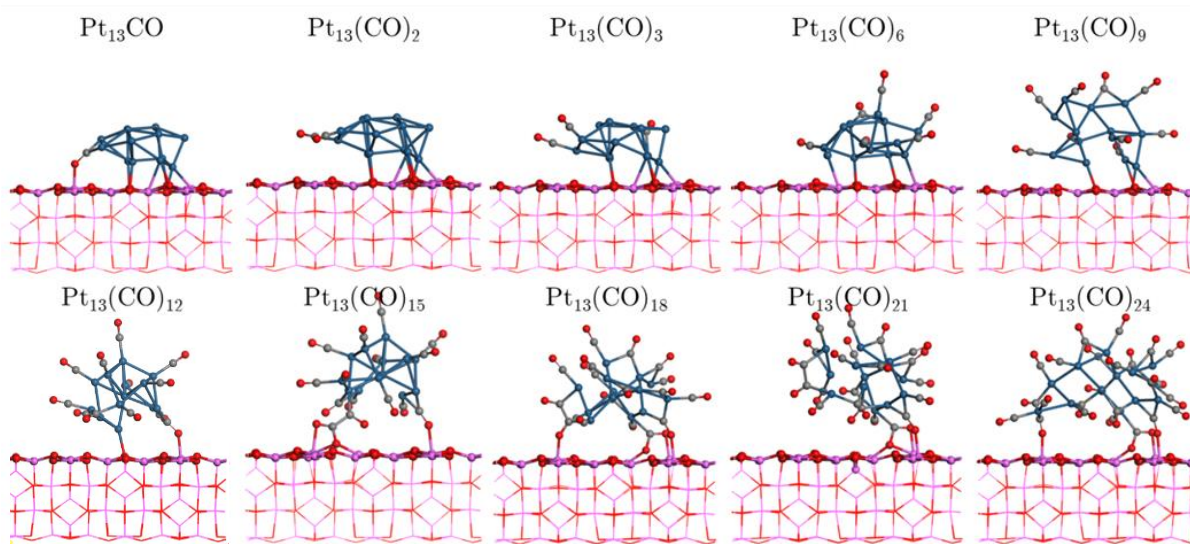


Figure S4. Illustrations of the most stable supported $\text{Pt}_{13}(\text{CO})_m$ structures.

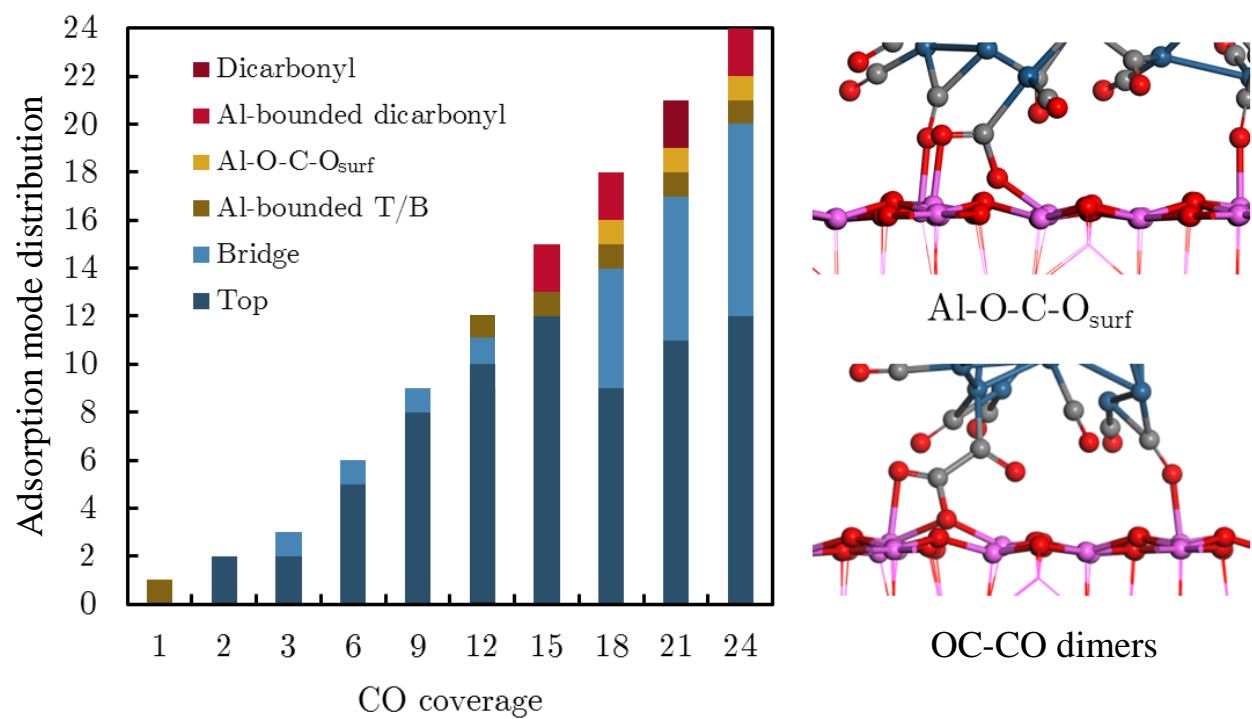


Figure S5. Population of adsorbed carbon monoxide according to their adsorption mode. The Al-bounded modes are characteristic of carbon monoxide linked to aluminum of the support.

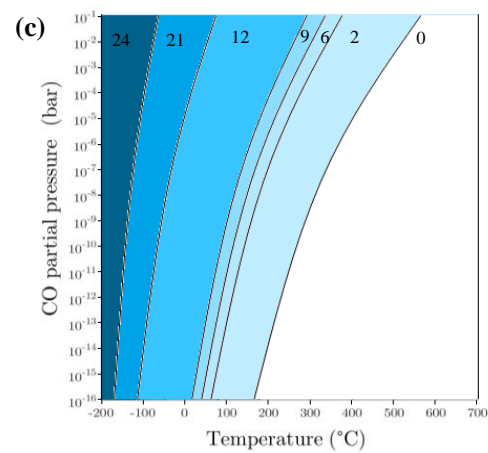
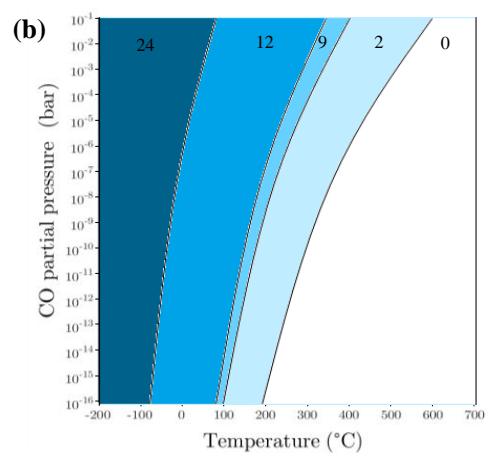
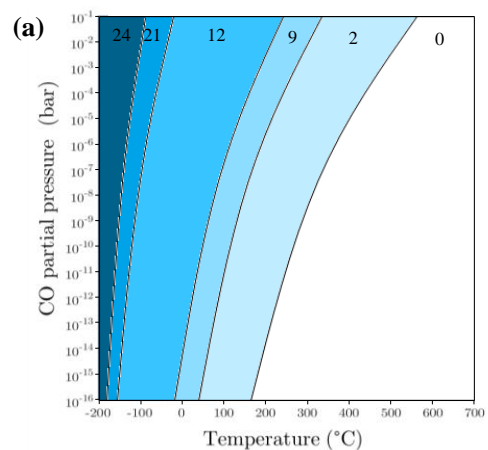


Figure S6. Phase diagram of supported $\text{Pt}_{13}(\text{CO})_m$ structures according to temperature and partial pressure of CO obtained with the (a) RPBE, (b) PBE-dDsC and (c) opt-PBE functionals.

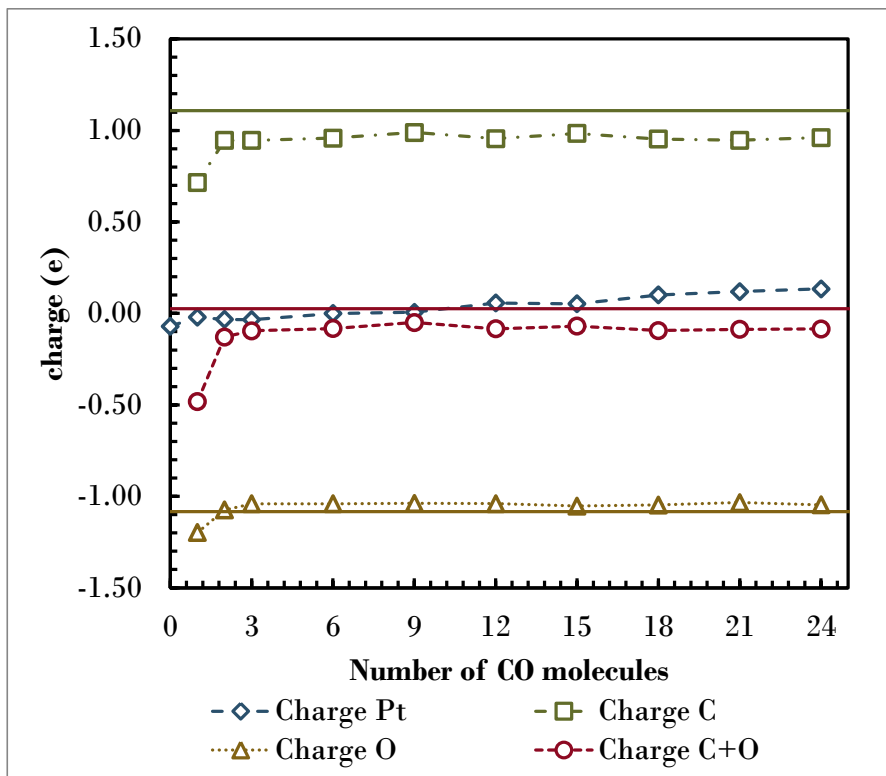


Figure S7. Bader charges of the elements present on the supported clusters calculated with the PBE functional. The straight lines deals with the isolated CO molecule charge.

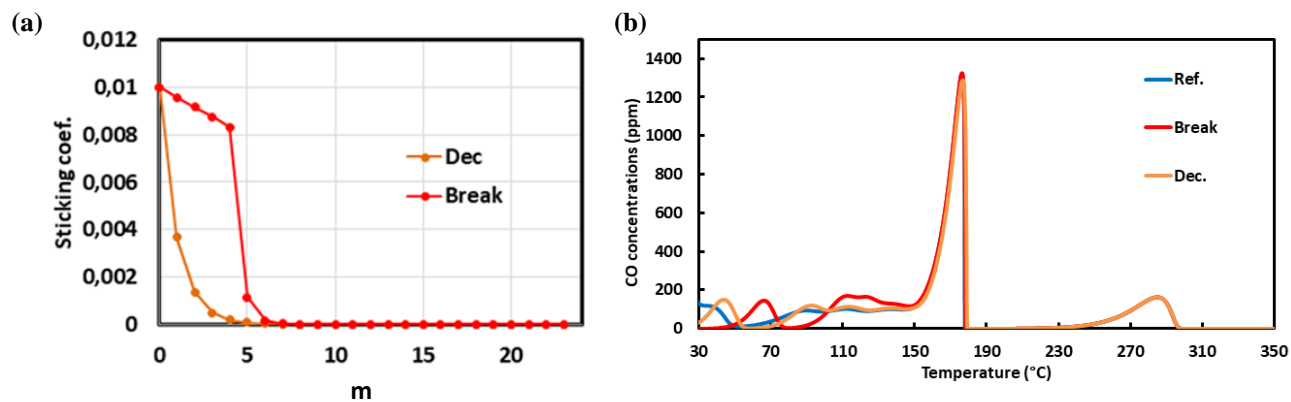


Figure S8. (a) Alternative models for the evolution of the sticking coefficient implemented in the kinetic model. (b) TPD simulations using these alternative evolutions, compared to the reference calculation ($s = 0.01$, independent on the coverage). All calculations were made starting from the PBE DFT calculations.

Table S1. Reactions and kinetic parameters of the $\text{Pt}_{13}(\text{CO})_m$ model with a constant sticking coefficient, computed starting from PBE DFT calculations. The pre-exponential factor and activation energies are given by the fit of $k_{\text{desorption}}$ (calculated from DFT) with respect to temperature (see equations 5 and 6 in the main text).

Adsorption reactions	Forward parameters		Backward parameters	
	Sticking coefficient s_t	$E_{\text{adsorption}}$ (kcal.mol ⁻¹)	Pre-exponential factor A (s ⁻¹)	E_{act} (kcal.mol ⁻¹)
$\text{CO} + \text{Pt}_{13} \leftrightarrow \text{Pt}_{13}(\text{CO})$	0.01	0.00	1.99E+28	67.0
$\text{CO} + \text{Pt}_{13}(\text{CO}) \leftrightarrow \text{Pt}_{13}(\text{CO})_2$	0.01	0.00	6.76E+25	62.9
$\text{CO} + \text{Pt}_{13}(\text{CO})_2 \leftrightarrow \text{Pt}_{13}(\text{CO})_3$	0.01	0.00	1.09E+28	48.6
$\text{CO} + \text{Pt}_{13}(\text{CO})_3 \leftrightarrow \text{Pt}_{13}(\text{CO})_4$	0.01	0.00	3.40E+27	49.5
$\text{CO} + \text{Pt}_{13}(\text{CO})_4 \leftrightarrow \text{Pt}_{13}(\text{CO})_5$	0.01	0.00	1.06E+27	50.5
$\text{CO} + \text{Pt}_{13}(\text{CO})_5 \leftrightarrow \text{Pt}_{13}(\text{CO})_6$	0.01	0.00	3.32E+26	51.4
$\text{CO} + \text{Pt}_{13}(\text{CO})_6 \leftrightarrow \text{Pt}_{13}(\text{CO})_7$	0.01	0.00	4.71E+26	51.4
$\text{CO} + \text{Pt}_{13}(\text{CO})_7 \leftrightarrow \text{Pt}_{13}(\text{CO})_8$	0.01	0.00	6.68E+26	51.2
$\text{CO} + \text{Pt}_{13}(\text{CO})_8 \leftrightarrow \text{Pt}_{13}(\text{CO})_9$	0.01	0.00	7.20E+26	50.2
$\text{CO} + \text{Pt}_{13}(\text{CO})_9 \leftrightarrow \text{Pt}_{13}(\text{CO})_{10}$	0.01	0.00	8.08E+26	47.6
$\text{CO} + \text{Pt}_{13}(\text{CO})_{10} \leftrightarrow \text{Pt}_{13}(\text{CO})_{11}$	0.01	0.00	9.07E+26	44.7
$\text{CO} + \text{Pt}_{13}(\text{CO})_{11} \leftrightarrow \text{Pt}_{13}(\text{CO})_{12}$	0.01	0.00	1.02E+27	41.9
$\text{CO} + \text{Pt}_{13}(\text{CO})_{12} \leftrightarrow \text{Pt}_{13}(\text{CO})_{13}$	0.01	0.00	5.47E+27	36.8
$\text{CO} + \text{Pt}_{13}(\text{CO})_{13} \leftrightarrow \text{Pt}_{13}(\text{CO})_{14}$	0.01	0.00	2.94E+28	31.8
$\text{CO} + \text{Pt}_{13}(\text{CO})_{14} \leftrightarrow \text{Pt}_{13}(\text{CO})_{15}$	0.01	0.00	1.58E+29	26.8
$\text{CO} + \text{Pt}_{13}(\text{CO})_{15} \leftrightarrow \text{Pt}_{13}(\text{CO})_{16}$	0.01	0.00	1.97E+28	36.6
$\text{CO} + \text{Pt}_{13}(\text{CO})_{16} \leftrightarrow \text{Pt}_{13}(\text{CO})_{17}$	0.01	0.00	5.17E+27	31.1
$\text{CO} + \text{Pt}_{13}(\text{CO})_{17} \leftrightarrow \text{Pt}_{13}(\text{CO})_{18}$	0.01	0.00	1.36E+27	25.6
$\text{CO} + \text{Pt}_{13}(\text{CO})_{18} \leftrightarrow \text{Pt}_{13}(\text{CO})_{19}$	0.01	0.00	2.18E+27	25.1
$\text{CO} + \text{Pt}_{13}(\text{CO})_{19} \leftrightarrow \text{Pt}_{13}(\text{CO})_{20}$	0.01	0.00	3.49E+27	24.6
$\text{CO} + \text{Pt}_{13}(\text{CO})_{20} \leftrightarrow \text{Pt}_{13}(\text{CO})_{21}$	0.01	0.00	5.59E+27	24.2
$\text{CO} + \text{Pt}_{13}(\text{CO})_{21} \leftrightarrow \text{Pt}_{13}(\text{CO})_{22}$	0.01	0.00	7.40E+27	24.6
$\text{CO} + \text{Pt}_{13}(\text{CO})_{22} \leftrightarrow \text{Pt}_{13}(\text{CO})_{23}$	0.01	0.00	9.79E+27	25.4
$\text{CO} + \text{Pt}_{13}(\text{CO})_{23} \leftrightarrow \text{Pt}_{13}(\text{CO})_{24}$	0.01	0.00	1.30E+28	25.8