Electronic Supplementary Material

Machine learning-guided discovery of γ-Al_2O_3 as defect-rich structural ensemble governs single-atom pt catalysis

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1 Computational Details

1.1 Calculation Parameters for Database Construction

Additional computational details are provided here to complement the main text. Spin-polarized DFT calculations were performed using Vienna Ab initio Simulation Package (VASP, 5.4.4 version), [1] with the Perdew–Burke–Ernzerhof (PBE). [2] The projector augmented wave (PAW) [3, 4] method was employed to describe core electrons. Plane wave expansion was used for valence electronic wave functions with a cutoff energy of 520 eV, while the convergence of force as well as energy was set as 0.02 eV/Å and 10^{-6} eV respectively. Periodic boundary conditions are set, resulting in a periodically repeated infinite system. A vacuum layer of at least 15Å was added to avoid interactions between periodic image and gaussian smearing was used. The self-consistent electronic energy is achieved through iterative matrix diagonalization scheme, following a constrained band-by-band residuum minimization technique. Brillouin zone integrations were performed using a Γ-centered $1 \times 1 \times 1$ Monkhorst–Pack grid [5] for DFT-SSW sampling, Γ-centered $3 \times 3 \times 3$ Monkhorst–Pack grid is used for global dataset refining, the geometry optimization is performed with a conjugate–gradient

algorithm, the cell shape and atomic positions were optimized while keeping the cell volume fixed.

1.2 Calculation Details for Transition State

Transition states were determined using the climbing image nudged elastic band (CI−NEB) method, [6, 7] followed by further refinement using the dimer method. The initial reaction pathways were constructed with six intermediate images between the initial and final states. A spring constant of -5 eV/$Å^2$ was used to maintain an even distribution of images along the reaction pathway. The forces acting on each image were minimized to below 0.02 eV/Å.

The dimer method [8] was employed to accurately locate saddle points without requiring a predefined reaction coordinate. The improved dimer algorithm was used, with a rotational force convergence criterion of 5×10^{-3} eV/Å and a maximum rotation step of 4. The initial guess for transition states was obtained from CI−NEB calculations.

All calculations were performed using spin-polarized density functional theory as implemented in VASP. The exchange–correlation interactions were described using the BEEF-vdW functional. [9] which incorporates van der Waals interactions self-consistently. The BEEF-vdW functional was employed due to its improved description of surface energetics and adsorption properties. The PAW method was used to describe core electrons, and a plane-wave cutoff energy of 400 eV was applied.

2. Neural Network Potential Details

The initial raw dataset contains over 450,000 structures generated from SSW−DFT simulations. [10] To construct a high-quality training database while maintaining computational efficiency, configurations were randomly selected and recalculated using high-accuracy DFT settings. This procedure yielded a refined dataset of around 10,000 structures, which captures the most representative atomic environments on the potential energy surface. The resulting dataset was then used as the training set for fitting a fourth-generation high-dimensional neural network potential (HDNNP) [11, 12] by LASP platform, [13] in which the total energy of the system is expressed as a sum of atomic contributions described by local structural descriptors. This framework enables an accurate and transferable representation of the potential energy surface for complex oxide systems. The details of the structural descriptors we used are shown in Table S2 and Table S3.

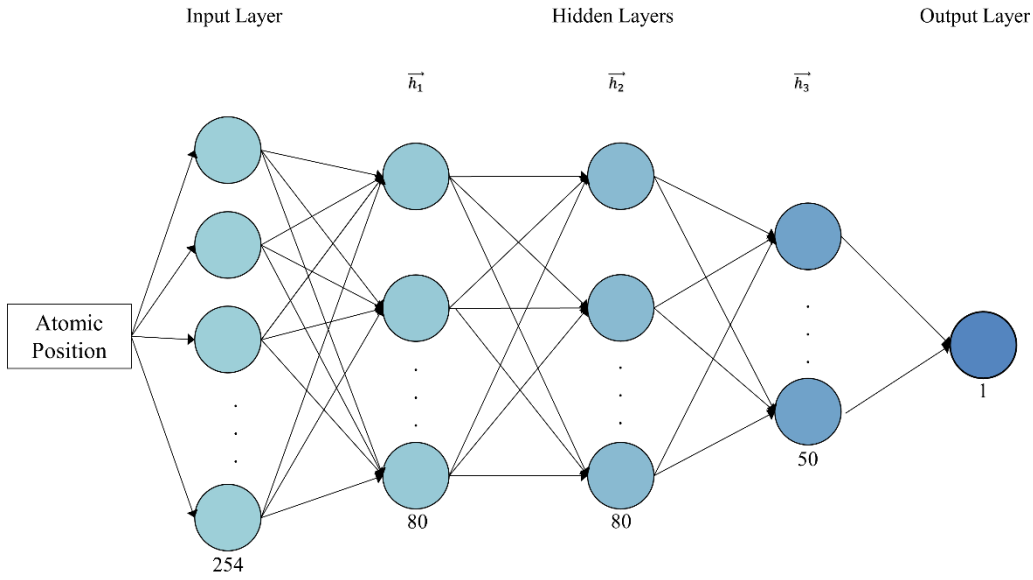

Fig. S1 Neural Network's Architecture

Table S1 Number of nodes for each layer

Layers	Input	Hidden 1	Hidden 2	Hidden 3	Output
Number of Nodes	254	80	80	50	1

Table S2 Number of SD-type for each PTSDs descriptor

	S1	S2	S3	S4	S5	S6
Number of SD-type	54	40	46	48	36	10

Table S3 Range of the adjustable parameters of PTSDs

	S1	S2	S3	S4	S5	S6
rc	1.3~7.5	2~6.8	2~6.5	3~6.5	2.8~4.5	2~3.4
n	-2~8	2~8	2~4	2	-2~2	2

m	–	–	-2~8	-2~8	2~4	2
p	–		–	4~8	2~4	2~4
L	–	2~6	–	–	2~6	–
ξ	–	–	2~4	2~4	–	4
λ	–	–	-1~1	-1~1	–	-1~1

Table S4 Result of the NN potential

	Energy/(meV/atom)	Force/(eV/Å)
RMS	3.601	0.139
max	169.338	9.931

2.1 Initial Structures for SSW

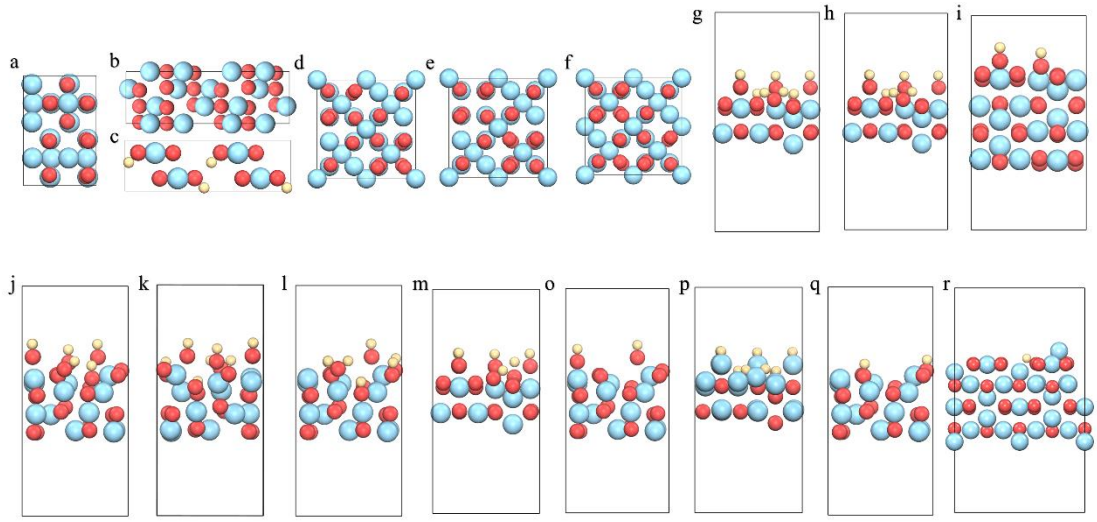

Fig. S2 Initial input structures for DFT-SSW sampling: (a) θ-Al_2O_3 (b) α-Al_2O_3 (c) AlOOH (d to f) Self-build spinel models with vacancies (g to f) surface structures of Digne's model

Table S5 Details of selected structures from initial SSW-generated database for NNP training

Types of Structures	Structural Configuration	Atoms	Number of structures selected

AlOOH	Bulk	4Al+8O+4h	2000
Digne's Model	Bulk	16Al+24O	1500
Digne's Model	Hydroxylated surface model with 2H	16Al+24O+2H	100
Digne's Model	Hydroxylated surface model with 2H+2O	16Al+26O+2H	100
Digne's Model	Hydroxylated surface model with 7H+7O	16Al+31O+7H	300
Digne's Model	Hydroxylated surface model with 10H+2O	16Al+26O+10H	100
Digne's Model	Hydroxylated surface model with 10H+6O	16Al+30O+10H	400
θ-Al_2O_3	Bulk	8Al+12O	1000
α-Al_2O_3	Bulk	12Al+18O	1000
Spinel-based Model	Bulk with mixed defects at 1Td and 2Oh sites	24Al+32O	1000
Spinel-based Model	Bulk with mixed defects at 2Td and 1Oh sites	24Al+32O	1000
Spinel-based Model	Bulk with mixed defects at 3Oh sites	24Al+32O	1000

2.2 Structural Parameters and Full-view of Newly Identified Models

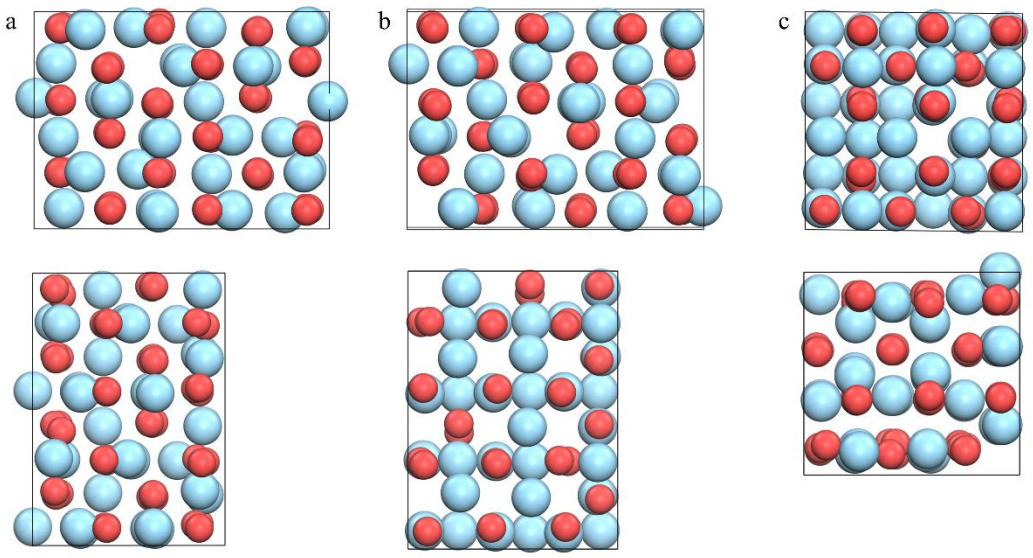

Fig. S3 Structural views of the γ-NAV and γ-AV models (a) Front view, (b) Side view, and (c) Top view, the upper row shows the γ-NAV, and the lower row shows the γ-AV model.

Table S6 Fractional coordinates of γ-NAV Bulk

Atoms	x	y	z
Al1	0.006	0.602	0.245
Al2	0.575	0.586	0.424
Al3	0.172	0.262	0.909
Al4	0.849	0.074	0.410
Al5	0.075	0.762	0.570
Al6	0.101	0.096	0.572
Al7	0.494	0.761	0.098
Al8	0.674	0.432	0.088
Al9	0.672	0.086	0.085
Al10	0.422	0.077	0.900
Al11	0.413	0.088	0.240
Al12	0.083	0.423	0.574
Al13	0.349	0.275	0.584

Atoms	x	y	z
Al14	0.170	0.265	0.255
Al15	0.172	0.919	0.252
Al16	0.422	0.419	0.242
Al17	0.672	0.430	0.742
Al18	0.261	0.597	0.748
Al19	0.761	0.751	0.246
Al20	0.269	0.601	0.409
Al21	0.506	0.746	0.749
Al22	0.242	0.600	0.076
Al23	0.431	0.418	0.911
Al24	0.338	0.927	0.569
Al25	0.838	0.422	0.425
Al26	0.931	0.931	0.084
Al27	0.742	0.749	0.918
Al28	0.994	0.588	0.897
Al29	0.922	0.930	0.752
Al30	0.174	0.917	0.906
Al31	0.601	0.253	0.423
Al32	0.922	0.272	0.095
Al33	0.913	0.261	0.754
Al34	0.769	0.748	0.585
Al35	0.670	0.084	0.739
Al36	0.583	0.926	0.420
O1	0.918	0.092	0.226
O2	0.758	0.910	0.081

Atoms	x	y	z
O3	0.586	0.090	0.261
O4	0.426	0.946	0.079
O5	0.255	0.093	0.249
O6	0.089	0.922	0.078
O7	0.930	0.091	0.594
O8	0.752	0.904	0.415
O9	0.597	0.086	0.561
O10	0.426	0.938	0.403
O11	0.261	0.103	0.582
O12	0.099	0.928	0.433
O13	0.922	0.084	0.907
O14	0.756	0.909	0.747
O15	0.587	0.087	0.912
O16	0.422	0.920	0.742
O17	0.257	0.089	0.909
O18	0.087	0.924	0.731
O19	0.918	0.768	0.233
O20	0.747	0.610	0.085
O21	0.592	0.757	0.267
O22	0.414	0.577	0.081
O23	0.245	0.738	0.244
O24	0.083	0.589	0.069
O25	0.922	0.777	0.599
O26	0.755	0.603	0.418
O27	0.589	0.753	0.568

Atoms	x	y	z
O28	0.422	0.572	0.395
O29	0.255	0.746	0.576
O30	0.089	0.595	0.426
O31	0.914	0.771	0.913
O32	0.745	0.611	0.750
O33	0.583	0.760	0.925
O34	0.418	0.581	0.761
O35	0.247	0.738	0.909
O36	0.091	0.592	0.727
O37	0.922	0.429	0.252
O38	0.757	0.260	0.085
O39	0.587	0.425	0.263
O40	0.422	0.264	0.087
O41	0.256	0.440	0.247
O42	0.087	0.262	0.083
O43	0.926	0.411	0.591
O44	0.761	0.246	0.412
O45	0.599	0.421	0.561
O46	0.429	0.258	0.400
O47	0.252	0.444	0.580
O48	0.097	0.262	0.433
O49	0.926	0.403	0.915
O50	0.755	0.256	0.745
O51	0.589	0.426	0.916
O52	0.418	0.257	0.768

Atoms	x	y	z
O53	0.258	0.439	0.913
O54	0.086	0.258	0.733

Table S7 Fractional coordinates of γ-AV Bulk

Atoms	x	y	z
Al1	0.495	0.319	0.763
Al2	0.250	0.559	0.760
Al3	0.366	0.193	0.097
Al4	0.629	0.566	0.255
Al5	0.243	0.067	0.760
Al6	0.608	0.062	0.582
Al7	0.495	0.819	0.413
Al8	0.752	0.312	0.095
Al9	0.893	0.686	0.763
Al10	0.148	0.316	0.580
Al11	0.871	0.203	0.750
Al12	0.111	0.321	0.927
Al13	0.637	0.059	0.257
Al14	0.628	0.066	0.921
Al15	0.250	0.059	0.416
Al16	0.364	0.438	0.096
Al17	0.148	0.816	0.596
Al18	0.884	0.439	0.432
Al19	0.752	0.812	0.081

Atoms	x	y	z
Al20	0.884	0.939	0.744
Al21	0.002	0.569	0.092
Al22	0.609	0.562	0.594
Al23	0.364	0.938	0.080
Al24	0.512	0.813	0.765
Al25	0.111	0.821	0.249
Al26	0.871	0.703	0.426
Al27	0.243	0.567	0.416
Al28	0.637	0.559	0.919
Al29	0.512	0.314	0.411
Al30	0.366	0.693	0.079
Al31	0.001	0.069	0.084
Al32	0.893	0.186	0.413
O1	0.114	0.942	0.737
O2	0.393	0.816	0.937
O3	0.630	0.952	0.752
O4	0.853	0.819	0.897
O5	0.151	0.920	0.420
O6	0.385	0.811	0.594
O7	0.609	0.952	0.418
O8	0.897	0.806	0.600
O9	0.134	0.943	0.104
O10	0.372	0.814	0.236
O11	0.621	0.949	0.088
O12	0.880	0.803	0.251

Atoms	x	y	z
O13	0.122	0.685	0.741
O14	0.386	0.566	0.936
O15	0.632	0.678	0.756
O16	0.866	0.579	0.927
O17	0.116	0.700	0.420
O18	0.376	0.568	0.584
O19	0.627	0.687	0.415
O20	0.847	0.576	0.574
O21	0.140	0.691	0.109
O22	0.386	0.563	0.246
O23	0.615	0.680	0.090
O24	0.866	0.563	0.269
O25	0.151	0.420	0.756
O26	0.372	0.314	0.941
O27	0.609	0.452	0.758
O28	0.879	0.303	0.925
O29	0.115	0.442	0.439
O30	0.385	0.311	0.582
O31	0.630	0.452	0.424
O32	0.897	0.306	0.576
O33	0.135	0.443	0.073
O34	0.393	0.316	0.239
O35	0.621	0.449	0.088
O36	0.853	0.318	0.279
O37	0.115	0.200	0.756

Atoms	x	y	z
O38	0.386	0.063	0.930
O39	0.627	0.187	0.761
O40	0.866	0.063	0.907
O41	0.122	0.185	0.435
O42	0.376	0.068	0.593
O43	0.632	0.178	0.420
O44	0.846	0.076	0.602
O45	0.139	0.191	0.067
O46	0.386	0.066	0.240
O47	0.615	0.180	0.086
O48	0.866	0.079	0.249

3. Coordination of Surface Al atoms

The distribution of Al coordination environments on γ-Al_2O_3 surfaces shows a clear dependence on surface termination. [14-16] As indicated in the figure S4, solid-filled bars represent the top surface, while dashed bars correspond to the bottom surface. For the γ-NAV and γ-AV models, the presence of bulk defects leads to non-equivalent surface terminations, resulting in distinct coordination environments of surface Al atoms.

In contrast, for the Digne's [15] and Liu's [17] models, the absence of bulk defects and their higher structural symmetry give rise to equivalent surface terminations, leading to similar coordination distributions between the two surfaces.

Overall, these results highlight that the fraction of penta-coordinated Al sites is strongly dependent on both surface structure and termination, reflecting the defect-sensitive nature of γ-Al_2O_3 surfaces.

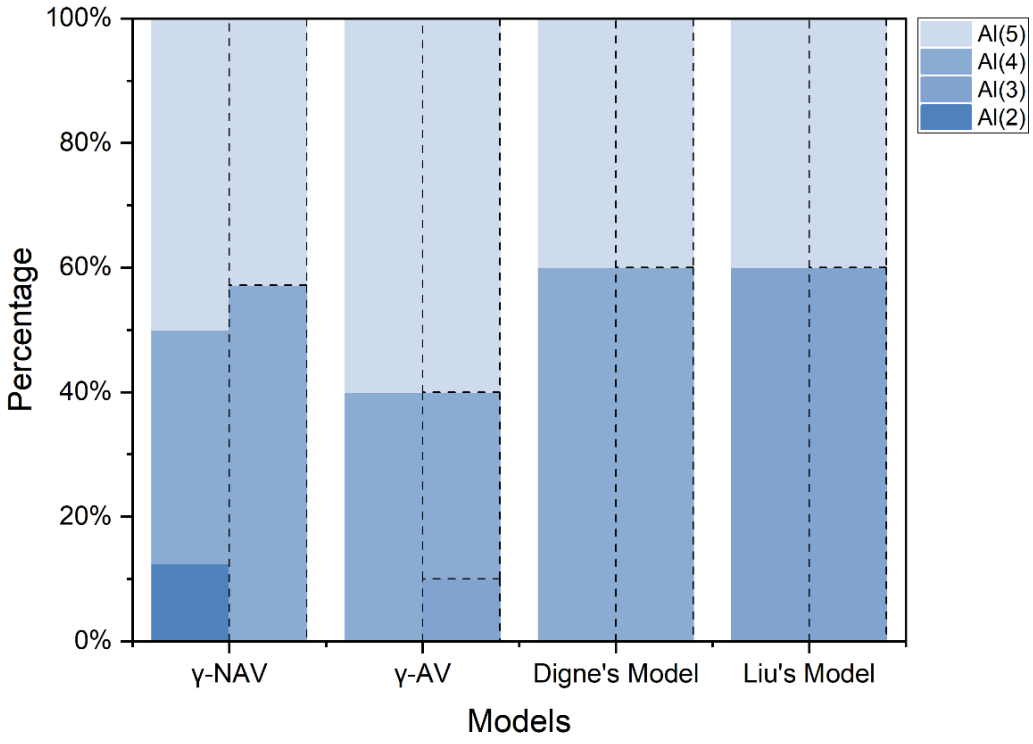

Fig. S4 Distribution of Aluminum Coordination Environments in γ-Al_2O_3 Structural Models

To further illustrate the local surface structures of the newly identified models, additional front and side views of the (100) surfaces of γ-NAV and γ-AV are provided in Fig. S5.

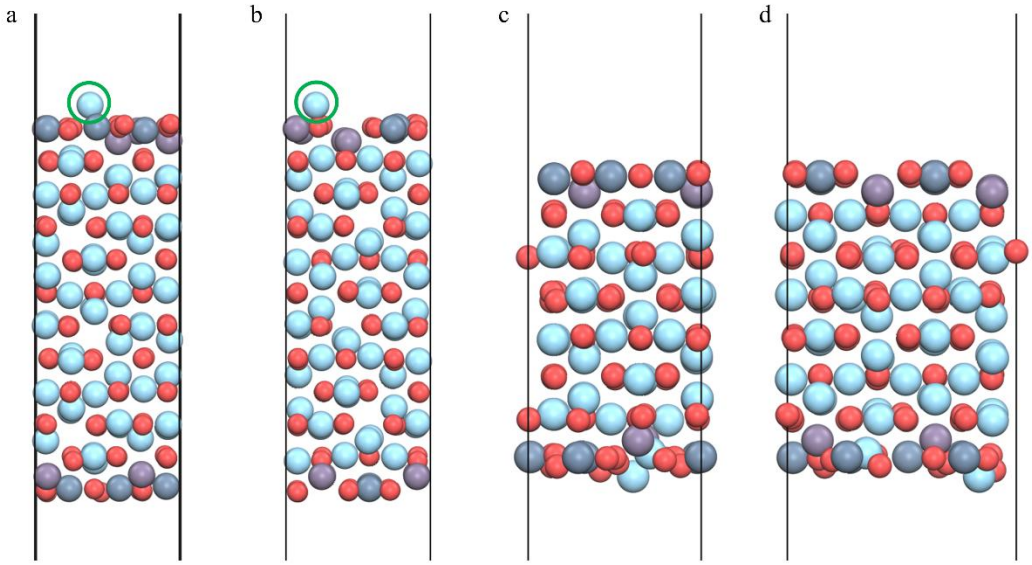

Fig. S5 Front and side views of the (100) surfaces of the γ-NAV and γ-AV models. (a) front view and (b) side view of the γ-NAV model; (c) front view and (d) side view of the γ-AV model. The green circles

indicate the exposed two-coordinated Al sites.

To further visualize the thermodynamically stable surface configurations identified from the phase diagram, the optimized γ-NAV and γ-AV surface structures were analyzed from different viewing directions, as shown in Fig. S6.

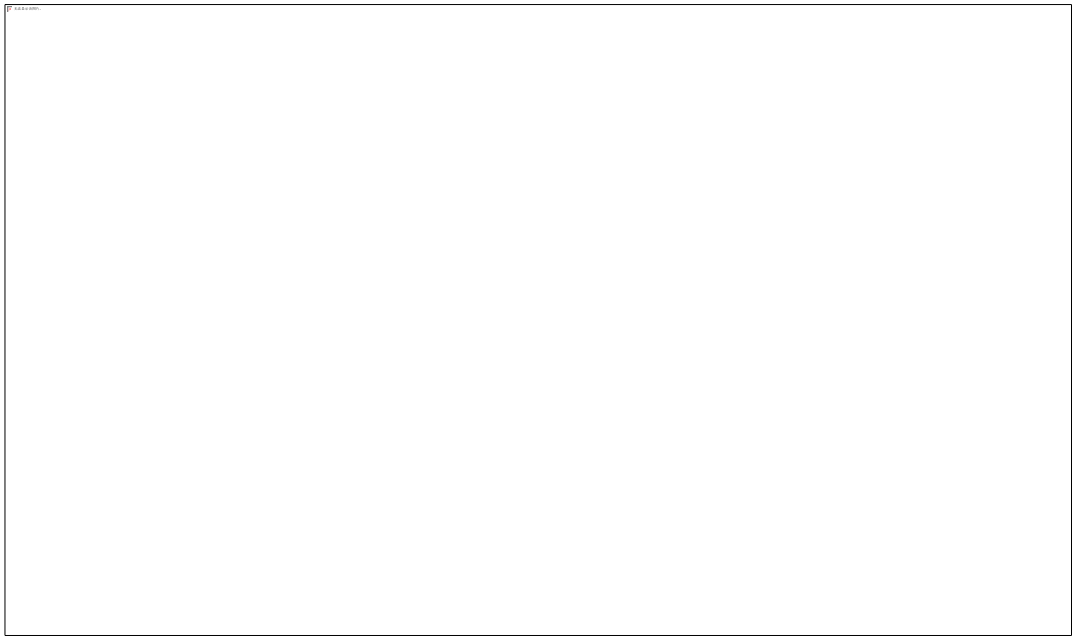

Fig. S6 Optimized surface structures obtained from the surface phase diagram. (a) top view and (b) front view (c) side view of the γ-NAV model; (d) top view and (e) front view (f) side view of the γ-AV model. The green box indicates the exposed penta-coordinated Al sites.

4. Details of XRD simulation

The XRD patterns were simulated using Diamond 5 software under Cu Kα radiation (λ = 1.541Å). The diffraction patterns were calculated in the 2θ range of 15°–75° with a step size of 0.05°, using a pseudo-Voigt peak profile (FWHM = 1°). Lorentz correction was applied, and the intensities were normalized to a maximum value of 100.

5. Pt adsorption structures and Bader charge calculation

5.1 Details of Pt adsorption structures

Table S8 Fractional coordinate of Digne's model with Pt adsorption

Model parameters: a= 11.162Å ; b= 16.807Å ; c= 34.511Å ; $\alpha = \beta = \gamma = 90.0°$

Atoms	x	y	z
Al1	0.189	0.300	0.416
Al2	0.321	0.051	0.588
Al3	0.437	0.050	0.503
Al4	0.062	0.298	0.504
Al5	0.438	0.300	0.416
Al6	0.065	0.050	0.589
Al7	0.288	0.299	0.565
Al8	0.192	0.050	0.447
Al9	0.174	0.461	0.529
Al10	0.315	0.213	0.478
Al11	0.315	0.388	0.478
Al12	0.184	0.138	0.531
Al13	0.036	0.217	0.586
Al14	0.442	0.465	0.419
Al15	0.442	0.136	0.419
Al16	0.033	0.381	0.585
Al17	0.189	0.800	0.416
Al18	0.319	0.513	0.588
Al19	0.433	0.550	0.503
Al20	0.063	0.801	0.504
Al21	0.438	0.800	0.416
Al22	0.055	0.550	0.589
Al23	0.290	0.800	0.565
Al24	0.192	0.550	0.447
Al25	0.184	0.962	0.531

Atoms	x	y	z
Al26	0.315	0.713	0.478
Al27	0.315	0.888	0.478
Al28	0.179	0.640	0.531
Al29	0.032	0.717	0.585
Al30	0.442	0.965	0.419
Al31	0.442	0.636	0.419
Al32	0.035	0.881	0.586
Al33	0.689	0.300	0.416
Al34	0.822	0.050	0.588
Al35	0.937	0.050	0.503
Al36	0.563	0.301	0.504
Al37	0.938	0.300	0.416
Al38	0.564	0.052	0.589
Al39	0.789	0.299	0.565
Al40	0.692	0.050	0.447
Al41	0.682	0.463	0.531
Al42	0.815	0.213	0.478
Al43	0.815	0.388	0.478
Al44	0.684	0.138	0.531
Al45	0.534	0.219	0.586
Al46	0.942	0.465	0.419
Al47	0.942	0.136	0.419
Al48	0.545	0.381	0.586
Al49	0.689	0.800	0.416
Al50	0.819	0.549	0.588

Atoms	x	y	z
Al51	0.934	0.550	0.502
Al52	0.563	0.800	0.505
Al53	0.938	0.800	0.416
Al54	0.569	0.555	0.592
Al55	0.790	0.802	0.564
Al56	0.692	0.550	0.447
Al57	0.684	0.963	0.530
Al58	0.815	0.713	0.478
Al59	0.815	0.888	0.478
Al60	0.683	0.639	0.531
Al61	0.550	0.726	0.590
Al62	0.942	0.965	0.419
Al63	0.942	0.636	0.419
Al64	0.538	0.886	0.586
O1	0.427	0.301	0.591
O2	0.059	0.050	0.416
O3	0.310	0.051	0.535
O4	0.192	0.300	0.471
O5	0.150	0.300	0.595
O6	0.319	0.050	0.413
O7	0.069	0.050	0.533
O8	0.432	0.300	0.474
O9	0.450	0.127	0.598
O10	0.056	0.378	0.411
O11	0.056	0.222	0.411

Atoms	x	y	z
O12	0.459	0.470	0.600
O13	0.293	0.383	0.532
O14	0.196	0.134	0.477
O15	0.196	0.466	0.477
O16	0.297	0.218	0.531
O17	0.183	0.127	0.588
O18	0.322	0.378	0.421
O19	0.322	0.222	0.421
O20	0.171	0.469	0.588
O21	0.057	0.385	0.534
O22	0.431	0.134	0.472
O23	0.431	0.467	0.472
O24	0.061	0.213	0.534
O25	0.430	0.804	0.592
O26	0.059	0.550	0.416
O27	0.303	0.544	0.536
O28	0.192	0.800	0.471
O29	0.151	0.802	0.594
O30	0.319	0.550	0.413
O31	0.066	0.550	0.533
O32	0.432	0.800	0.474
O33	0.503	0.640	0.618
O34	0.056	0.878	0.411
O35	0.056	0.722	0.411
O36	0.450	0.977	0.599

Atoms	x	y	z
O37	0.297	0.882	0.531
O38	0.196	0.634	0.477
O39	0.196	0.966	0.477
O40	0.294	0.718	0.531
O41	0.154	0.637	0.589
O42	0.322	0.878	0.421
O43	0.322	0.722	0.421
O44	0.186	0.976	0.588
O45	0.061	0.887	0.534
O46	0.431	0.634	0.472
O47	0.431	0.967	0.472
O48	0.057	0.715	0.533
O49	0.926	0.299	0.592
O50	0.559	0.050	0.416
O51	0.810	0.050	0.535
O52	0.692	0.300	0.471
O53	0.653	0.299	0.595
O54	0.819	0.050	0.413
O55	0.569	0.051	0.533
O56	0.932	0.300	0.474
O57	0.950	0.125	0.599
O58	0.556	0.378	0.411
O59	0.556	0.222	0.411
O60	0.945	0.473	0.598
O61	0.795	0.382	0.531

Atoms	x	y	z
O62	0.696	0.134	0.477
O63	0.696	0.466	0.477
O64	0.797	0.218	0.531
O65	0.685	0.126	0.588
O66	0.822	0.378	0.421
O67	0.822	0.222	0.421
O68	0.683	0.474	0.589
O69	0.561	0.387	0.534
O70	0.931	0.134	0.472
O71	0.931	0.467	0.472
O72	0.562	0.215	0.534
O73	0.926	0.800	0.592
O74	0.559	0.550	0.416
O75	0.807	0.547	0.534
O76	0.692	0.800	0.471
O77	0.658	0.806	0.596
O78	0.819	0.550	0.413
O79	0.563	0.552	0.535
O80	0.932	0.800	0.474
O81	0.938	0.624	0.598
O82	0.556	0.878	0.411
O83	0.556	0.722	0.411
O84	0.950	0.974	0.598
O85	0.798	0.883	0.531
O86	0.696	0.634	0.477

Atoms	x	y	z
O87	0.696	0.966	0.477
O88	0.796	0.719	0.531
O89	0.694	0.625	0.586
O90	0.822	0.878	0.421
O91	0.822	0.722	0.421
O92	0.683	0.975	0.588
O93	0.562	0.887	0.534
O94	0.931	0.634	0.472
O95	0.931	0.967	0.472
O96	0.562	0.716	0.537
Pt1	0.323	0.641	0.613

Table S9 Fractional coordinate of Liu's model with Pt adsorption

Model parameters: a= 18.728Å; b= 11.365Å ; c= 33.236Å ; $\alpha = \beta = \gamma = 90.0°$

Atoms	x	y	z
Al1	0.062	0.114	0.657
Al2	0.062	0.619	0.652
Al3	0.547	0.126	0.655
Al4	0.547	0.625	0.655
Al5	0.482	0.369	0.652
Al6	0.484	0.869	0.652
Al7	0.982	0.358	0.646
Al8	0.987	0.861	0.653
Al9	0.322	0.240	0.646
Al10	0.325	0.739	0.649

Atoms	x	y	z
Al11	0.823	0.235	0.649
Al12	0.825	0.737	0.649
Al13	0.321	0.487	0.647
Al14	0.324	0.989	0.649
Al15	0.823	0.486	0.647
Al16	0.826	0.985	0.648
Al17	0.168	0.351	0.666
Al18	0.192	0.860	0.642
Al19	0.688	0.342	0.645
Al20	0.689	0.841	0.645
Al21	0.213	0.114	0.617
Al22	0.212	0.609	0.618
Al23	0.710	0.099	0.619
Al24	0.710	0.601	0.618
Al25	0.431	0.111	0.587
Al26	0.430	0.612	0.587
Al27	0.933	0.111	0.588
Al28	0.931	0.613	0.587
Al29	0.094	0.484	0.581
Al30	0.092	0.985	0.581
Al31	0.592	0.480	0.581
Al32	0.592	0.979	0.581
Al33	0.094	0.235	0.580
Al34	0.092	0.737	0.579
Al35	0.591	0.231	0.580

Atoms	x	y	z
Al36	0.591	0.731	0.580
Al37	0.255	0.362	0.571
Al38	0.256	0.862	0.568
Al39	0.754	0.364	0.568
Al40	0.754	0.864	0.569
Al41	0.473	0.362	0.544
Al42	0.474	0.863	0.544
Al43	0.974	0.363	0.543
Al44	0.974	0.864	0.544
Al45	0.209	0.108	0.517
Al46	0.209	0.607	0.518
Al47	0.708	0.107	0.518
Al48	0.708	0.607	0.518
Al49	0.362	0.238	0.510
Al50	0.364	0.737	0.509
Al51	0.863	0.237	0.510
Al52	0.863	0.737	0.510
Al53	0.361	0.487	0.509
Al54	0.362	0.988	0.508
Al55	0.862	0.488	0.509
Al56	0.862	0.988	0.509
Al57	0.123	0.356	0.504
Al58	0.122	0.856	0.504
Al59	0.622	0.353	0.504
Al60	0.622	0.854	0.504

Atoms	x	y	z
Al61	0.023	0.107	0.500
Al62	0.023	0.606	0.499
Al63	0.523	0.104	0.499
Al64	0.523	0.604	0.499
Al65	0.239	0.248	0.444
Al66	0.239	0.747	0.444
Al67	0.739	0.247	0.444
Al68	0.739	0.747	0.444
Al69	0.138	0.498	0.439
Al70	0.138	0.998	0.439
Al71	0.638	0.497	0.439
Al72	0.638	0.997	0.439
Al73	0.401	0.367	0.435
Al74	0.402	0.867	0.434
Al75	0.901	0.367	0.434
Al76	0.901	0.868	0.435
Al77	0.400	0.116	0.433
Al78	0.400	0.616	0.433
Al79	0.900	0.116	0.433
Al80	0.900	0.616	0.433
Al81	0.052	0.246	0.425
Al82	0.052	0.746	0.425
Al83	0.552	0.245	0.425
Al84	0.552	0.745	0.425
Al85	0.287	0.491	0.401

Atoms	x	y	z
Al86	0.288	0.991	0.401
Al87	0.787	0.491	0.401
Al88	0.787	0.991	0.401
Al89	0.006	0.494	0.371
Al90	0.006	0.994	0.371
Al91	0.506	0.494	0.371
Al92	0.506	0.994	0.371
Al93	0.169	0.118	0.364
Al94	0.169	0.618	0.364
Al95	0.669	0.118	0.364
Al96	0.669	0.618	0.364
Al97	0.169	0.368	0.364
Al98	0.169	0.868	0.364
Al99	0.669	0.368	0.364
Al100	0.669	0.868	0.364
Al101	0.332	0.242	0.357
Al102	0.332	0.742	0.357
Al103	0.832	0.242	0.357
Al104	0.832	0.742	0.357
Al105	0.050	0.245	0.326
Al106	0.050	0.745	0.326
Al107	0.550	0.245	0.326
Al108	0.550	0.745	0.326
Al109	0.285	0.490	0.302
Al110	0.285	0.990	0.302

Atoms	x	y	z
Al111	0.785	0.490	0.302
Al112	0.785	0.990	0.302
Al113	0.437	0.120	0.294
Al114	0.437	0.620	0.294
Al115	0.937	0.120	0.294
Al116	0.937	0.620	0.294
Al117	0.436	0.369	0.293
Al118	0.436	0.869	0.293
Al119	0.936	0.369	0.293
Al120	0.936	0.869	0.293
Al121	0.200	0.238	0.288
Al122	0.200	0.738	0.288
Al123	0.700	0.238	0.288
Al124	0.700	0.738	0.288
Al125	0.098	0.489	0.284
Al126	0.098	0.989	0.284
Al127	0.598	0.489	0.284
Al128	0.598	0.989	0.284
O1	0.509	0.245	0.676
O2	0.510	0.745	0.676
O3	0.008	0.236	0.672
O4	0.016	0.731	0.674
O5	0.263	0.363	0.667
O6	0.267	0.863	0.672
O7	0.767	0.360	0.672

Atoms	x	y	z
O8	0.768	0.860	0.672
O9	0.009	0.492	0.671
O10	0.017	0.990	0.673
O11	0.519	0.493	0.672
O12	0.520	0.993	0.673
O13	0.267	0.114	0.664
O14	0.267	0.613	0.665
O15	0.767	0.108	0.665
O16	0.767	0.609	0.664
O17	0.387	0.366	0.645
O18	0.389	0.866	0.646
O19	0.887	0.363	0.644
O20	0.891	0.861	0.647
O21	0.139	0.224	0.631
O22	0.138	0.727	0.632
O23	0.634	0.211	0.635
O24	0.634	0.711	0.635
O25	0.386	0.113	0.633
O26	0.384	0.615	0.633
O27	0.885	0.115	0.633
O28	0.885	0.613	0.633
O29	0.135	0.498	0.635
O30	0.141	-0.007	0.631
O31	0.645	0.475	0.629
O32	0.646	0.974	0.629

Atoms	x	y	z
O33	0.271	0.234	0.598
O34	0.262	0.749	0.604
O35	0.757	0.249	0.605
O36	0.757	0.750	0.605
O37	0.032	0.112	0.598
O38	0.031	0.610	0.598
O39	0.530	0.109	0.598
O40	0.530	0.609	0.598
O41	0.268	0.490	0.599
O42	0.266	0.978	0.602
O43	0.772	0.486	0.599
O44	0.774	0.985	0.600
O45	0.029	0.362	0.596
O46	0.030	0.859	0.595
O47	0.529	0.357	0.595
O48	0.529	0.857	0.595
O49	0.158	0.109	0.564
O50	0.158	0.610	0.565
O51	0.658	0.107	0.566
O52	0.658	0.607	0.566
O53	0.155	0.361	0.561
O54	0.156	0.860	0.561
O55	0.655	0.355	0.560
O56	0.655	0.855	0.560
O57	0.417	0.487	0.557

Atoms	x	y	z
O58	0.416	0.987	0.557
O59	0.917	0.488	0.557
O60	0.917	0.988	0.557
O61	0.418	0.236	0.557
O62	0.417	0.737	0.557
O63	0.918	0.238	0.558
O64	0.917	0.738	0.558
O65	0.050	0.475	0.528
O66	0.050	0.975	0.528
O67	0.550	0.473	0.528
O68	0.550	0.973	0.528
O69	0.303	0.363	0.526
O70	0.304	0.862	0.524
O71	0.804	0.362	0.525
O72	0.804	0.862	0.525
O73	0.052	0.243	0.527
O74	0.053	0.742	0.526
O75	0.553	0.239	0.526
O76	0.552	0.739	0.526
O77	0.302	0.109	0.521
O78	0.302	0.612	0.522
O79	0.802	0.111	0.522
O80	0.802	0.611	0.522
O81	0.425	0.364	0.493
O82	0.427	0.863	0.492

Atoms	x	y	z
O83	0.926	0.364	0.493
O84	0.926	0.864	0.493
O85	0.176	0.488	0.490
O86	0.176	0.987	0.490
O87	0.676	0.486	0.490
O88	0.676	0.986	0.490
O89	0.189	0.239	0.490
O90	0.189	0.739	0.490
O91	0.689	0.237	0.490
O92	0.689	0.737	0.490
O93	0.430	0.112	0.488
O94	0.430	0.612	0.488
O95	0.930	0.113	0.489
O96	0.930	0.613	0.489
O97	0.332	0.241	0.455
O98	0.333	0.741	0.454
O99	0.833	0.241	0.455
O100	0.833	0.741	0.455
O101	0.072	0.116	0.453
O102	0.072	0.615	0.453
O103	0.572	0.114	0.453
O104	0.572	0.614	0.453
O105	0.085	0.366	0.453
O106	0.085	0.866	0.453
O107	0.585	0.365	0.453

Atoms	x	y	z
O108	0.585	0.865	0.453
O109	0.337	0.490	0.451
O110	0.337	0.990	0.450
O111	0.837	0.490	0.451
O112	0.837	0.990	0.451
O113	0.459	0.243	0.421
O114	0.459	0.743	0.421
O115	0.959	0.243	0.421
O116	0.959	0.743	0.421
O117	0.208	0.112	0.417
O118	0.208	0.612	0.417
O119	0.709	0.111	0.417
O120	0.709	0.611	0.417
O121	0.211	0.379	0.416
O122	0.211	0.878	0.416
O123	0.711	0.378	0.416
O124	0.711	0.878	0.416
O125	0.459	0.491	0.416
O126	0.459	0.991	0.416
O127	0.959	0.491	0.416
O128	0.959	0.992	0.416
O129	0.344	0.367	0.387
O130	0.344	0.867	0.386
O131	0.844	0.367	0.387
O132	0.844	0.867	0.387

Atoms	x	y	z
O133	0.343	0.116	0.386
O134	0.343	0.616	0.386
O135	0.843	0.116	0.386
O136	0.843	0.616	0.386
O137	0.106	0.494	0.382
O138	0.106	0.994	0.382
O139	0.606	0.494	0.382
O140	0.606	0.994	0.382
O141	0.103	0.243	0.377
O142	0.103	0.743	0.377
O143	0.603	0.243	0.377
O144	0.603	0.743	0.377
O145	0.234	0.493	0.349
O146	0.234	0.993	0.349
O147	0.734	0.493	0.349
O148	0.734	0.993	0.349
O149	0.231	0.242	0.345
O150	0.231	0.742	0.345
O151	0.731	0.242	0.345
O152	0.731	0.742	0.345
O153	0.495	0.120	0.341
O154	0.495	0.620	0.341
O155	0.995	0.120	0.341
O156	0.995	0.620	0.341
O157	0.494	0.370	0.341

Atoms	x	y	z
O158	0.494	0.870	0.341
O159	0.994	0.370	0.341
O160	0.994	0.870	0.341
O161	0.126	0.358	0.312
O162	0.126	0.858	0.312
O163	0.626	0.358	0.312
O164	0.626	0.858	0.312
O165	0.379	0.245	0.311
O166	0.379	0.745	0.311
O167	0.879	0.245	0.311
O168	0.879	0.745	0.311
O169	0.128	0.125	0.311
O170	0.128	0.625	0.311
O171	0.628	0.125	0.311
O172	0.628	0.625	0.311
O173	0.378	0.493	0.306
O174	0.378	0.993	0.306
O175	0.878	0.493	0.306
O176	0.878	0.993	0.306
O177	0.001	0.246	0.276
O178	0.001	0.746	0.276
O179	0.501	0.246	0.276
O180	0.501	0.746	0.276
O181	0.265	0.121	0.274
O182	0.265	0.621	0.274

Atoms	x	y	z
O183	0.765	0.121	0.274
O184	0.765	0.621	0.274
O185	0.252	0.370	0.274
O186	0.252	0.870	0.274
O187	0.752	0.370	0.274
O188	0.752	0.870	0.274
O189	0.005	0.495	0.273
O190	0.005	0.995	0.273
O191	0.505	0.495	0.273
O192	0.505	0.995	0.273
Pt1	0.095	0.277	0.716

Table S10 Fractional coordinate of γ-NAV with Pt adsorption

Model parameters: a= 17.154Å ; b= 8.577Å ; c= 42.594Å $\alpha = \beta = 90.0°$; γ =89.4°

Atoms	x	y	z
Al1	0.129	0.577	0.624
Al2	0.626	0.581	0.624
Al3	0.294	0.577	0.623
Al4	0.796	0.581	0.623
Al5	0.459	0.579	0.620
Al6	0.961	0.577	0.620
Al7	0.049	0.257	0.605
Al8	0.549	0.258	0.605
Al9	0.049	0.898	0.605
Al10	0.549	0.901	0.605

Atoms	x	y	z
Al11	0.374	0.252	0.606
Al12	0.873	0.256	0.606
Al13	0.375	0.904	0.605
Al14	0.873	0.902	0.605
Al15	0.208	0.078	0.580
Al16	0.711	0.075	0.585
Al17	0.210	0.752	0.580
Al18	0.710	0.755	0.579
Al19	0.209	0.408	0.578
Al20	0.709	0.408	0.578
Al21	0.044	0.574	0.557
Al22	0.544	0.575	0.557
Al23	0.371	0.579	0.553
Al24	0.870	0.579	0.553
Al25	0.464	0.232	0.537
Al26	0.964	0.232	0.537
Al27	0.469	0.891	0.535
Al28	0.969	0.891	0.535
Al29	0.298	0.240	0.535
Al30	0.798	0.240	0.535
Al31	0.299	0.909	0.532
Al32	0.799	0.909	0.532
Al33	0.127	0.103	0.515
Al34	0.627	0.103	0.515
Al35	0.134	0.754	0.512

Atoms	x	y	z
Al36	0.634	0.754	0.512
Al37	0.214	0.425	0.493
Al38	0.714	0.425	0.493
Al39	0.045	0.429	0.490
Al40	0.545	0.429	0.490
Al41	0.381	0.417	0.485
Al42	0.881	0.417	0.485
Al43	0.466	0.731	0.467
Al44	0.966	0.731	0.467
Al45	0.464	0.076	0.466
Al46	0.964	0.076	0.466
Al47	0.293	0.740	0.466
Al48	0.793	0.740	0.466
Al49	0.292	0.086	0.465
Al50	0.792	0.086	0.465
Al51	0.133	0.923	0.447
Al52	0.633	0.923	0.447
Al53	0.132	0.251	0.442
Al54	0.632	0.251	0.442
Al55	0.134	0.590	0.439
Al56	0.634	0.590	0.439
Al57	0.297	0.424	0.420
Al58	0.797	0.424	0.420
Al59	0.471	0.402	0.417
Al60	0.971	0.402	0.417

Atoms	x	y	z
Al61	0.377	0.749	0.400
Al62	0.877	0.749	0.400
Al63	0.372	0.090	0.397
Al64	0.872	0.090	0.397
Al65	0.043	0.761	0.397
Al66	0.543	0.761	0.397
Al67	0.042	0.092	0.395
Al68	0.542	0.092	0.395
Al69	0.214	0.898	0.377
Al70	0.714	0.898	0.377
Al71	0.206	0.247	0.374
Al72	0.706	0.247	0.374
O1	0.380	0.076	0.626
O2	0.872	0.080	0.628
O3	0.040	0.078	0.629
O4	0.536	0.079	0.628
O5	0.377	0.434	0.627
O6	0.878	0.434	0.627
O7	0.045	0.719	0.626
O8	0.544	0.723	0.626
O9	0.045	0.435	0.626
O10	0.544	0.438	0.626
O11	0.376	0.723	0.626
O12	0.880	0.720	0.626
O13	0.211	0.719	0.624

Atoms	x	y	z
O14	0.712	0.734	0.626
O15	0.212	0.436	0.623
O16	0.712	0.451	0.624
O17	0.139	0.921	0.586
O18	0.638	0.916	0.584
O19	0.139	0.239	0.585
O20	0.641	0.241	0.586
O21	0.461	0.254	0.582
O22	0.961	0.249	0.583
O23	0.464	0.903	0.581
O24	0.963	0.906	0.582
O25	0.287	0.241	0.581
O26	0.789	0.247	0.580
O27	0.286	0.917	0.580
O28	0.791	0.909	0.577
O29	0.287	0.578	0.579
O30	0.787	0.581	0.579
O31	0.133	0.578	0.578
O32	0.634	0.582	0.579
O33	0.456	0.578	0.578
O34	0.956	0.576	0.578
O35	0.219	0.082	0.537
O36	0.719	0.082	0.537
O37	0.217	0.762	0.536
O38	0.717	0.762	0.536

Atoms	x	y	z
O39	0.379	0.763	0.536
O40	0.879	0.763	0.536
O41	0.375	0.082	0.535
O42	0.875	0.082	0.535
O43	0.048	0.751	0.535
O44	0.548	0.751	0.535
O45	0.222	0.396	0.535
O46	0.722	0.396	0.535
O47	0.035	0.088	0.534
O48	0.535	0.088	0.534
O49	0.039	0.412	0.533
O50	0.539	0.412	0.533
O51	0.379	0.395	0.533
O52	0.879	0.395	0.533
O53	0.128	0.930	0.490
O54	0.628	0.930	0.490
O55	0.462	0.253	0.490
O56	0.962	0.253	0.490
O57	0.464	0.903	0.489
O58	0.964	0.903	0.489
O59	0.295	0.261	0.489
O60	0.795	0.261	0.489
O61	0.131	0.574	0.489
O62	0.631	0.574	0.489
O63	0.294	0.914	0.489

Atoms	x	y	z
O64	0.794	0.914	0.489
O65	0.129	0.272	0.488
O66	0.629	0.272	0.488
O67	0.464	0.553	0.487
O68	0.964	0.553	0.487
O69	0.297	0.559	0.486
O70	0.797	0.559	0.486
O71	0.202	0.753	0.446
O72	0.702	0.753	0.446
O73	0.202	0.087	0.445
O74	0.702	0.087	0.445
O75	0.055	0.423	0.444
O76	0.555	0.423	0.444
O77	0.206	0.420	0.443
O78	0.706	0.420	0.443
O79	0.380	0.740	0.443
O80	0.880	0.740	0.443
O81	0.053	0.755	0.443
O82	0.553	0.755	0.443
O83	0.378	0.080	0.443
O84	0.878	0.080	0.443
O85	0.052	0.089	0.442
O86	0.552	0.089	0.442
O87	0.384	0.407	0.441
O88	0.884	0.407	0.441

Atoms	x	y	z
O89	0.122	0.919	0.399
O90	0.622	0.919	0.399
O91	0.124	0.239	0.398
O92	0.624	0.239	0.398
O93	0.462	0.217	0.398
O94	0.962	0.217	0.398
O95	0.293	0.250	0.397
O96	0.793	0.250	0.397
O97	0.465	0.898	0.397
O98	0.965	0.898	0.397
O99	0.119	0.605	0.397
O100	0.619	0.605	0.397
O101	0.306	0.913	0.396
O102	0.806	0.913	0.396
O103	0.302	0.589	0.396
O104	0.802	0.589	0.396
O105	0.462	0.586	0.395
O106	0.962	0.586	0.395
H1	0.478	0.078	0.634
H2	0.988	0.079	0.639
Pt1	0.757	0.965	0.638

Table S11 Fractional coordinate of γ-AV with Pt adsorption

Model parameters: a= 11.271Å ; b= 17.042Å ; c= 35.048Å; $\alpha = \beta = \gamma = 90°$

Atoms	x	y	z

Atoms	x	y	z
Al1	0.352	0.238	0.572
Al2	0.361	0.738	0.572
Al3	0.852	0.411	0.572
Al4	0.857	0.914	0.576
Al5	0.351	0.413	0.572
Al6	0.360	0.912	0.572
Al7	0.851	0.237	0.572
Al8	0.856	0.735	0.575
Al9	0.355	0.075	0.568
Al10	0.355	0.575	0.568
Al11	0.855	0.076	0.568
Al12	0.855	0.574	0.568
Al13	0.104	0.163	0.552
Al14	0.107	0.662	0.552
Al15	0.604	0.487	0.552
Al16	0.606	0.987	0.552
Al17	0.104	0.487	0.549
Al18	0.106	0.988	0.549
Al19	0.604	0.162	0.549
Al20	0.606	0.662	0.549
Al21	0.227	0.321	0.517
Al22	0.226	0.820	0.514
Al23	0.726	0.328	0.517
Al24	0.726	0.829	0.515
Al25	0.484	0.330	0.514

Atoms	x	y	z
Al26	0.484	0.829	0.516
Al27	0.984	0.320	0.514
Al28	0.983	0.820	0.515
Al29	0.362	0.161	0.488
Al30	0.362	0.661	0.488
Al31	0.862	0.488	0.488
Al32	0.862	0.988	0.488
Al33	0.353	0.489	0.487
Al34	0.853	0.161	0.487
Al35	0.353	0.988	0.487
Al36	0.853	0.661	0.487
Al37	0.605	0.071	0.466
Al38	0.605	0.571	0.466
Al39	0.105	0.079	0.466
Al40	0.105	0.579	0.466
Al41	0.100	0.405	0.458
Al42	0.100	0.905	0.458
Al43	0.600	0.244	0.458
Al44	0.600	0.744	0.458
Al45	0.352	0.327	0.433
Al46	0.352	0.827	0.433
Al47	0.852	0.323	0.433
Al48	0.852	0.823	0.433
Al49	0.735	0.487	0.408
Al50	0.235	0.162	0.408

Atoms	x	y	z
Al51	0.735	0.987	0.408
Al52	0.235	0.662	0.408
Al53	0.982	0.153	0.406
Al54	0.482	0.496	0.406
Al55	0.982	0.653	0.406
Al56	0.482	0.996	0.406
Al57	0.218	0.494	0.403
Al58	0.218	0.994	0.403
Al59	0.718	0.156	0.403
Al60	0.718	0.656	0.403
Al61	0.609	0.328	0.376
Al62	0.609	0.828	0.376
Al63	0.109	0.321	0.376
Al64	0.109	0.821	0.376
O1	0.244	0.157	0.578
O2	0.247	0.659	0.578
O3	0.744	0.491	0.578
O4	0.745	0.992	0.578
O5	0.964	0.159	0.578
O6	0.967	0.655	0.578
O7	0.464	0.491	0.578
O8	0.467	0.993	0.578
O9	0.241	0.492	0.576
O10	0.244	0.990	0.576
O11	0.741	0.158	0.576

Atoms	x	y	z
O12	0.743	0.658	0.576
O13	0.966	0.489	0.576
O14	0.968	0.993	0.575
O15	0.466	0.160	0.576
O16	0.469	0.657	0.576
O17	0.754	0.324	0.574
O18	0.742	0.823	0.573
O19	0.254	0.326	0.574
O20	0.248	0.825	0.579
O21	0.965	0.325	0.578
O22	0.960	0.824	0.576
O23	0.465	0.325	0.578
O24	0.458	0.825	0.573
O25	0.104	0.250	0.525
O26	0.105	0.751	0.525
O27	0.604	0.399	0.525
O28	0.605	0.901	0.524
O29	0.108	0.077	0.522
O30	0.108	0.577	0.523
O31	0.608	0.073	0.522
O32	0.608	0.572	0.522
O33	0.357	0.248	0.520
O34	0.351	0.748	0.520
O35	0.857	0.401	0.519
O36	0.855	0.901	0.521

Atoms	x	y	z
O37	0.605	0.251	0.520
O38	0.607	0.750	0.520
O39	0.105	0.399	0.520
O40	0.106	0.898	0.520
O41	0.860	0.246	0.519
O42	0.858	0.746	0.520
O43	0.360	0.404	0.519
O44	0.354	0.903	0.519
O45	0.355	0.073	0.517
O46	0.355	0.573	0.517
O47	0.854	0.076	0.517
O48	0.854	0.576	0.517
O49	0.501	0.159	0.467
O50	0.501	0.659	0.467
O51	0.001	0.491	0.467
O52	0.001	0.991	0.467
O53	0.730	0.314	0.464
O54	0.230	0.335	0.464
O55	0.730	0.814	0.464
O56	0.230	0.835	0.464
O57	0.978	0.333	0.463
O58	0.978	0.833	0.463
O59	0.478	0.317	0.463
O60	0.478	0.817	0.463
O61	0.736	0.498	0.460

Atoms	x	y	z
O62	0.236	0.151	0.460
O63	0.736	0.998	0.460
O64	0.236	0.651	0.460
O65	0.721	0.159	0.459
O66	0.721	0.659	0.459
O67	0.221	0.491	0.459
O68	0.221	0.991	0.459
O69	0.479	0.000	0.459
O70	0.979	0.149	0.459
O71	0.479	0.500	0.459
O72	0.979	0.649	0.459
O73	0.115	0.081	0.409
O74	0.115	0.581	0.409
O75	0.615	0.068	0.409
O76	0.615	0.568	0.409
O77	0.618	0.243	0.405
O78	0.118	0.406	0.405
O79	0.618	0.743	0.405
O80	0.118	0.906	0.405
O81	0.842	0.405	0.402
O82	0.342	0.244	0.402
O83	0.842	0.905	0.402
O84	0.342	0.744	0.402
O85	0.858	0.234	0.402
O86	0.358	0.415	0.402

Atoms	x	y	z
O87	0.858	0.734	0.402
O88	0.358	0.915	0.402
O89	0.603	0.420	0.399
O90	0.103	0.229	0.399
O91	0.603	0.920	0.399
O92	0.103	0.729	0.399
O93	0.845	0.082	0.398
O94	0.345	0.068	0.398
O95	0.845	0.582	0.398
O96	0.345	0.568	0.398
H1	0.661	0.824	0.584
H2	0.167	0.825	0.589
H3	0.550	0.325	0.585
H4	0.049	0.324	0.585
Pt1	0.940	0.827	0.632

5.2 Results of Bader charge calculation

Table S12 Bader charge analysis of Pt atoms anchored on γ-NAV, γ-AV and Digne's models

Model	Bader electron population of Pt (e)	Net Bader charge of Pt (e)
Pt/γ-NAV	10.28	-0.28
Pt/γ-NAV	10.25	-0.25
Pt/Digne	10.30	-0.30

6. Phase Diagram Calculation Gibbs Free Energy

Table S13 Gibbs free energy of Digne's model (Units: eV)

	$0O_v$	$1O_v$	$2O_v$	$3O_v$	$4O_v$	$5O_v$

	$0O_v$	$1O_v$	$2O_v$	$3O_v$	$4O_v$	$5O_v$
0OH	-1164.75	-1153.95	-1143.13	-1132.28	-1122.28	-1111.97
1OH	-1166.83	-1156.25	-1145.40	-1134.89	-1124.95	-1114.23
2OH	-1169.23	-1158.03	-1147.16	-1137.17	-1126.78	-1116.05
3OH	-1171.59	-1160.05	-1149.52	-1139.18	-1129.23	-1118.96
4OH	-1173.36	-1161.98	-1151.44	-1140.83	-1131.50	-1121.70
5OH	-1175.74	-1164.34	-1153.47	-1143.59	-1133.51	-1124.01

Table S14 Gibbs free energy of Liu's model (Units: eV)

	$0O_v$	$1O_v$	$2O_v$	$3O_v$	$4O_v$	$5O_v$
0OH	-2342.46	-2332.75	-2322.89	-2312.69	-2302.41	-2292.20
1OH	-2345.63	-2335.72	-2338.60	-2341.46	-2343.85	-2346.36
2OH	-2348.52	-2326.24	-2328.90	-2331.79	-2333.99	-2335.85
3OH	-2351.69	-2315.65	-2318.31	-2320.80	-2322.99	-2325.55
4OH	-2355.06	-2305.28	-2307.58	-2310.26	-2312.65	-2314.62
5OH	-2357.60	-2295.10	-2297.25	-2299.76	-2302.73	-2304.68

Table S15 Gibbs free energy of γ-NAV model (Units: eV)

	$0O_v$	$1O_v$	$2O_v$	$3O_v$	$4O_v$	$5O_v$
0OH	-1293.31	-1290.66	-1286.21	-1280.33	-1270.22	-1259.94
1OH	-1299.58	-1296.29	-1301.50	-1307.06	-1312.35	-1314.45

2OH	-1305.95	-1291.89	-1297.18	-1299.31	-1301.24	-1303.28
3OH	-1311.39	-1283.16	-1286.33	-1288.44	-1290.36	-1292.16
4OH	-1316.66	-1272.93	-1275.60	-1277.59	-1279.57	-1281.58
5OH	-1322.19	-1262.46	-1264.80	-1266.97	-1268.98	-1270.77

Table S16 Gibbs free energy of γ-AV model (Units: eV)

	$0O_v$	$1O_v$	$2O_v$	$3O_v$	$4O_v$	$5O_v$
0OH	-1151.08	-1146.02	-1140.42	-1129.67	-1118.82	-1108.01
1OH	-1156.46	-1150.68	-1155.72	-1158.42	-1160.96	-1163.02
2OH	-1161.87	-1142.69	-1145.03	-1147.23	-1149.80	-1151.87
3OH	-1167.24	-1131.86	-1134.15	-1136.59	-1138.32	-1140.31
4OH	-1172.59	-1121.1	-1123.17	-1125.61	-1127.37	-1129.32
5OH	-1173.45	-1110.3	-1112.58	-1114.37	-1116.30	-1118.69

Table S17 Calculated energies along the PDH pathway on different structural models (Units: eV)

	C_3H_8*	TS1	C_3H_7*+H*	C_3H_7*	TS2	C_3H_6*+H*
γ-NAV	-1106.72	-1106.28	-1107.86	-1104.38	-1103.62	-1104.21
γ-AV	-1006.08	-1006.04	-1006.24	-1002.01	-1001.22	-1001.66
Digne	-997.67	-996.73	-997.79	-993.11	-992.46	-992.89

* The energies of C_3H_7*, TS2 and C_3H_6*+ H* were corrected by adding $\frac{1}{2}H_2$, because the surface H* generated in the first dehydrogenation step was removed and referenced to molecular hydrogen. No H_2 correction was applied to C_3H_8*, TS1 and C_3H_7*+ H*, where all hydrogen atoms are explicitly included in the surface model.

7. References

1. Sun, G., Kürti, J., Rajczy, P., Kertesz, M., Hafner, J., and Kresse, G., Performance of the Vienna ab initio simulation package (VASP) in chemical applications. Journal of Molecular Structure: THEOCHEM, 2003. 624(1): p. 37-45.

2. Perdew, J.P., Burke, K., and Ernzerhof, M., Generalized Gradient Approximation Made Simple. Physical Review Letters, 1996. 77(18): p. 3865-3868.

3. Blöchl, P.E., Projector augmented-wave method. Physical Review B, 1994. 50(24): p. 17953-17979.

4. Kresse, G. and Joubert, D., From ultrasoft pseudopotentials to the projector augmented-wave method. Physical Review B, 1999. 59(3): p. 1758-1775.

5. Monkhorst, H.J. and Pack, J.D., Special points for Brillouin-zone integrations. Physical Review B, 1976. 13(12): p. 5188-5192.

6. Henkelman, G. and Jónsson, H., Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. The Journal of Chemical Physics, 2000. 113(22): p. 9978-9985.

7. Henkelman, G., Uberuaga, B.P., and Jónsson, H., A climbing image nudged elastic band method for finding saddle points and minimum energy paths. The Journal of Chemical Physics, 2000. 113(22): p. 9901-9904.

8. Henkelman, G. and Jónsson, H., A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives. The Journal of Chemical Physics, 1999. 111(15): p. 7010-7022.

9. Wellendorff, J., Lundgaard, K.T., Møgelhøj, A., Petzold, V., Landis, D.D., Nørskov, J.K., Bligaard, T., and Jacobsen, K.W., Density functionals for surface science: Exchange-correlation model development with Bayesian error estimation. Physical Review B, 2012. 85(23).

10. Shang, C. and Liu, Z.-P., Stochastic Surface Walking Method for Structure Prediction and Pathway Searching. Journal of Chemical Theory and Computation, 2013. 9(3): p. 1838-1845.

11. Behler, J. and Parrinello, M., Generalized Neural-Network Representation of High-Dimensional Potential-Energy Surfaces. Physical Review Letters, 2007. 98(14).

12. Behler, J., Four Generations of High-Dimensional Neural Network Potentials. Chemical Reviews, 2021. 121(16): p. 10037-10072.

13. Kang, P.-L., Shang, C., and Liu, Z.-P., Recent implementations in LASP 3.0: Global neural network potential with multiple elements and better long-range description. Chinese Journal of Chemical Physics, 2021. 34(5): p. 583-590.

14. Busca, G., The surface of transitional aluminas: A critical review. Catalysis Today, 2014. 226: p. 2-13.

15. Digne, M., Use of DFT to achieve a rational understanding of acid-basic properties of γ-alumina surfaces. Journal of Catalysis, 2004. 226(1): p. 54-68.

16. Busca, G., Catalytic materials based on silica and alumina: Structural features and generation of surface acidity. Progress in Materials Science, 2019. 104: p. 215-249.

17. Yang, X., Shang, C., and Liu, Z.-P., Resolving the atomic structure of γ-alumina: a non-spinel phase with a distorted anion lattice and three adjacent long channels. Journal of Materials Chemistry A, 2025. 13(23): p. 17429-17433.