

Supporting Information

Atomic scale insight into the formation, size and location of platinum nanoparticles supported on γ -alumina

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S.I. 1. DFT edge model

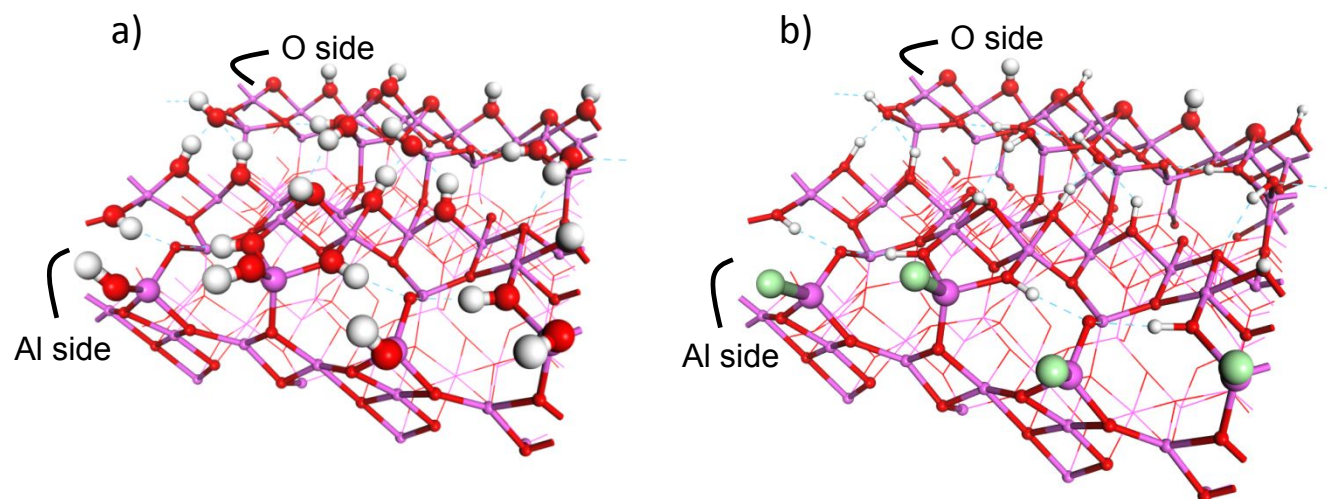


Figure S1. γ -Alumina (110)-(100) edge models a) hydrated with $6\text{H}_2\text{O}$ and b) chlorinated with 2 Cl reported in reference 1.

S.I. 2. EXAFS spectra and fitting

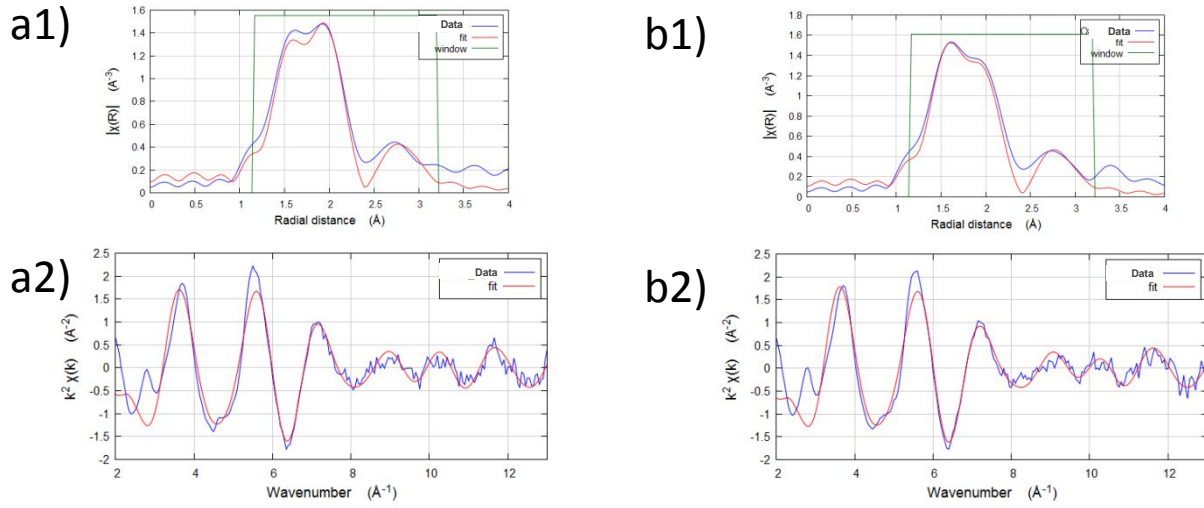


Figure S2. Fourier Transform $|\chi(R)|$ of the Pt L₃ edge EXAFS magnitude spectra (no phase correction) (1) and EXAFS $\chi(k)$ (2), both weighted by k^2 , the red line represents the best fit and the fitting range is represented by the green line: a) oxide 0.3%Pt/ γ -Al₂O₃-Cl, b) oxide 1%Pt/ γ -Al₂O₃-Cl.

Table S1. EXAFS fitting results for oxide catalysts at 1.4%Cl. $S_0^2=0.88$; $E_0=11566.1$ eV; $1.15 < R < 3.2$ Å; $N_{ind}=12$; $N_{var}=8$.

Oxide catalyst	k-range (Å ⁻¹)	Path	Coordination number	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	R-factor
0.3%Pt/ γ -Al ₂ O ₃ -Cl	4.2 – 12	Pt-O	3.3±0.2	2.00±0.02	0.001±0.001	11.1±0.6	0.03
		Pt-Cl	2.7±0.2	2.31±0.01			
		Pt-O _{long} or Pt-Al _{long}	5±1	3.11±0.03	0.003±0.003		
1%Pt/ γ -Al ₂ O ₃ -Cl	4.2 – 11.8	Pt-O	3.8±0.4	2.00±0.03	0.001±0.001	11.1±0.5	0.02
		Pt-Cl	2.2±0.4	2.31±0.03			
		Pt-O _{long} or Pt-Al _{long}	4.6±0.9	3.10±0.02	0.003±0.002		

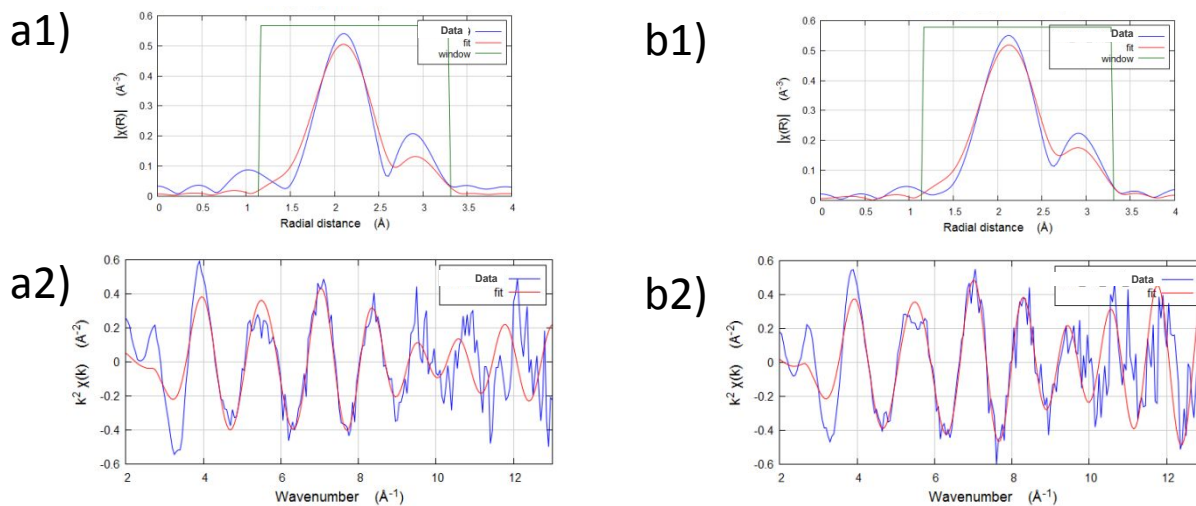


Figure S3. Fourier Transform $|\chi(R)|$ of the Pt L_3 edge EXAFS magnitude spectra (no phase correction) (1) and EXAFS $\chi(k)$ (2), both weighted by k^2 , the red line represents the best fit and the fitting range is represented by the green line: a) reduced 0.3%Pt/ γ - Al_2O_3 -Cl, b) reduced 1%Pt/ γ - Al_2O_3 -Cl.

Table S2. EXAFS fitting results for reduced catalysts considering Pt-Al coordination for the light scatterer. $S_0^2=0.79$ $E_0=11566.1$ eV; $1.15 < R < 3.2$ Å; $N_{ind}=8$; $N_{var}=7$ (* $N_{var}=6$).

Reduced catalyst	k-range (Å ⁻¹)	Path	Coordination number	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	R-factor
0.3%Pt/ γ - Al_2O_3 -Cl	3.9 – 8.3	Pt-Al or Pt-O _{long}	1.4±0.5	2.43±0.05	0.004±0.004	6±1	0.06
		Pt-Pt	3±1	2.73±0.05	0.006±0.004		
1%Pt/ γ - Al_2O_3 -Cl*	4 – 8.3	Pt-Al or Pt-O _{long}	1.2±0.4	2.41±0.05	0.003±0.001	5.0±0.9	0.03
		Pt-Pt	3.2±0.7	2.73±0.03			

S.I. 3. Tomographic volumes

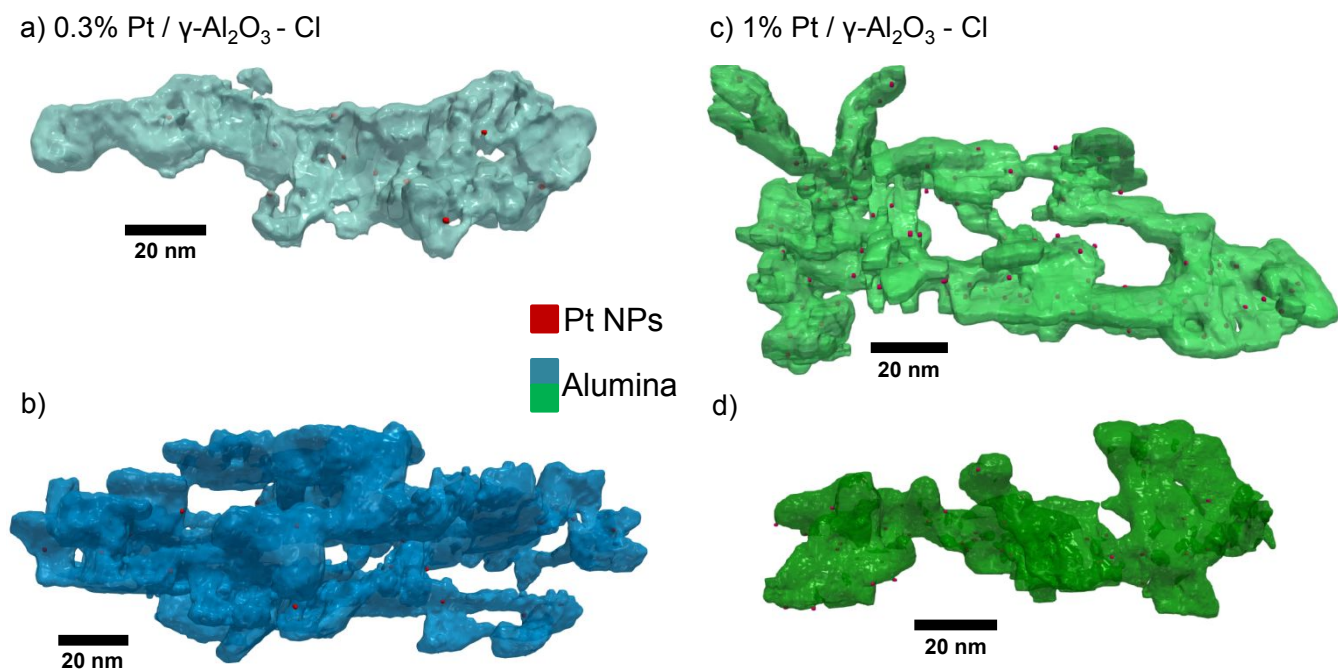


Figure S4. Segmented volumes obtained for the two objects for both reduced catalysts: a) and b) 0.3%Pt/ γ -Al₂O₃-Cl; c) and d) 1%Pt/ γ -Al₂O₃-Cl.

Table S3. Detail, for each volume, of the total number of NPs, the number of NPs for which their location was evaluated and of which how many were located on edges of edge like structures (steps, kinks), on surface planes and for how many the location could not be unambiguously determined (called “Undetermined”, due to deviations during segmentation the NP could be *floating* in the emptiness or *inside* the alumina).

# of NPs:	0.3%Pt/ γ -Al ₂ O ₃ -Cl		1%Pt/ γ -Al ₂ O ₃ -Cl	
	a)	b)	c)	d)
Total in volume	13	30	131	55
Evaluated for location*	13	12	61	18
On edges/kinks/steps	11	7	38	7
On surface planes	2	2	9	4
Undetermined	0	3	14	7

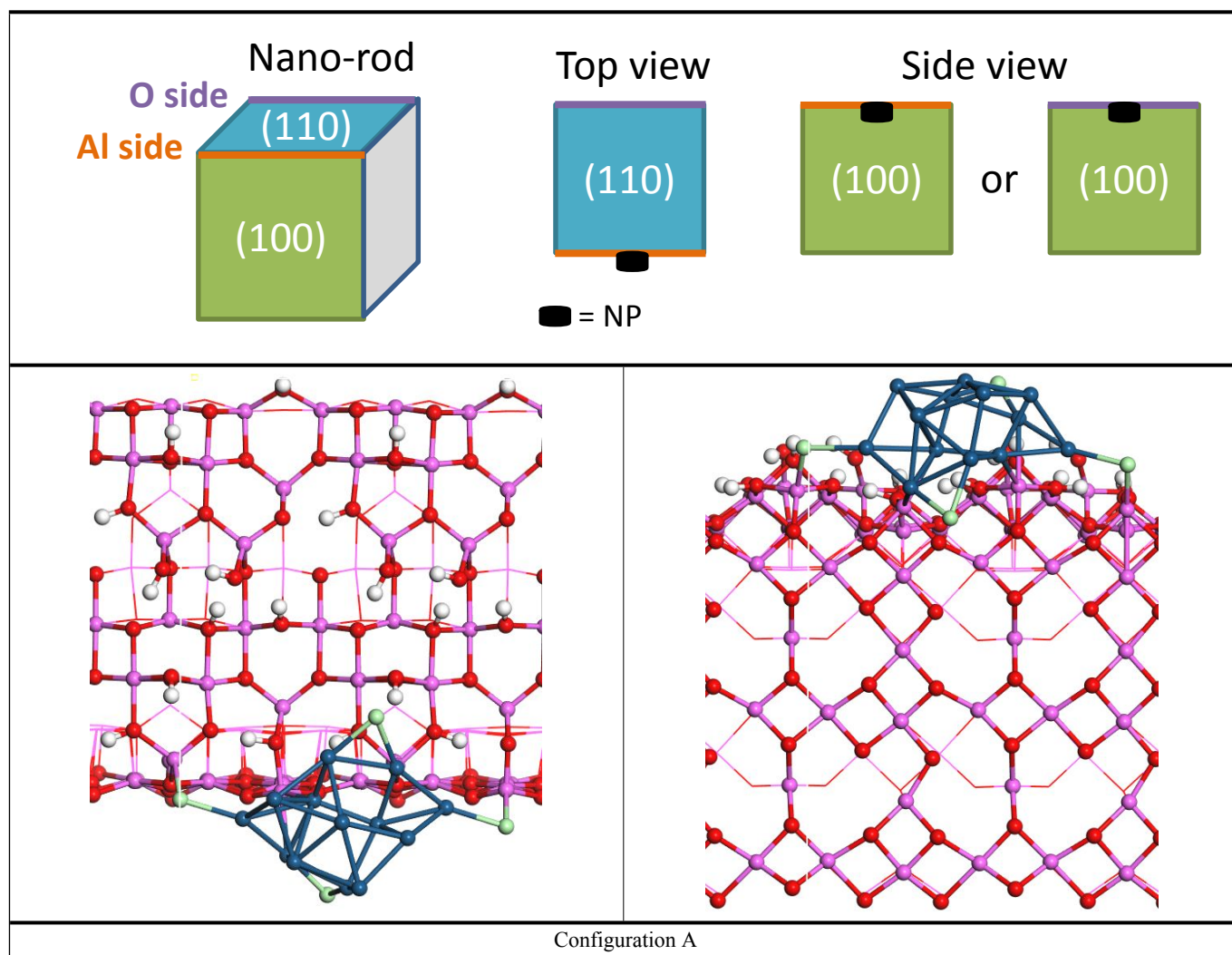
*Arbitrarily, the location was assessed for the NPs that remain visible when the alumina surface in the volume is set as completely opaque, except for the volume of 0.3%Pt/ γ -Al₂O₃-Cl reduced with 13 NPs in which case all NPs were assessed. This is possible because due to deviations during segmentation some NPs may appear inside the alumina crystallites.

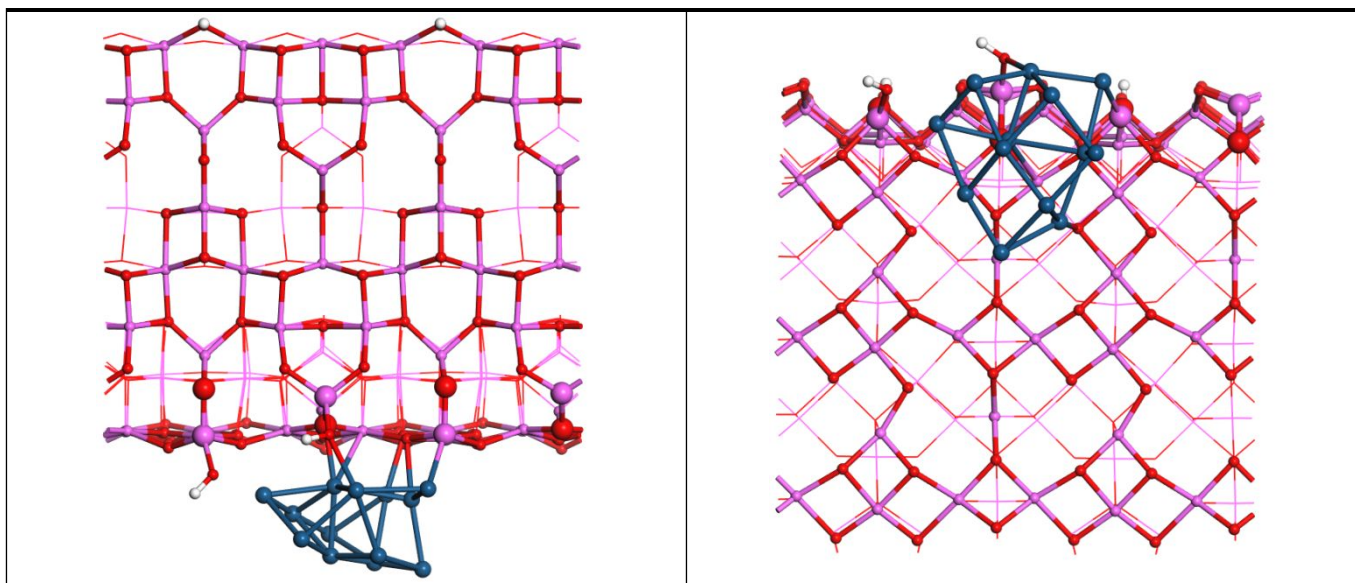
S.I. 4. DFT Pt₁₃/edge models and binding energy

Table S4. Binding energies of Pt₁₃/edge models. Each model is identified by a letter (ID) and further details of the model are given, namely the hydration degree of the edge, the chlorination of the Al side, in which edge termination the NP was grafted and if an edge OH was migrated onto the NP. The models are ranked by order of stability. For reference, binding energies for the previously published models² of Pt₁₃/(100) (dehydrated) and Pt₁₃/(110) (with 11.8 OH/nm²) are -416 and -397 kJ/mol respectively.

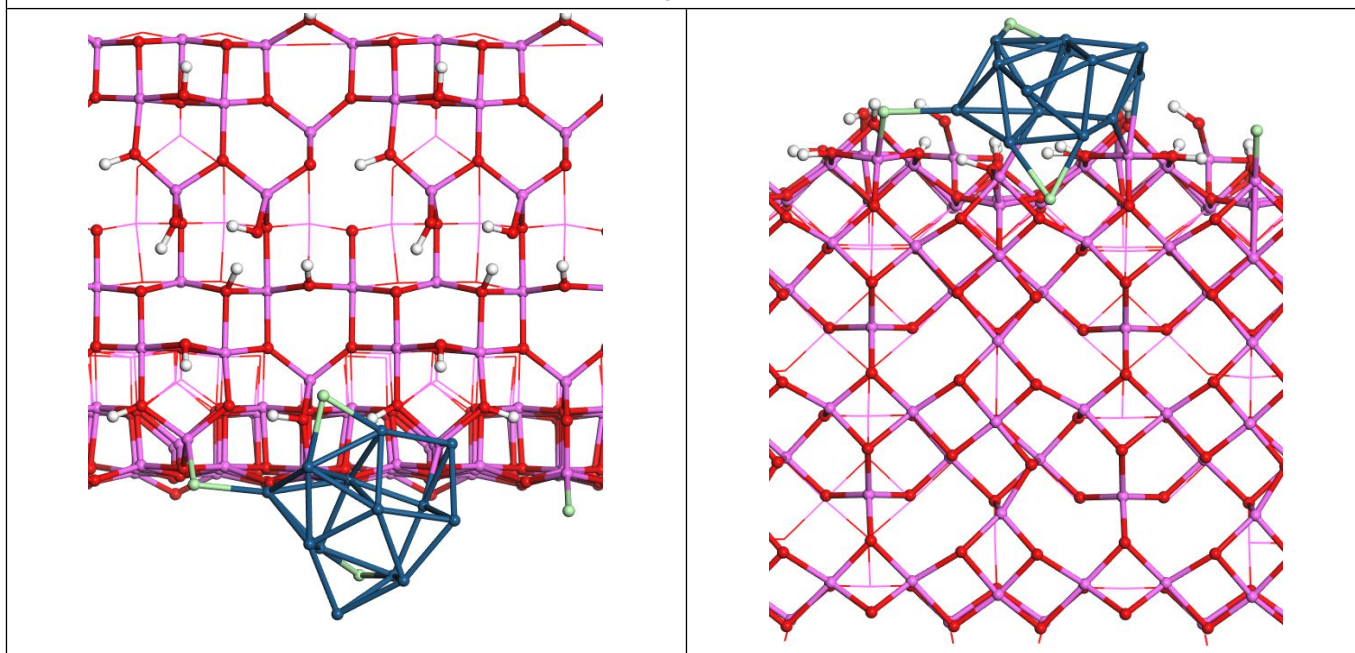
ID	Position	Edge hydration	Edge chlorination	Edge termination	Cl migration	OH migration	E _b (kJ.mol ⁻¹ .Pt atom ⁻¹)
A	Edge	6H ₂ O	2 Cl	Al side	yes	-	-414
B	Near edge	1H ₂ O	-	Al side	-	-	-409
C	Edge	6H ₂ O	2 Cl	Al side	yes	-	-406
D	Near edge	6H ₂ O	1 Cl	Al side	-	-	-404
E	Near edge	6H ₂ O	2 Cl	Al side	-	-	-404
F	Near edge	6H ₂ O	-	O side	-	-	-403
G	Near edge	6H ₂ O	-	Al side	-	-	-400
H	Near edge	6H ₂ O	-	Al side	-	yes	-397
I	Near edge	6H ₂ O	-	Al side	-	yes	-395
J	Near edge	6H ₂ O	-	Al side	-	yes	-394
K	Near edge	6H ₂ O	-	Al side	-	yes	-393

Table S5. Optimized $\text{Pt}_{13}/\text{edge}$ models as identified in Table 1 (ID). The first scheme illustrates the views of the nano-rod that are presented which are as follows: left - top view of the (110) side with Al-side edge facing down and O-side edge facing up; right - side view of the (100) side with edge facing up on the right side. Models color coded white – H; red – O; pink – Al; green – Cl; blue – Pt.

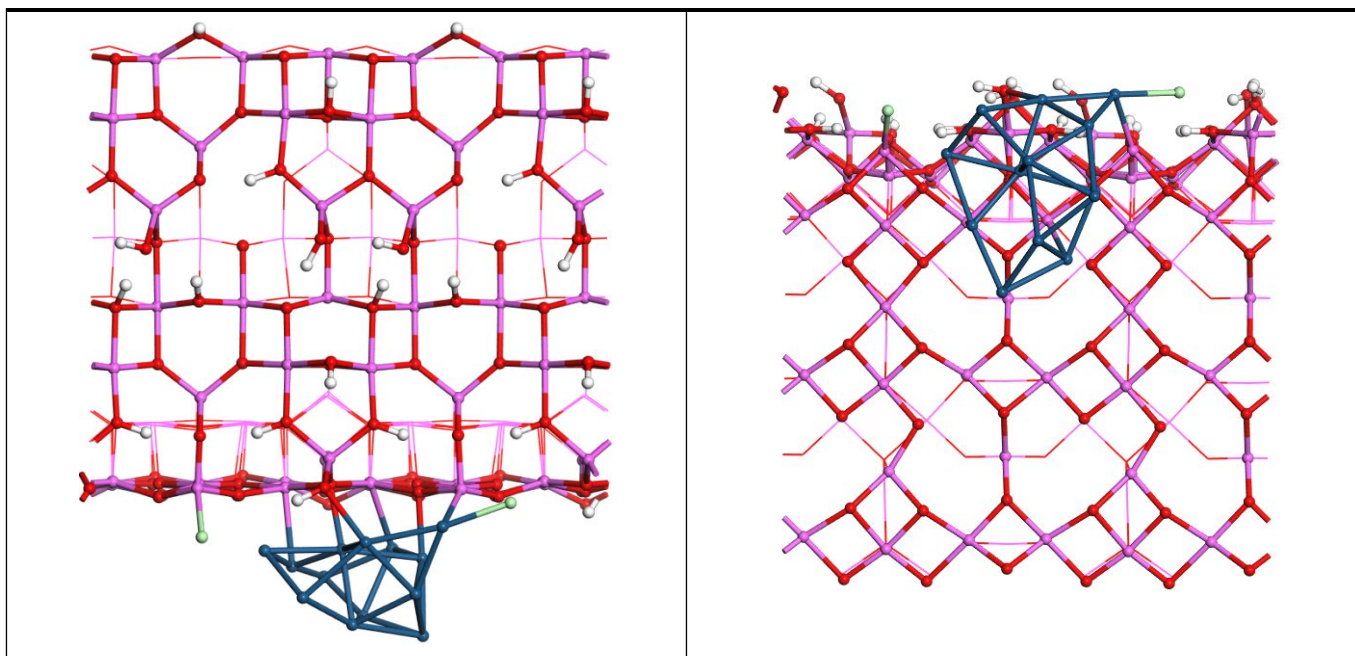




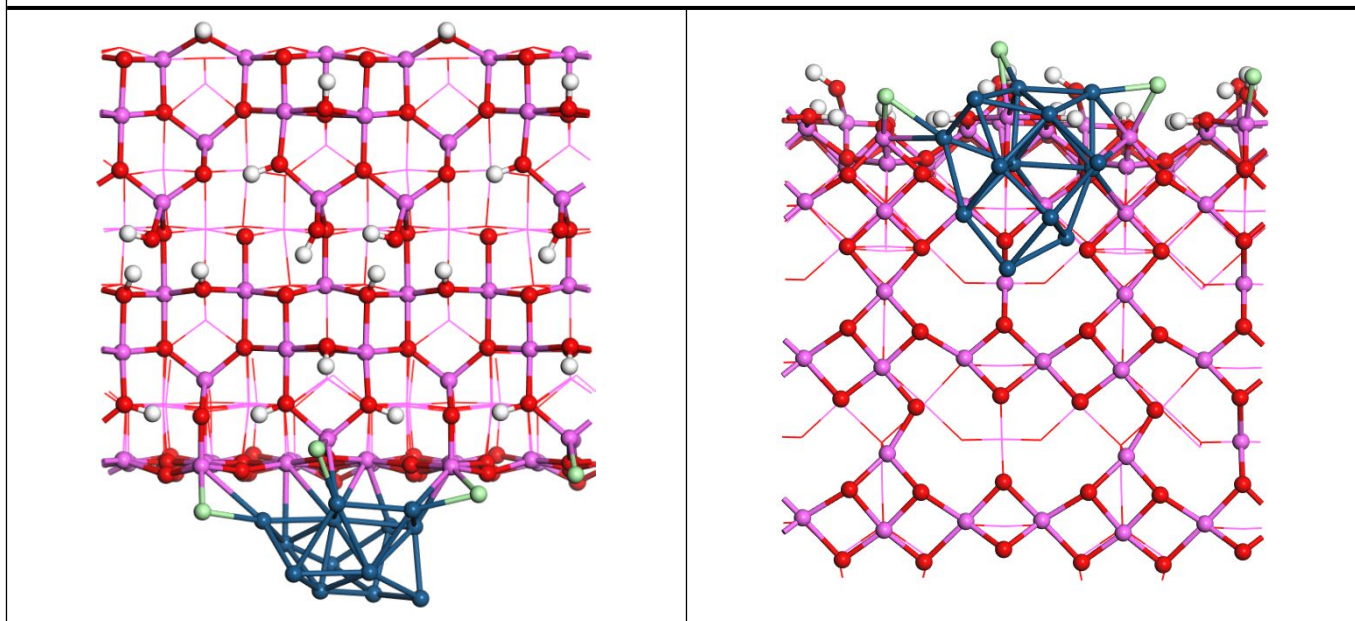
Configuration B



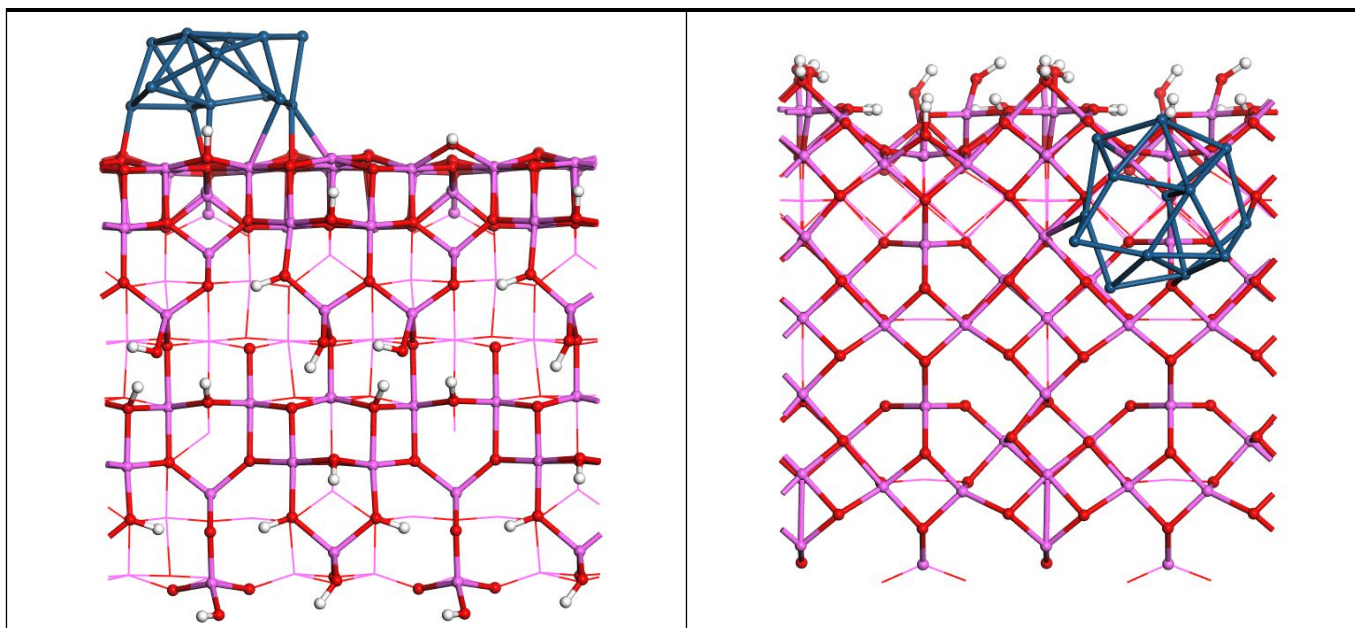
Configuration C



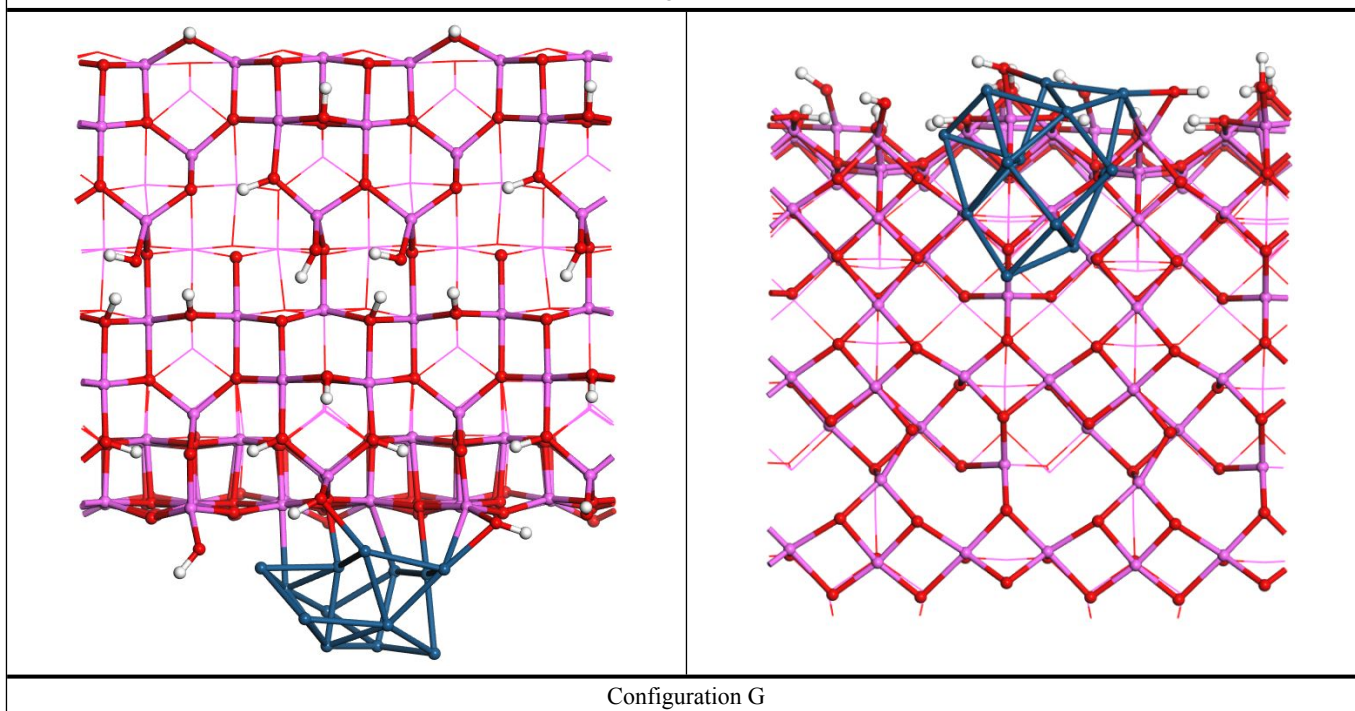
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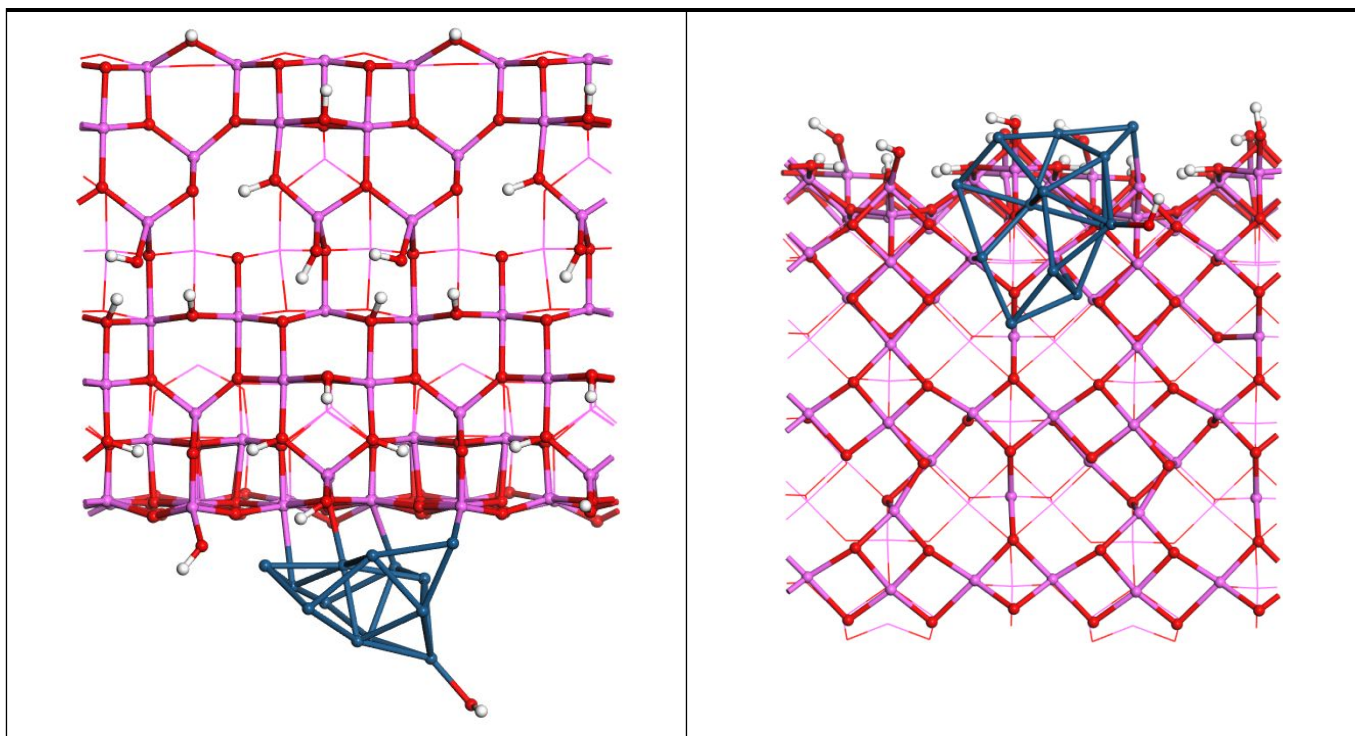
Configuration E



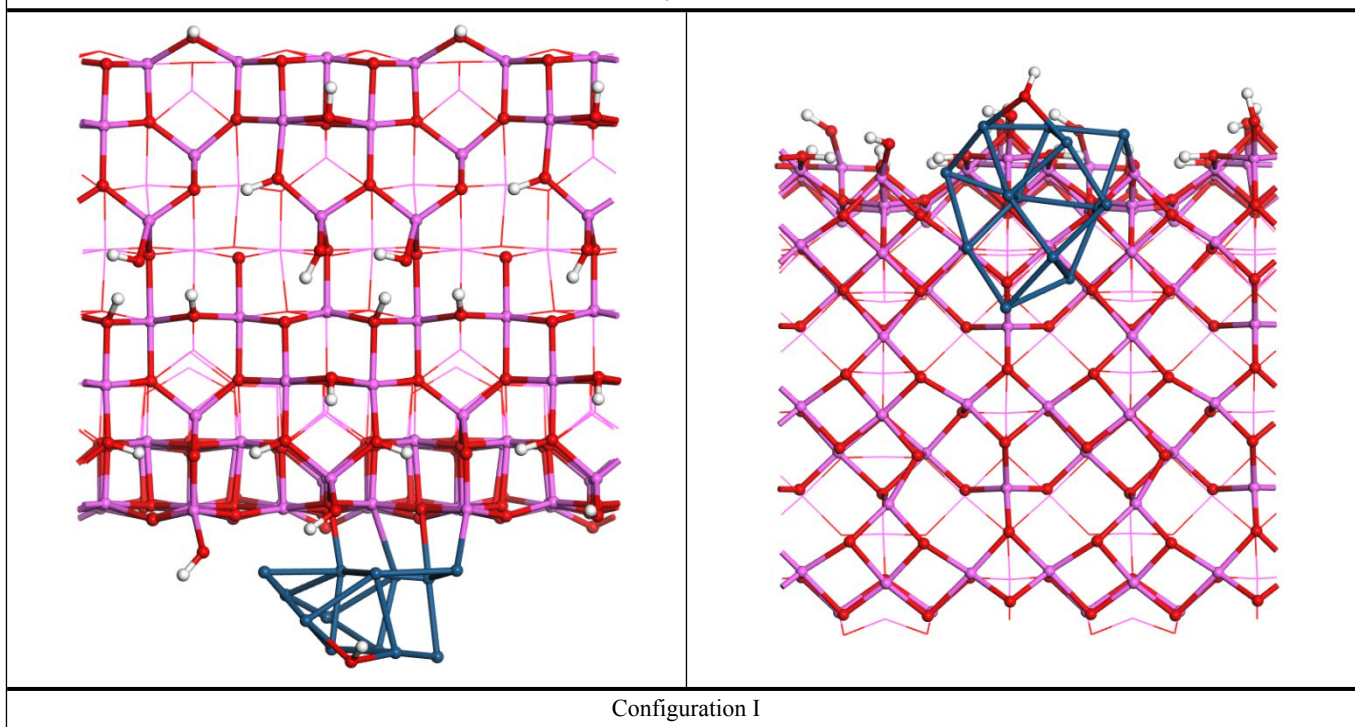
Configuration F



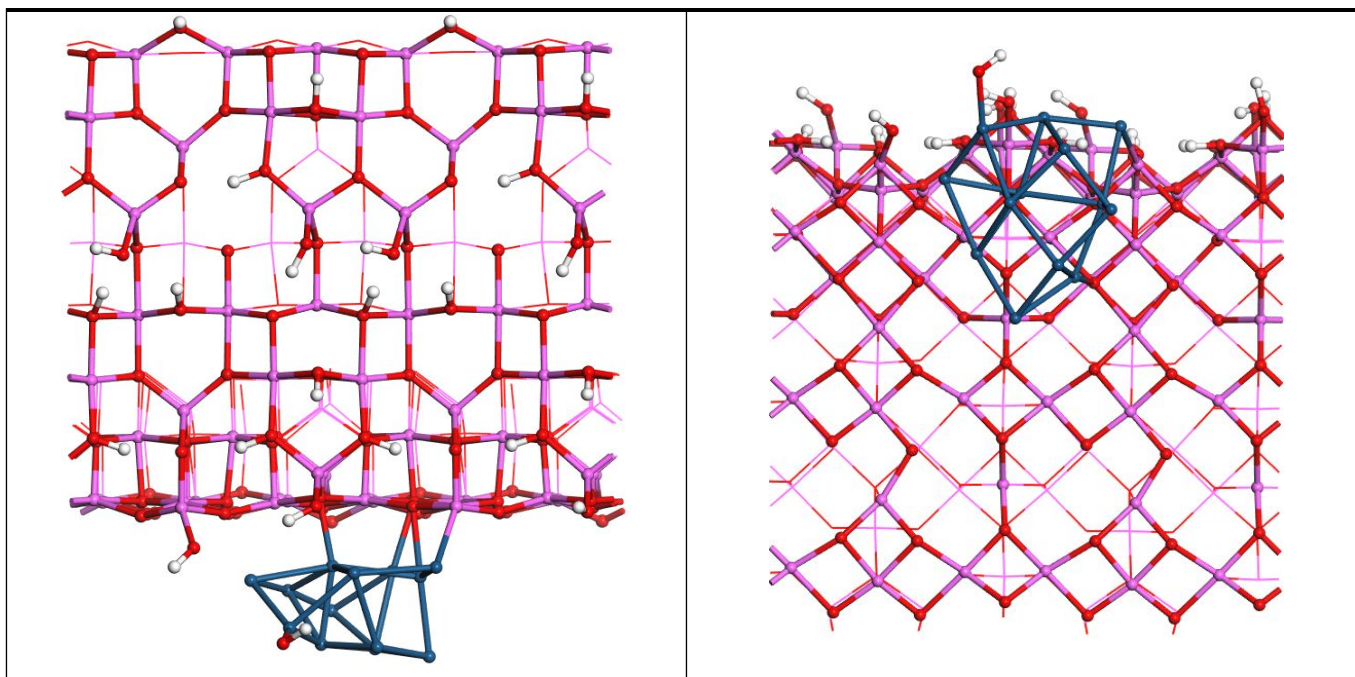
Configuration G



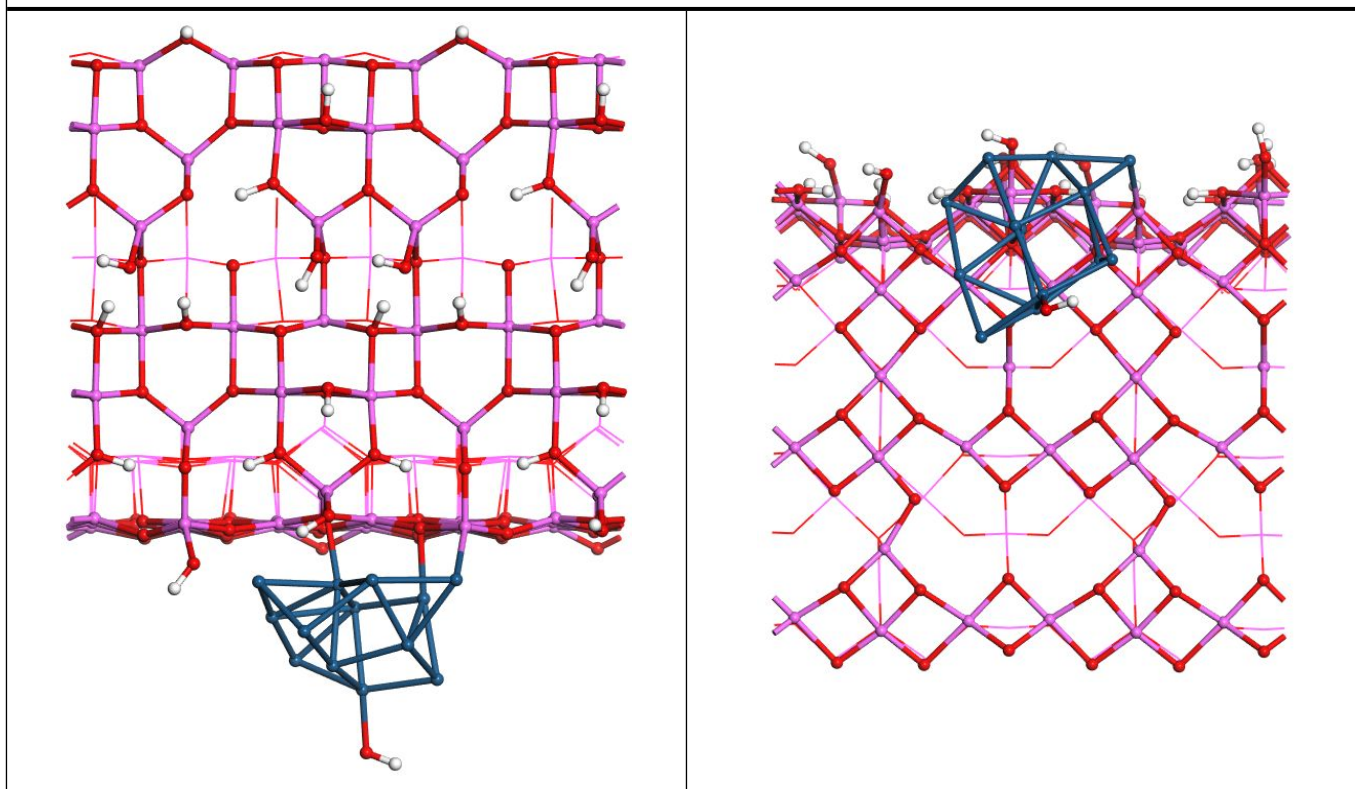
Configuration H



Configuration I



Configuration J



Configuration K

S.I. 5. M-Tortuosity and σ_C

Table S6. M-Tortuosity values and σ_C obtained for the segmented object of each catalyst shown in Figure 7 of the main text using either the Pt nanoparticle positions or the uniformly distributed points set.

	M-Tortuosity			
	NP positions	σ_C	Point set	σ_C
0.3%Pt/ γ -Al ₂ O ₃ -Cl	1.27 ^a	0.07	1.25 ^c	0.01
1%Pt/ γ -Al ₂ O ₃ -Cl	1.20 ^b	0.02	1.22 ^d	0.01

Number of NPs: a – 13, b – 131; Number of points in set: c – 182, d – 147

References

- (1) Batista, A. T. F.; Wisser, D.; Pigeon, T.; Gajan, D.; Diehl, F.; Rivallan, M.; Catita, L.; Gay, A.-S.; Lesage, A.; Chizallet, C.; Raybaud, P. Beyond gamma-Al₂O₃ Crystallite Surfaces: the Hidden Features of Edges Revealed by Solid-State ¹H NMR and DFT Calculations. *J. Catal.* **2019**, 378, 140–143.
- (2) Mager-Maury, C.; Chizallet, C.; Sautet, P.; Raybaud, P. Platinum Nanoclusters Stabilized on γ -Alumina by Chlorine Used As a Capping Surface Ligand: A Density Functional Theory Study. *ACS Catal.* **2012**, 2, 1346–1357.