Electronic Supplementary Material (ESI) for Nanoscale.

Evaluating acid and metallic site proximity in Pt/γ-Al_2O_3-Cl bifunctional catalysts through an atomic scale geometrical model

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Supplementary Information

1. (S)TEM study of the experimental catalysts

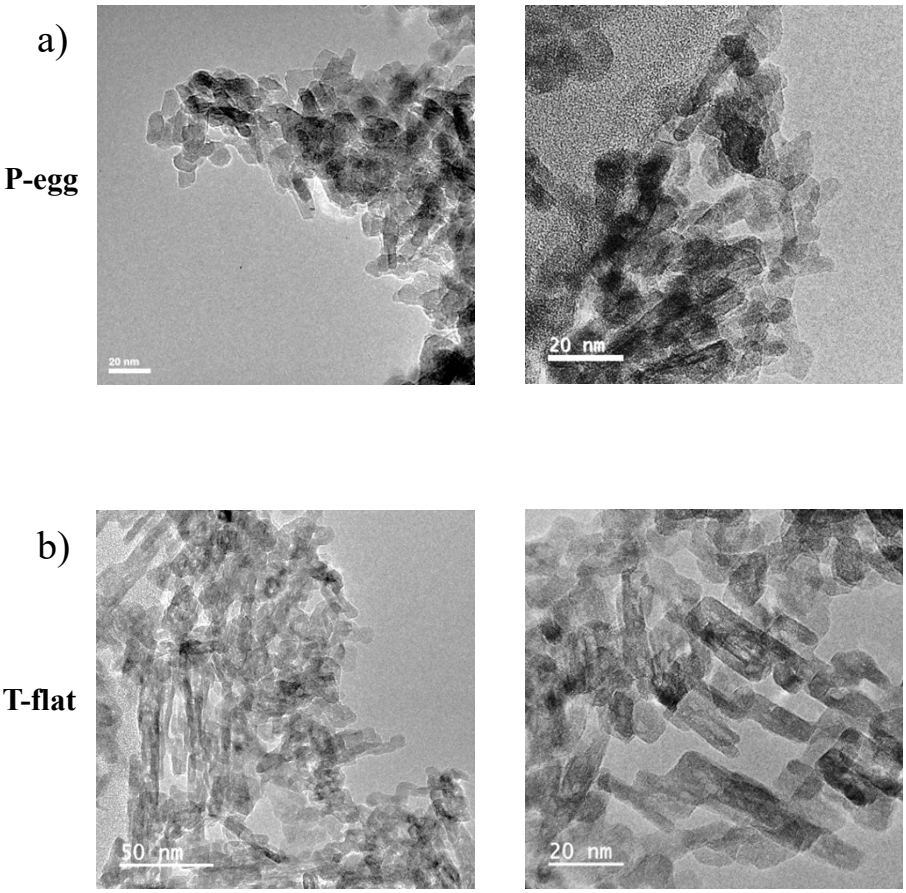
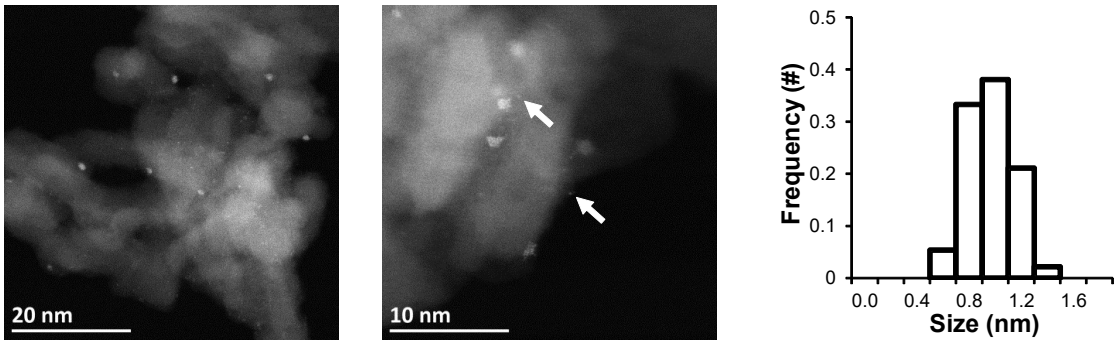
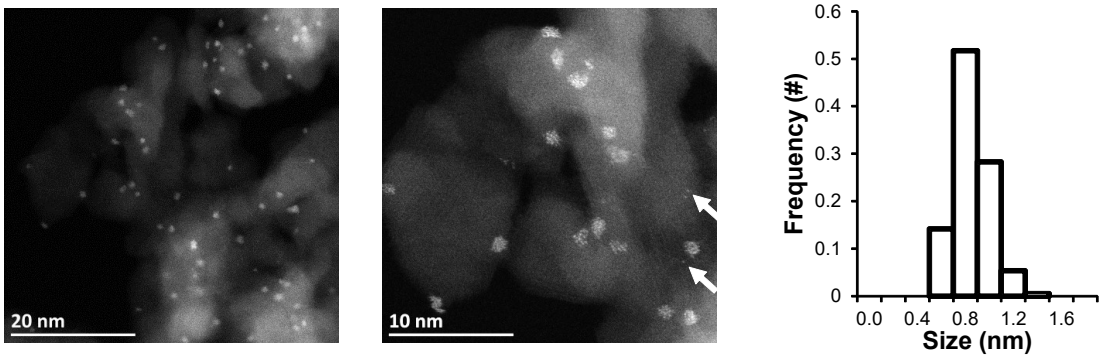


Figure S1. TEM images of a) P-egg and b) T-flat aluminas. From ref. [1] with permission.

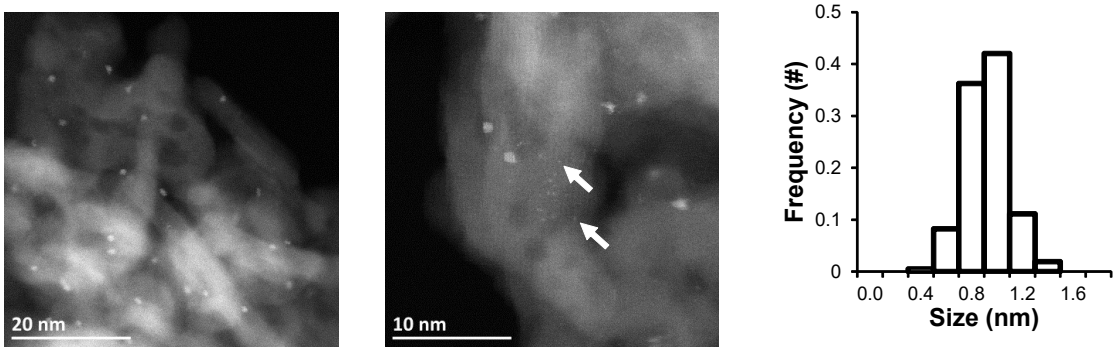
a) 0.3%Pt/P-egg-0.1%Cl reduced



b) 1%Pt/P-egg-0.1%Cl reduced



c) 0.3%Pt/T-flat-0.1%Cl reduced



d) 1%Pt/T-flat-0.1%Cl reduced

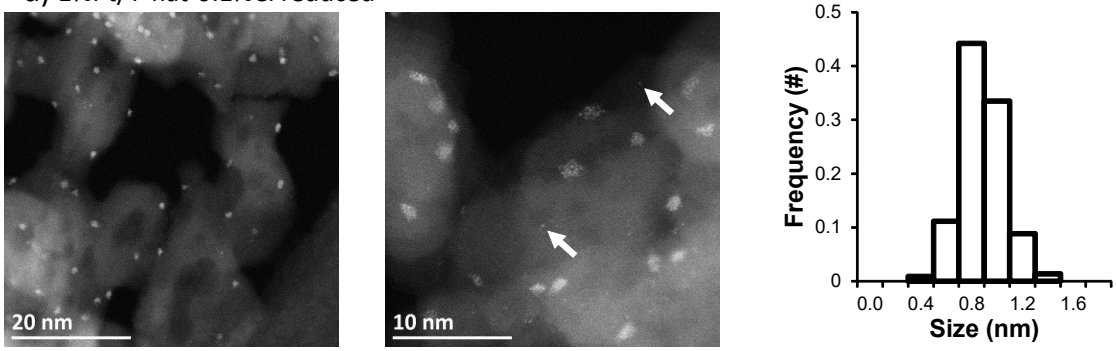
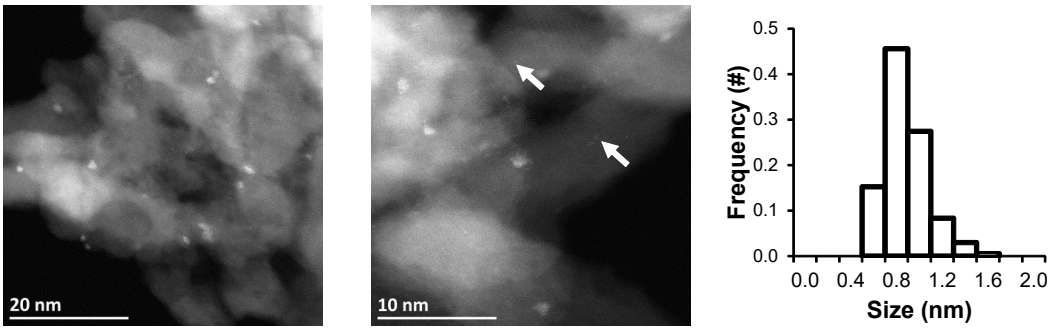
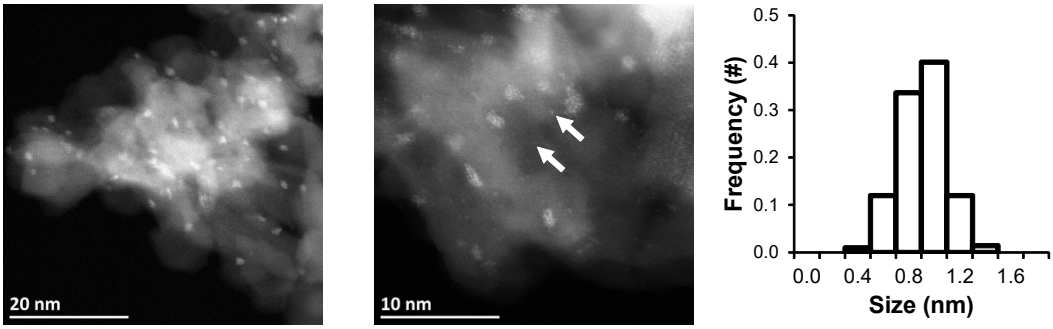


Figure S2. HR-HAADF-STEM images and nanoparticle size histograms of four reduced catalysts a) 0.3%Pt/P-egg-0.1%Cl, b) 1%Pt/P-egg-0.1%Cl, c) 0.3%Cl/T-flat0-0.1%Cl, d) 1%Pt/T-flat-0.1%Cl. White arrows highlight single atoms.

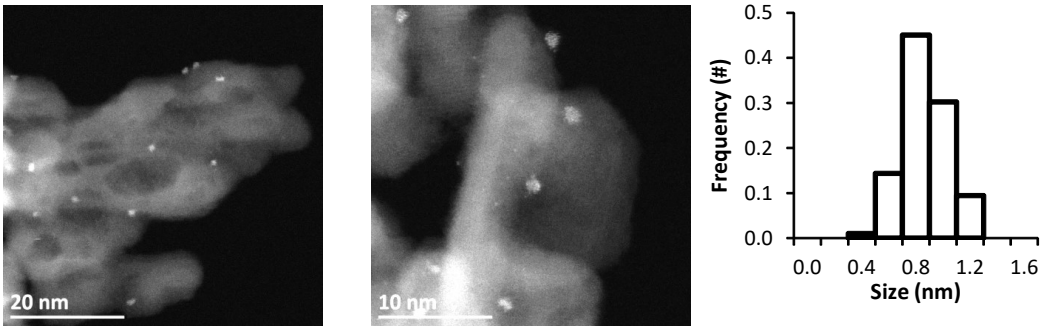
a) 0.3%Pt/P-egg-1.4%Cl reduced



b) 1%Pt/P-egg-1.4%Cl reduced



c) 0.3%Pt/T-flat-1.4%Cl reduced



d) 1%Pt/T-flat-1.4%Cl reduced

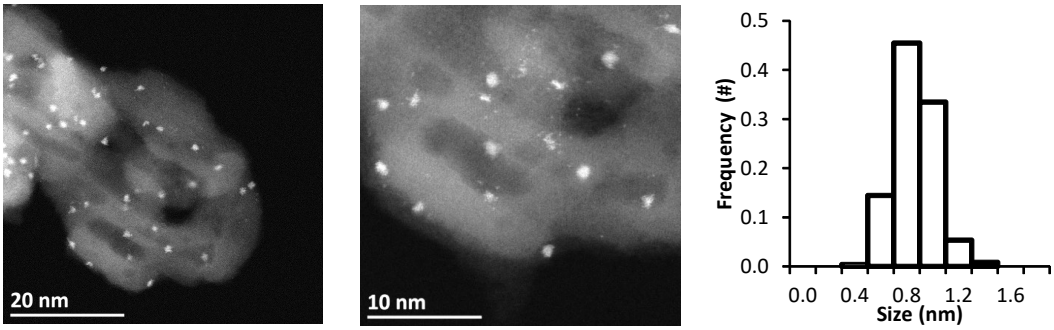


Figure S3. HR-HAADF-STEM images and nanoparticle size histograms of four reduced catalysts a) 0.3%Pt/P-egg-1.4%Cl, b) 1%Pt/P-egg-1.4%Cl, c) 0.3%Pt/T-flat-1.4%Cl, d) 1%Pt/T-flat-1.4%Cl. White arrows highlight single atoms. Figures c) and d) are from ref [2] (with permission).

Table S1. Detailed results of nanoparticle size study, complementary to histograms of Figures S2-S3

Sample	#measured NPS	Average NP size (nm)	Standard deviation (nm)	%[0.6; 1.2]nm
0.3%Pt/P-egg-1.4%Cl	204	0.87	0.19	72
0.3%Pt/ P-egg -0.1%Cl	171	0.87	0.16	75
1%Pt/ P-egg -1.4%Cl	214	0.91	0.18	69
1%Pt/ P-egg -0.1%Cl	205	0.86	0.15	76
0.3%Pt/T-flat-1.4%Cl	202	0.86	0.16	74
0.3%Pt/ T-flat -0.1%Cl	207	0.93	0.16	70
1%Pt/ T-flat -1.4%Cl	242	0.86	0.15	75
1%Pt/ T-flat -0.1%Cl	215	0.88	0.17	73

Images acquired at higher magnification allow the platinum atoms that compose the nanoparticles to be observed. Nanoparticle morphology was studied measuring HAADF intensity to estimate the number of Pt atoms stacked perpendicular to the electron beam (n) from the intensity of atomic column (I), as the image intensity is roughly proportional to the square of the mean atomic number of the analyzed area (Z).[3] As measurements were performed on thin areas, alumina contribution to intensity can be neglected in first approximation. The intensity of three single atoms was measured, to estimate I_{SA} proportional to Z_{SA}^2. Stating that the atomic number of a column composed of n Pt atoms is equal to nZ_{SA}, by measuring intensity of nanoparticles the *n* parameter can be obtained as $n \propto \sqrt{I/I_{SA}}$. At least one NP per sample was studied this way and it was consistently found that the NPs are composed of at most two layers of Pt atoms.

An example is given in Figure S4 for the 1%Pt/P-egg-0.1%Cl sample.

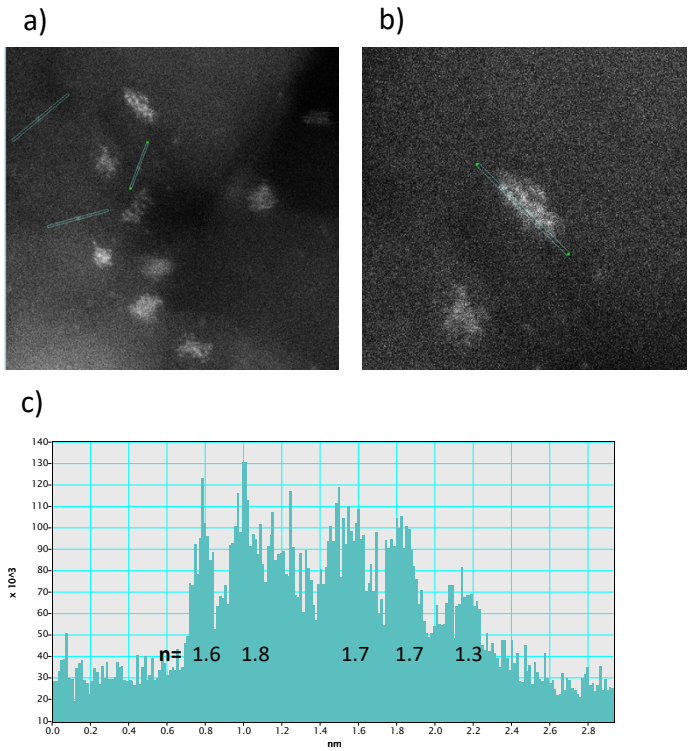


Figure S4. Detail of nanoparticle morphological study based on the analysis of the HAADF intensity for 1%Pt/P-egg-0.1%Cl, a) three single atom reference paths, b) path through nanoparticle including five potential "stacks" of atoms, c) intensity graph for path of b) with the calculated n for each "stack".

2. Pt and Cl loading of the experimental catalysts

Table S2. Platinum loading evaluated by XRF and calculated surface coverage of P-egg and T-flat impregnated and calcined materials.

	P-egg - Impregnated + calcined	
	$\%_{w/w}$Pt	Pt/nm²
0.3%Pt/ P-egg	1.37 ± 0.03	1.29 ± 0.07
1%Pt/ P-egg	1.41 ± 0.03	1.34 ± 0.07
	T-flat - Impregnated + calcined	
	$\%_{w/w}$Pt	Pt/nm²
0.3%Pt/ T-flat	1.18 ± 0.03	1.37 ± 0.08
1%Pt/ T-flat	1.12 ± 0.03	1.30 ± 0.07

Table S3. Chlorine loading measured by XRF and calculated surface coverage of oxide and reduced PuralSB3 and TH100 catalysts.

PuralSB3				
	Oxide		Reduced	
	$\%_{w/w}$Cl	Cl/nm²	$\%_{w/w}$Cl	Cl/nm²
0.3%Pt/PuralSB3-**1.4%Cl**	1.50 ± 0.04	1.42 ± 0.08	1.25 ± 0.03	1.18 ± 0.07
0.3%Pt/PuralSB3-**0.1%Cl**	0.108 ± 0.006	0.101 ± 0.008	0.107 ± 0.006	0.10 ± 0.01
1%Pt/PuralSB3-**1.4%Cl**	1.51 ± 0.04	1.44 ± 0.09	1.18 ± 0.03	1.11 ± 0.06
1%Pt/PuralSB3-**0.1%Cl**	0.163 ± 0.007	0.15 ± 0.01	0.150 ± 0.007	0.14 ± 0.01
TH100				
	Oxide		Reduced	
	$\%_{w/w}$Cl	Cl/nm²	$\%_{w/w}$Cl	Cl/nm²
0.3%Pt/TH100-**1.4%Cl**	1.33 ± 0.03	1.54 ± 0.08	1.08 ± 0.03	1.25 ± 0.07
0.3%Pt/TH100-**0.1%Cl**	0.132 ± 0.006	0.15 ± 0.01	0.132 ± 0.006	0.15 ± 0.01
1%Pt/TH100-**1.4%Cl**	1.27 ± 0.03	1.48 ± 0.08	1.02 ± 0.03	1.18 ± 0.07
1%Pt/TH100-**0.1%Cl**	0.212 ± 0.008	0.24 ± 0.02	0.214 ± 0.008	0.25 ± 0.02

3. Calculated Pt and Cl coverage for model platelets

The calculated Pt and Cl coverage listed in Table 1 is obtained as follows:

$$X/nm^2(for\ n\%_{w/w}X) = \frac{n/MM(X) * N_A}{(100-n) * Calculated\ specific\ area}$$

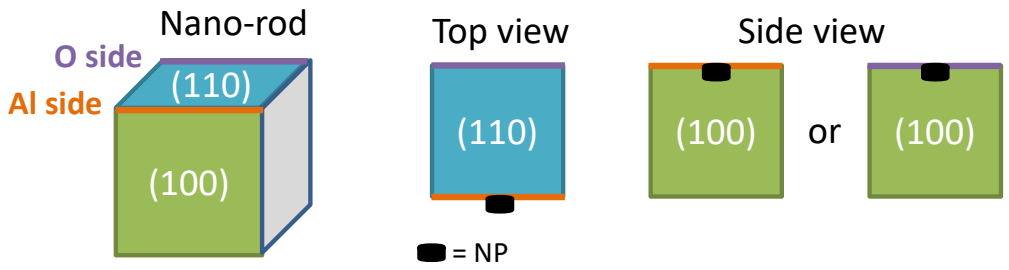
With:

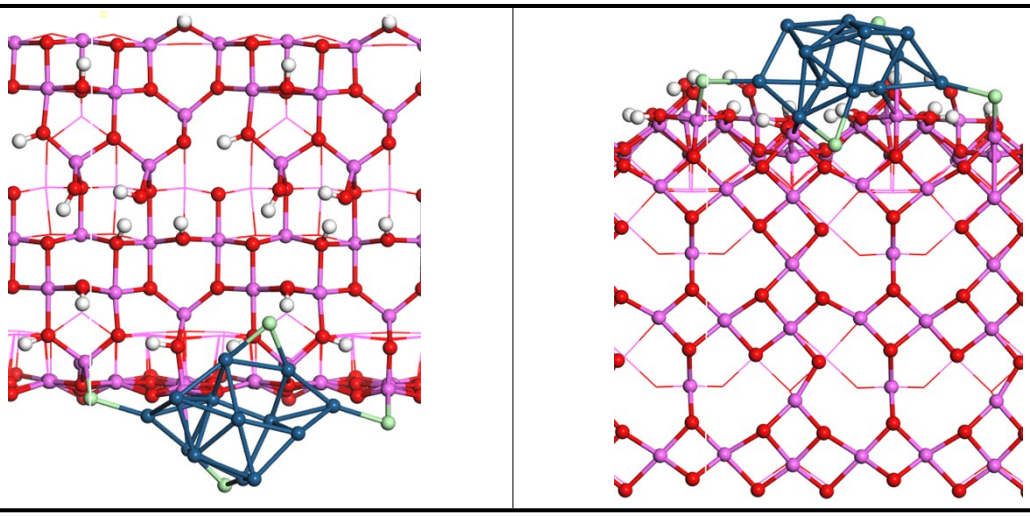
$$Calculated\ specific\ area = \frac{Platelet\ surface\ area}{Platelet\ volume * \rho}$$

MM(X) is the molar mass of the element X. Platelet surface area and volume are calculated from the model platelet dimensions (*a, b,c* for T-flat and *a* for P-egg) and the density ρ of gamma-alumina used was of 4 g/cm^3.

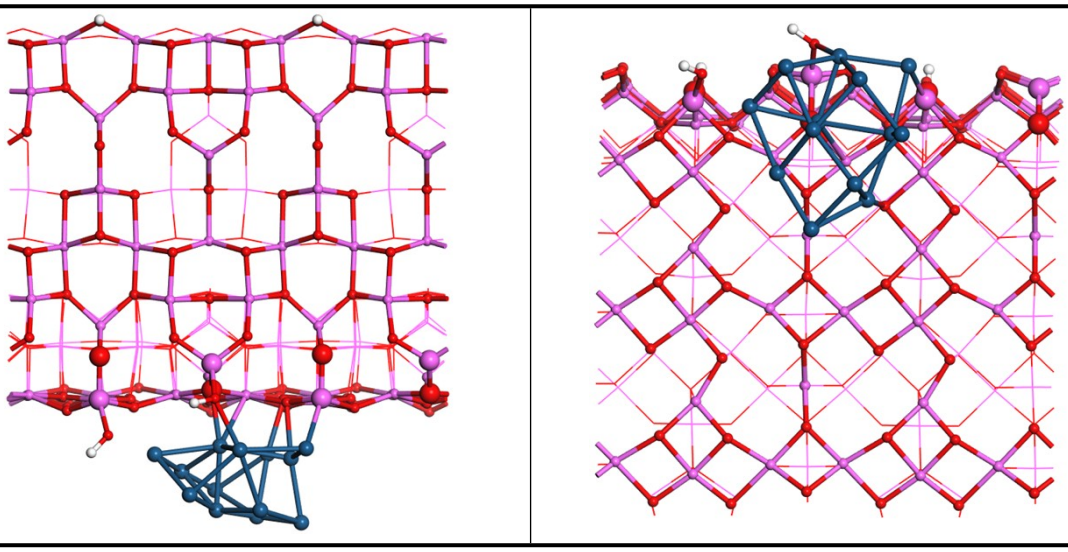
4. Pt_{13}/edge models described in ref 3

Table S4. Optimized Pt13/edge models, configuration A and B, from ref [2] (with permission). 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.





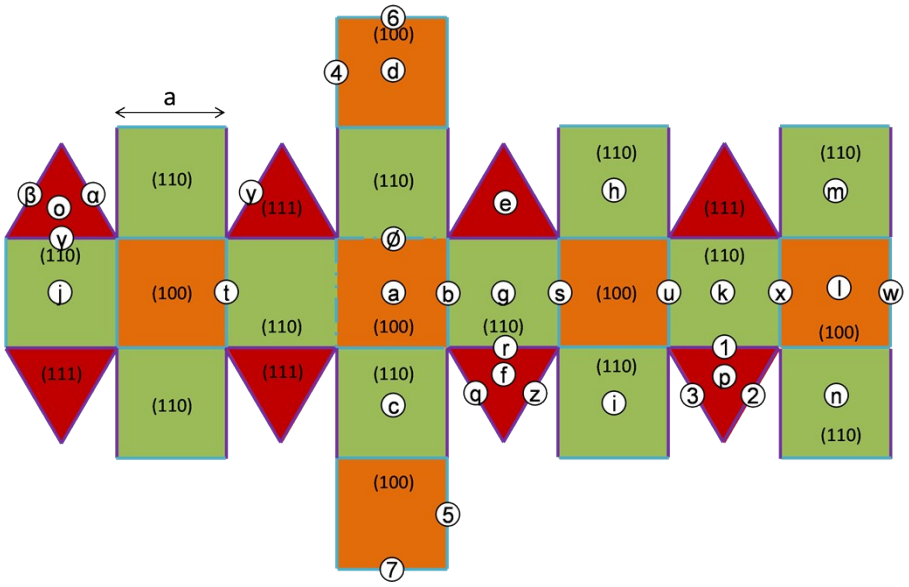
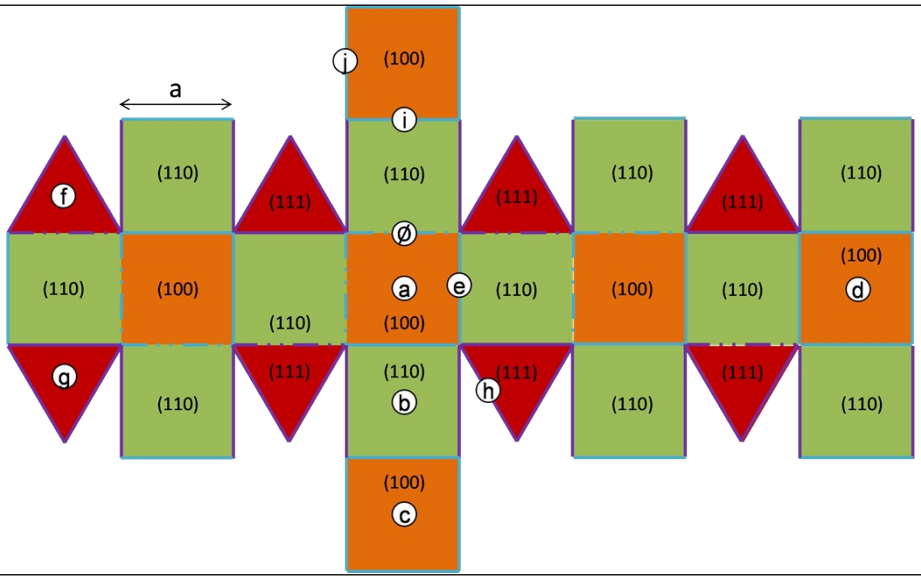
Configuration A

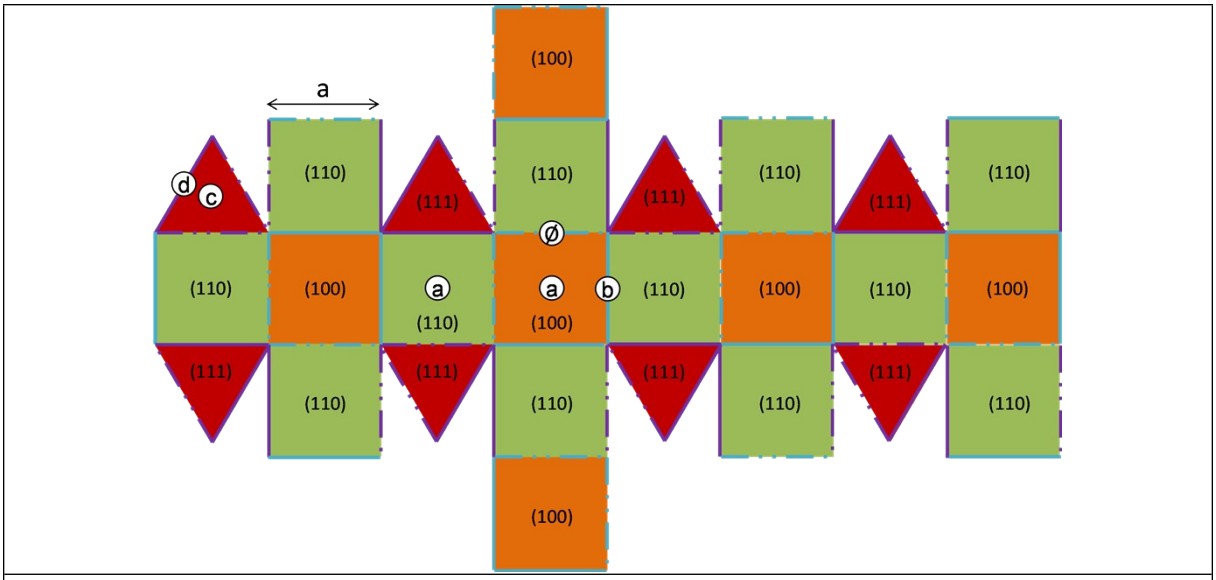


Configuration B

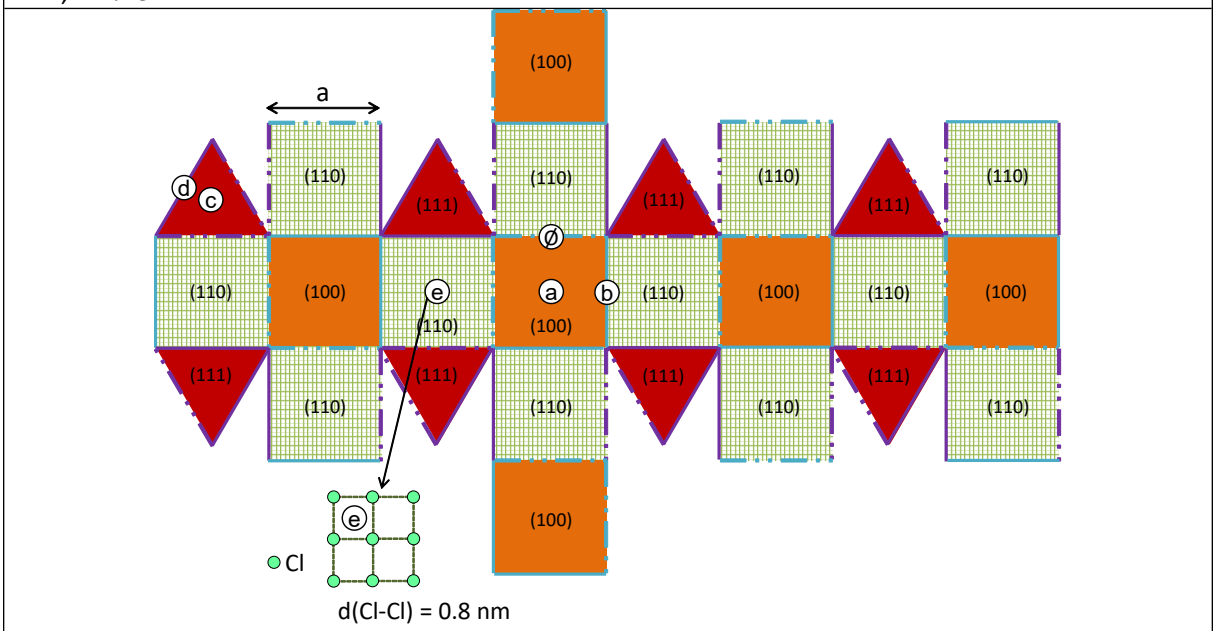
5. Polyhedral nets with Pt NP fixed positions

Table S5. Polyhedral net of the parallelepiped platelet model of P-egg morphology for all the k and %Cl explored, with fixed Pt NP positions considered for distance estimation shown in the white icons. Chlorinated edges are depicted by broken lines, non-chlorinated edges by full lines. Chlorinated surfaces are depicted by a mesh pattern.

P-egg
k=1; 0.1%Cl

k=1; 0.5%Cl

k=1; 1.2%Cl - k=1.5; 0.52%Cl - k=0.5; 4.5%Cl (edge saturation)

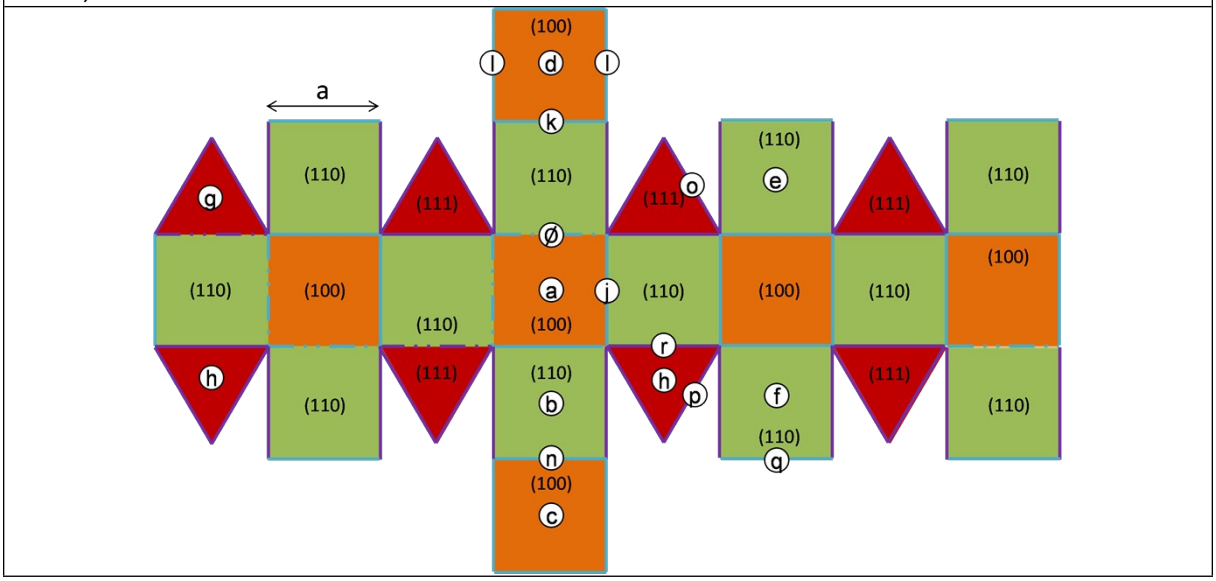


k=1; 1.4%Cl

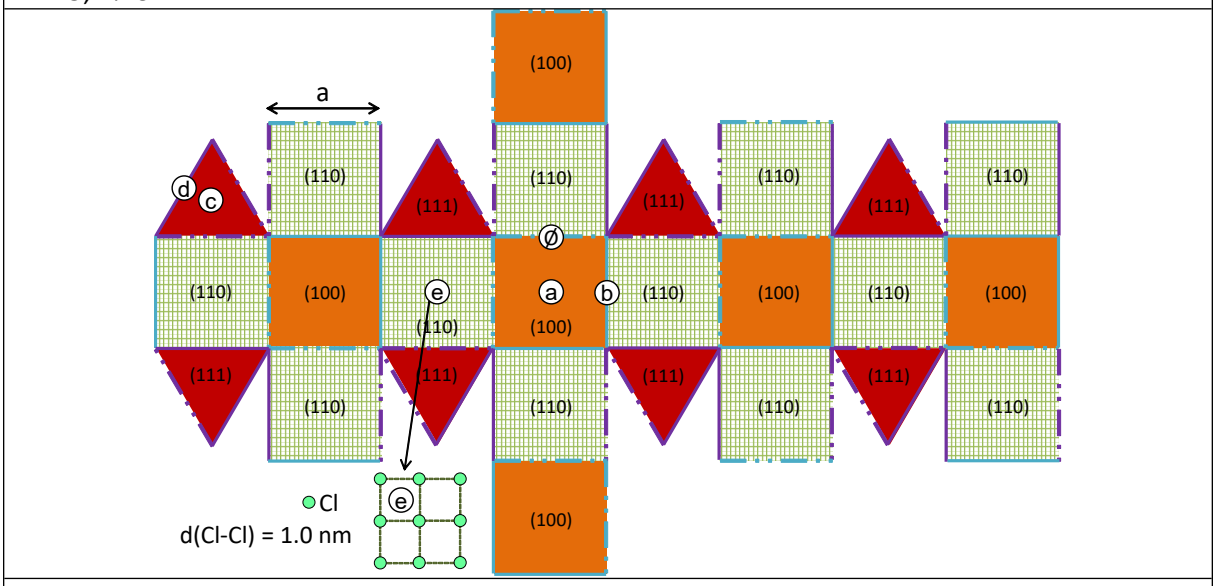


d(Cl-Cl) = 0.8 nm

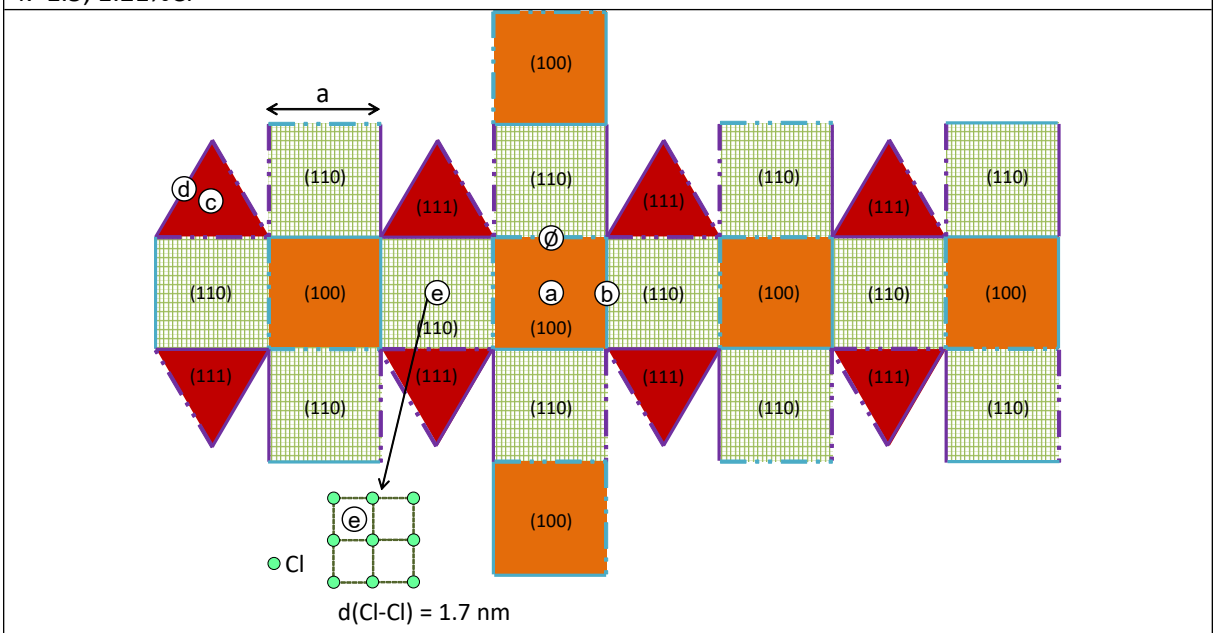
k=1.5; 0.5%Cl



k=1.5; 1%Cl



k=1.5; 1.21%Cl



k=0.5; 1%Cl

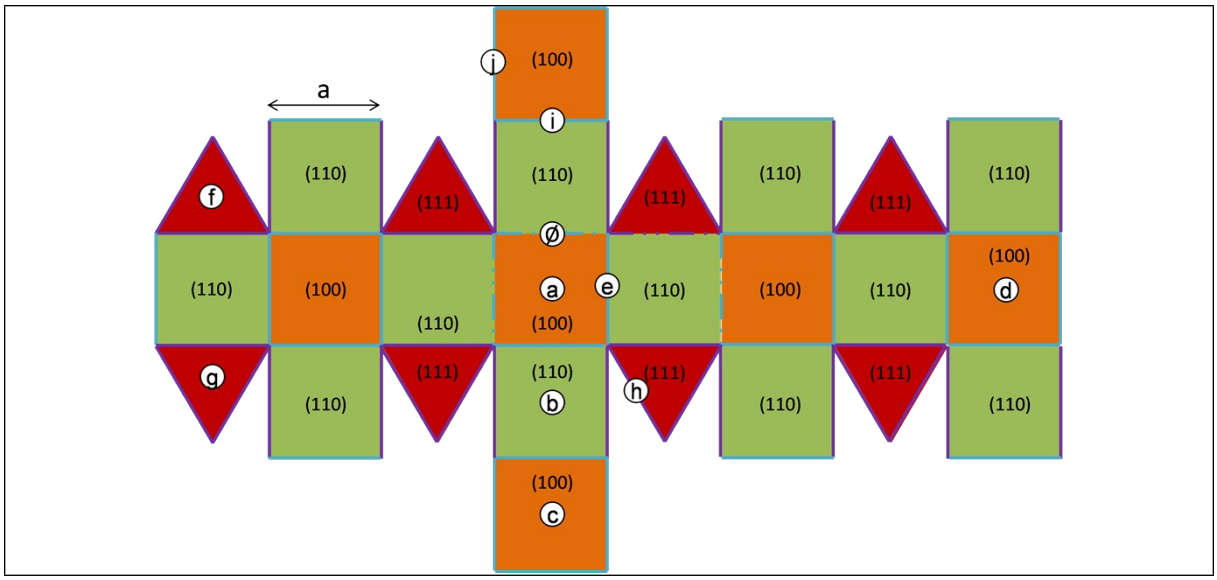
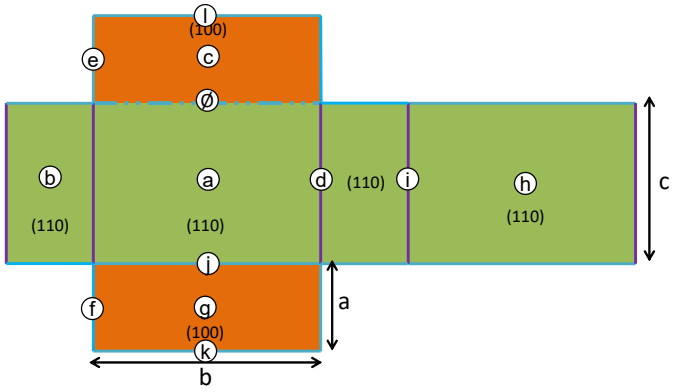
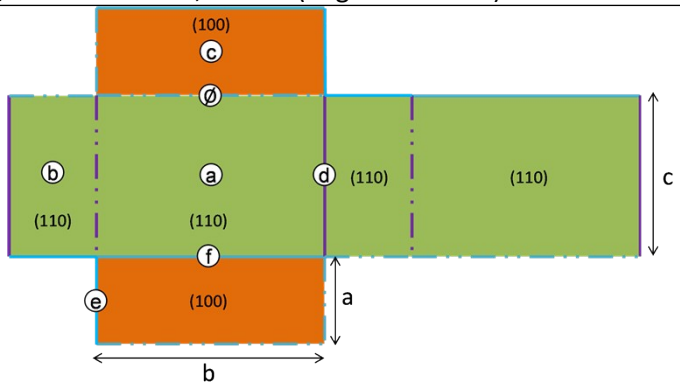
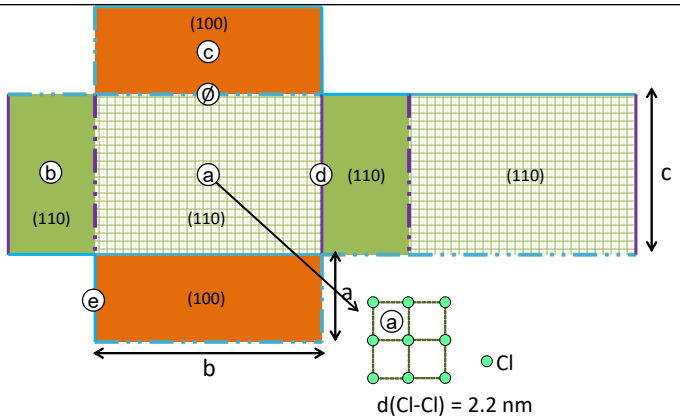


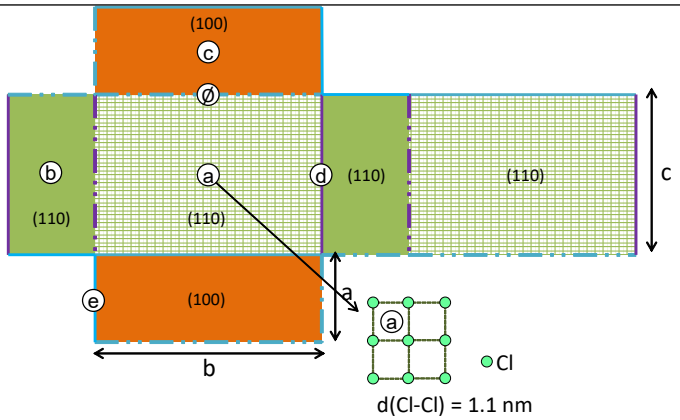
Table S6. Polyhedral net of the parallelepiped platelet model of T-flat morphology for all the k and %Cl explored, with fixed Pt NP positions considered for distance estimation shown in the white icons. Chlorinated edges are depicted by broken lines, non-chlorinated edges by full lines. Chlorinated surfaces are depicted by a mesh pattern.

T-flat
k=1; 0.1%Cl

k=1; 0.35%Cl - k=1.5; 0.15%Cl - k=0.5; 1.4%Cl (edge saturation)

k=1; 0.5%Cl



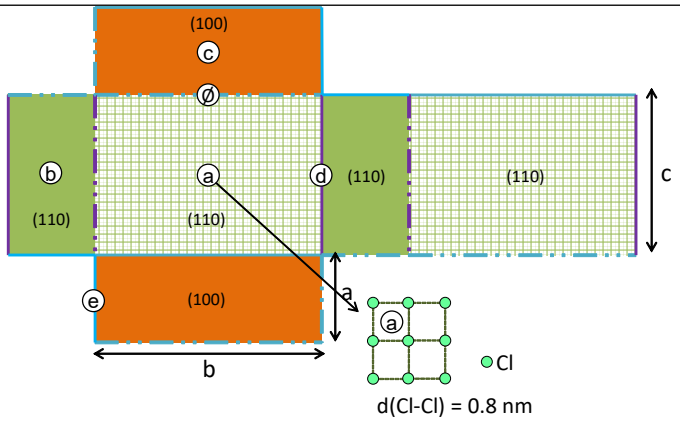
d(Cl-Cl) = 2.2 nm

k=1; 1%Cl



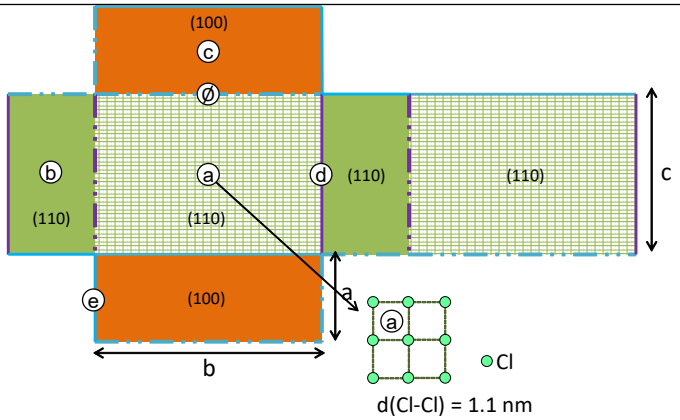
d(Cl-Cl) = 1.1 nm

k=1; 1.4%Cl



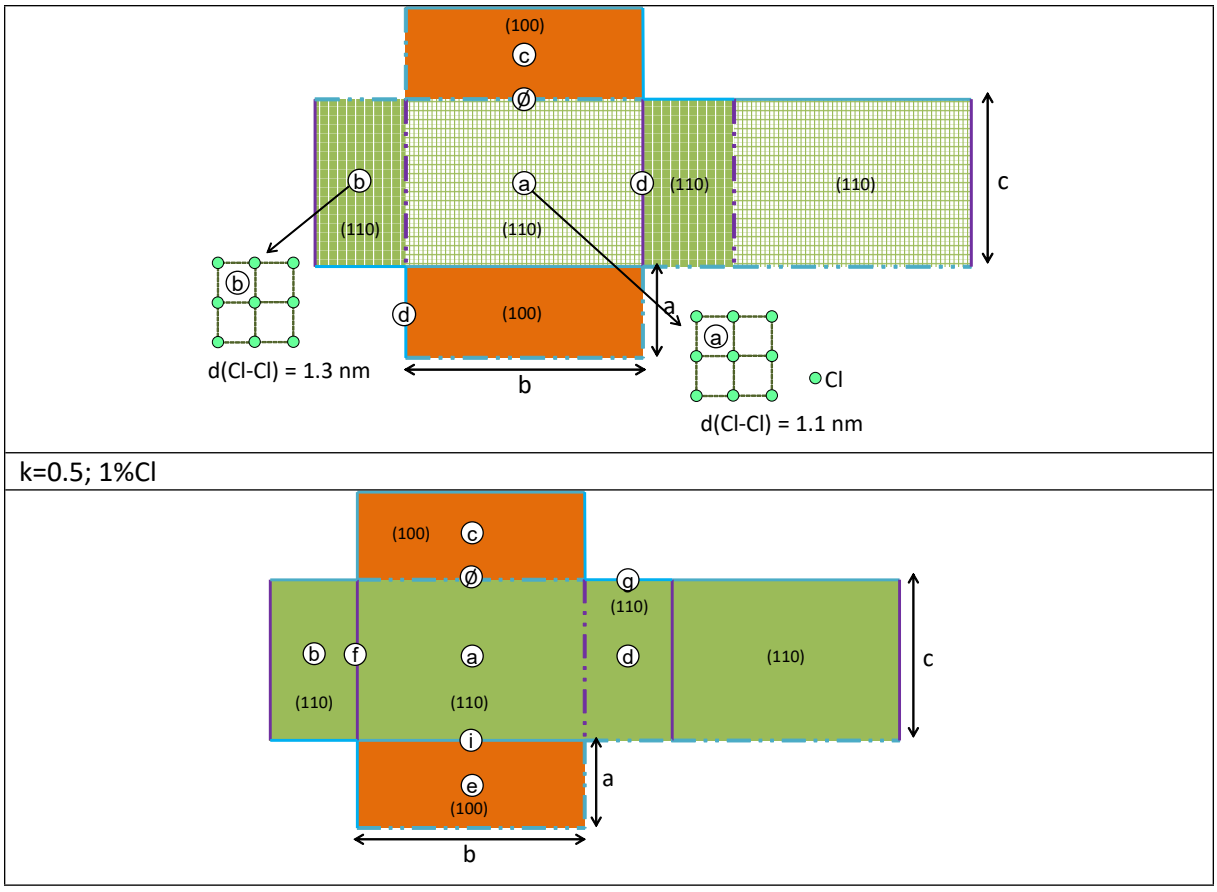
d(Cl-Cl) = 0.8 nm

k=1.5; 0.52%Cl



d(Cl-Cl) = 1.1 nm

k=1.5; 1%Cl



6. Estimation of Pt NP-Cl distances

Table S7. Estimation of Pt NP-Cl distances for P-egg for all k and %Cl considered.

P-egg								
k=1			**k=1.5**			**k=0.5**		
1.4%Cl			**1.21%Cl**			**1%Cl**		
Pt NP fixed position	**Distance PtNP-Cl (nm)**	**Exposition proportion**	**Pt NP fixed position**	**Distance PtNP-Cl (nm)**	**Exposition proportion**	**Pt NP fixed position**	**Distance PtNP-Cl (nm)**	**Exposition proportion**
Surface Positions			Surface Positions			Surface Positions		
e	1.23	0.56	e	0.58	0.56	a)	0.70	0.23
a	1.40	0.28	a	2.09	0.28	b)	0.18	0.14
c	0.81	0.16	c	1.20	0.16	c)	2.20	0.05
Surface average distance (nm)	1.21		Surface average distance (nm)	1.10		d)	2.09	0.14
Edge Positions			Edge Positions			e)	3.48	0.09
Ø	0.23	0.5	Ø	0.23	0.5	f)	1.90	0.09
b	0.90	0.25	b	0.9	0.25	g)	2.80	0.09
d	0.90	0.25	d	0.9	0.25	h)	0.40	0.02
Edge average distance (nm)	0.68		Edge average distance (nm)	0.57		i)	0.80	0.06
Global average distance	0.79		Global average distance	0.68		j)	1.92	0.04
						k)	3.00	0.04
1.2%Cl edge saturation			**1%Cl**			Surface	0.85	

Pt NP fixed position	Distance PtNP-Cl (nm)	Exposition proportion
Surface Positions		
a	1.40	0.84
c	0.80	0.16
Surface average distance (nm)	1.30	
Edge Positions		
Ø	0.23	0.5
b	1.40	0.25
d	1.40	0.25
Edge average distance (nm)	0.82	
Global average distance	0.92	

0.5%Cl

Pt NP fixed position	Distance PtNP-Cl (nm)	Exposition proportion
Surface Positions		
a)	1.40	0.42
b)	1.98	0.28
c)	4.20	0.09
d)	1.98	0.05
f)	0.81	0.08
g)	1.62	0.31
Surface average distance (nm)	1.82	
Edge Positions		
Ø	0.23	0.21
e)	1.40	0.54
h)	2.42	0.08
i)	2.80	0.06
j)	3.13	0.10
Edge average distance (nm)	1.51	
Global average distance	1.58	

0.1%Cl

Pt NP fixed position	Distance PtNP-Cl (nm)	Exposition proportion
Surface Positions		
e	2.09	0.56
a	0.70	0.28
c	1.20	0.16
Surface average distance (nm)	1.17	
Edge Positions		
Ø	0.23	0.5
b	0.90	0.25
d	0.90	0.25
Edge average distance (nm)	0.57	
Global average distance	0.70	

0.52%Cl edge saturation

Pt NP fixed position	Distance PtNP-Cl (nm)	Exposition proportion
Surface Positions		
a	2.09	0.84
c	1.20	0.16
Surface average distance (nm)	1.94	
Edge Positions		
Ø	0.23	0.5
b	2.09	0.25
d	2.09	0.25
Edge average distance (nm)	1.16	
Global average distance	1.33	

0.15%Cl

Pt NP fixed position	Distance PtNP-Cl (nm)	Exposition proportion
Surface Positions		
a)	2.09	0.37
b)	2.95	0.19
c)	8.60	0.09
d)	6.26	0.09
e)	5.70	0.05
average distance (nm)		
Edge Positions		
Ø	0.23	0.08
l)	0.70	0.25
m)	1.39	0.06
n)	1.56	0.10
o)	2.78	0.06
p)	4.17	0.02
q)	2.02	0.04
r)	2.87	0.02
s)	1.56	0.06
t)	2.03	0.04
u)	2.60	0.04
v)	3.17	0.04
x)	3.48	0.08
y)	2.09	0.08
Edge average distance (nm)	1.73	
Global average distance	1.54	

4.5%Cl edge saturation

Pt NP fixed position	Distance PtNP-Cl (nm)	Exposition proportion
Surface Positions		
a	0.70	0.84
c	0.40	0.16
Surface average distance (nm)	0.65	
Edge Positions		
Ø		0.23 0.5
b	0.70	0.25
d	0.70	0.25
Edge average distance (nm)	0.46	
Global average distance	0.50	

a)	1.40	0.14
c)	1.98	0.09
d)	4.20	0.09
e)	1.89	0.06
f)	3.87	0.02
g)	4.43	0.09
h)	3.82	0.14
i)	5.64	0.05
j)	7.00	0.05
k)	9.80	0.15
l)	9.80	0.05
m)	14.23	0.05
n)	7.14	0.05
o	6.03	0.06
p)	16.21	0.02
Surface average distance (nm)	4.91	
Edge Positions		
Ø	0.23	0.04
b)	1.40	0.17
q)	3.13	0.02
r)	4.20	0.02
s)	3.13	0.04
t)	2.80	0.04
u)	5.77	0.02
v)	5.60	0.02
x)	8.52	0.02
w)	8.40	0.02
z)	4.08	0.02
y)	2.42	0.06
α	5.22	0.06
β	6.48	0.06
γ	7.00	0.08
1)	9.80	0.06
2)	8.03	0.02
3)	6.76	0.02
4)	4.20	0.13
5)	5.05	0.02
6)	5.60	0.02
7)	5.77	0.02
Edge average distance (nm)	4.57	
Global average distance (nm)	4.65	

f)	8.41	0.05
g)	1.20	0.04
h)	2.41	0.08
i)	5.77	0.04
Surface average distance (nm)	2.57	
Edge Positions		
Ø	0.23	0.15
j)	2.09	0.42
k)	4.17	0.06
l)	6.07	0.02
n)	4.67	0.17
o)	3.61	0.04
p)	6.08	0.04
q)	7.52	0.02
r)	6.26	0.08
Edge average distance (nm)	3.15	
Global average distance (nm)	3.02	

Table S8. Estimation of Pt NP-Cl distances for P-egg for all k and %Cl considered.

T-flat								
k=1			**k=1.5**			**k=0.5**		
1%Cl			**1%Cl**			**1%Cl**		
Pt NP fixed position	**Distance PtNP-Cl (nm)**	**Exposition proportion**	**Pt NP fixed position**	**Distance PtNP-Cl (nm)**	**Exposition proportion**	**Pt NP fixed position**	**Distance PtNP-Cl (nm)**	**Exposition proportion**
Surface Positions			Surface Positions			Surface Positions		
a	0.74	0.58	a	0.58	0.58	a)	2.25	0.58
b	2.00	0.16	b	0.69	0.16	b)	3.76	0.08
c	2.00	0.26	c	3.00	0.26	c)	2.25	0.13
Surface average distance (nm)	1.27		**Surface average distance (nm)**	1.23		d)	1.00	0.08
Edge Positions			Edge Positions			e)	3.63	0.13
Ø	0.23	0.5	Ø	0.23	0.50	**Surface average distance (nm)**	2.45	
d	0.9	0.43	d	0.90	0.50	Edge Positions		
e	2.00	0.07	**Edge average distance (nm)**	0.57		Ø	0.23	0.38
Edge average distance (nm)	0.65		**Global average distance**	0.71		f)	2.25	0.25
Global average distance	0.78					g)	1.00	0.11
			0.15%Cl edge saturation			i)	3.63	0.13
0.35%Cl edge saturation			**Pt NP fixed position**	**Distance PtNP-Cl (nm)**	**Exposition proportion**	j)	4.14	0.13
Pt NP fixed position	**Distance PtNP-Cl (nm)**	**Exposition proportion**	Surface Positions			**Edge average distance (nm)**	1.77	
Surface Positions			a	6.75	0.58	**Global average distance**	1.92	
a	4.50	0.58	b	3.00	0.16			
b	2.00	0.16	c	3.00	0.26	**1.4%Cl edge saturation**		
c	2.00	0.26	**Surface average distance (nm)**	5.18		**Pt NP fixed position**	**Distance PtNP-Cl (nm)**	**Exposition proportion**
Surface average distance (nm)	3.45		Edge Positions			Surface Positions		
Edge Positions			Ø	0.23	0.50	a)	2.25	0.58
Ø	0.23	0.50	d	6.75	0.16	b)	1.00	0.16
d	4.50	0.16	e	3.00	0.07	c)	1.00	0.26
e	2.00	0.07	f	10.88	0.26	**Surface average distance (nm)**	1.73	
f	7.25	0.26	**Edge average distance (nm)**	4.30		Edge Positions		
Edge average distance (nm)	2.91		**Global average distance**	4.50		Ø	0.23	0.50
Global average distance	3.03					d)	2.25	0.16
			0.52%Cl			e)	1.00	0.07
0.5%Cl			Surface Positions			f)	3.63	0.26
Pt NP fixed position	**Distance PtNP-Cl (nm)**	**Exposition proportion**	a	0.81	0.58	**Edge average distance (nm)**	1.51	

Surface Positions		
a	1.53	0.58
b	2.00	0.16
c	2.00	0.26
Surface average distance (nm)	1.73	
Edge Positions		
Ø	0.23	0.50
d	0.90	0.43
e	2.00	0.07
Edge average distance (nm)	0.65	
Global average distance	0.88	

0.1%Cl

Pt NP fixed position	**Distance PtNP-Cl (nm)**	**Exposition proportion**
Surface Positions		
a)	4.50	0.29
h)	12.12	0.29
b)	4.92	0.16
c)	2.00	0.13
g)	11.00	0.13
Surface average distance (nm)	7.30	
Edge Positions		
Ø	0.23	0.13
d	7.25	0.16
j	2.00	0.13
e	2.00	0.07
f	11.00	0.07
i	6.02	0.16
l	4.00	0.13
k	13.00	0.13
Edge average distance (nm)	5.65	
Global average distance	6.01	

1.4%Cl

Pt NP fixed position	**Distance PtNP-Cl (nm)**	**Exposition proportion**
Surface Positions		
a	0.58	0.58
b	3.00	0.16
c	3.00	0.26
Surface average distance (nm)	1.73	
Edge Positions		
Ø	0.23	0.50
d	0.90	0.43
e	3.00	0.07
Edge average distance (nm)	0.72	
Global average distance	0.94	

Global average distance	1.56	

b	2.00	0.16
c	2.00	0.26
Surface average distance (nm)	1.18	
Edge Positions		
Ø	0.23	0.50
d	0.90	0.43
e	2.00	0.07
Edge average distance (nm)	0.65	
Global average distance	0.76	

Table S9. Calculated chlorine surface loadings for each model platelet morphology, k and %Cl.

Cl/nm²								
k=0.5			k=1			k=1.5		
%w/wCl	T-flat	P-egg	%w/wCl	T-flat	P-egg	%w/wCl	T-flat	P-egg
1	0.40	0.39	0.1	0.08	0.08	0.15	0.18	0.18
1.4	0.57	-	0.35	0.28	-	0.52	0.63	0.61
4.5	-	1.83	0.5	0.40	0.39	1	1.21	1.18
			1	0.81	-	1.21	1.47	1.43
			1.2	-	0.94			
			1.4	1.14	1.10			

References

1 A. T. F. Batista, D. Wisser, T. Pigeon, D. Gajan, F. Diehl, M. Rivallan, L. Catita, A.-S. Gay, A. Lesage, C. Chizallet and P. Raybaud, 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 A. T. F. Batista, W. Baaziz, A.-L. Taleb, J. Chaniot, M. Moreaud, C. Legens, A. Aguilar-Tapia, O. Proux, J.-L. Hazemann, F. Diehl, C. Chizallet, A.-S. Gay, O. Ersen and P. Raybaud, Atomic Scale Insight into the Formation, Size, and Location of Platinum Nanoparticles Supported on γ-Alumina, *ACS Catal.*, 2020, **10**, 4193–4204.

3 P. D. Nellist and S. J. Pennycook, Direct Imaging of the Atomic Configuration of Ultradispersed Catalysts, *Science*, 1996, **274**, 413–415.