Local Fluxionality of Surface-Deposited Cluster Catalysts: the Case of Pt_7 on Al_2O_3

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Supporting Information

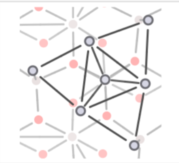
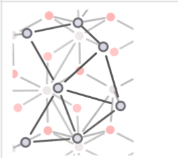
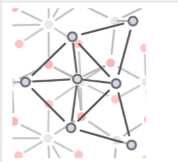
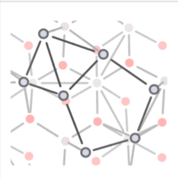
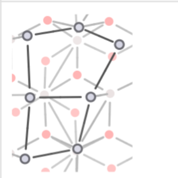
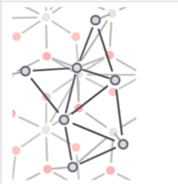
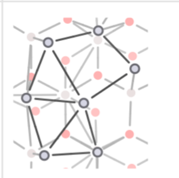
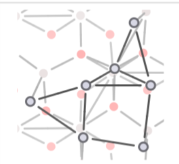
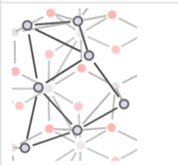
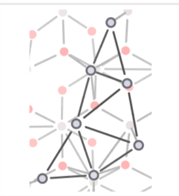
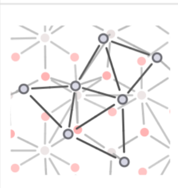
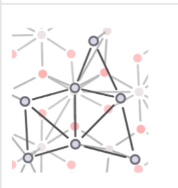
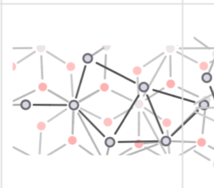
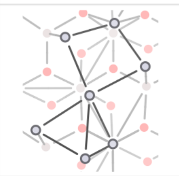
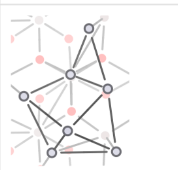
[**1**] E = 0.000 eV	[**2**] E = 0.073 eV	[**3**] E = 0.226 eV	[**4**] E = 0.249 eV	[**5**] E = 0.269 eV	[**6**] E = 0.287 eV	[**7**] E = 0.297 eV
						
[**8**] E = 0.384 eV	[**9**] E = 0.390 eV	[**10**] E = 0.391 eV	[**11**] E = 0.400 eV	[**12**] E = 0.401 eV	[**13**] E = 0.404 eV	[**14**] E = 0.432 eV
						
[**15**] E = 0.443 eV	[**16**] E = 0.468 eV	[**17**] E = 0.526 eV	[**18**] E = 0.540 eV	[**19**] E = 0.541 eV	[**20**] E = 0.547 eV	[**21**] E = 0.552 eV
						
[**22**] E = 0.571 eV	[**23**] E = 0.577 eV	[**24**] E = 0.582 eV	[**25**] E = 0.631 eV	[**26**] E = 0.678 eV	[**27**] E = 0.686 eV	[**28**] E = 0.782 eV
						
[**29**] E = 0.809 eV	[**30**] E = 0.894 eV					
						

Table S1. The Pt_7 cluster supported on Al_2O_3 isomers considered in this work. First, we included 20 isomers with energy lower than 0.6 eV relative to global minimum (GM). Second, some intermediates found along the optimized paths, which are necessary to build the isomerization graph, are included.

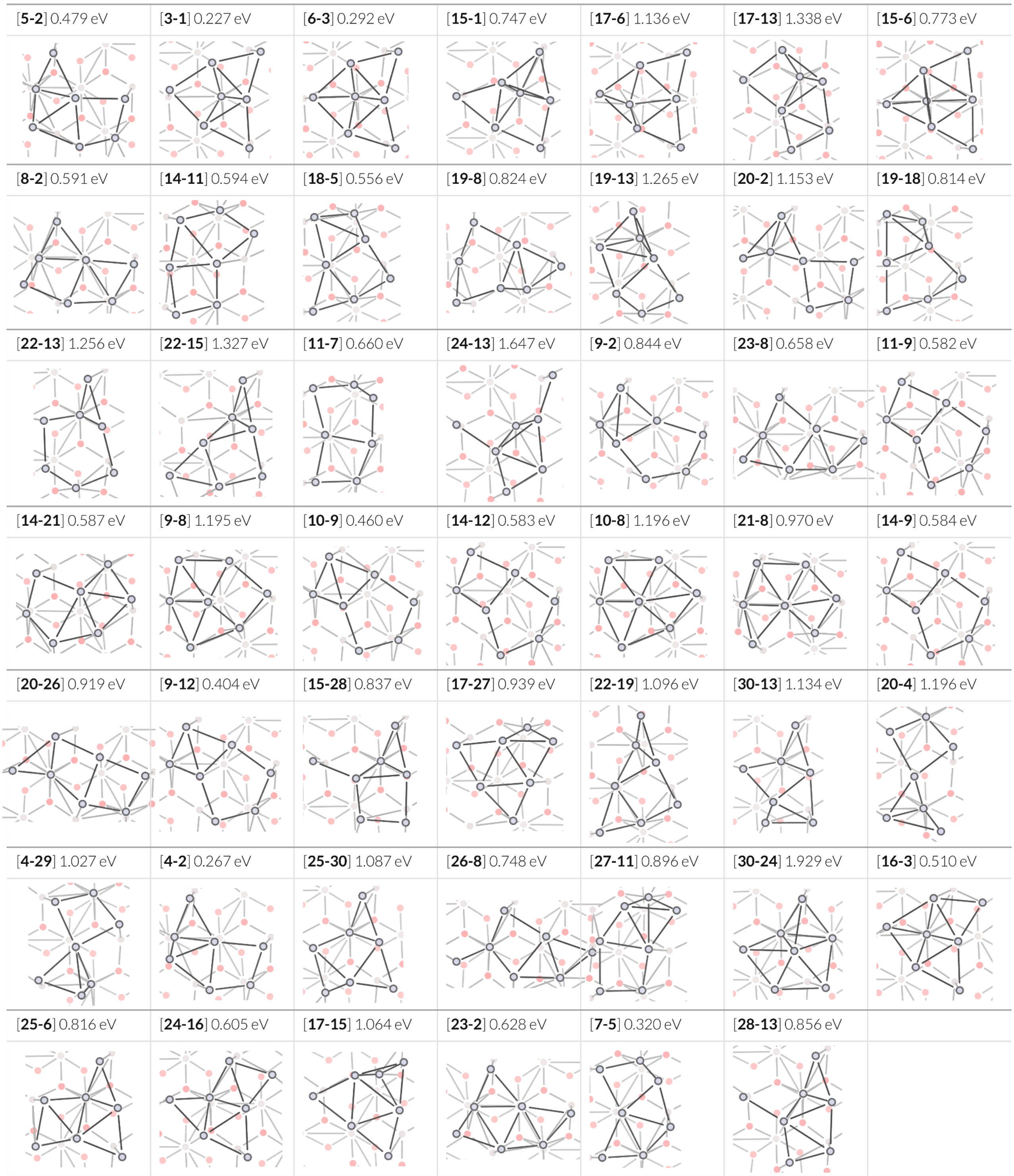


Table S2. The energy and geometry of transition states in direct paths between Pt_7 cluster supported on Al_2O_3 isomers considered in this work. The two numbers in bracket indicate the index (in Table S1) of the two isomers connected by the direct path. The energies are relative to the global minimum energy.

$\#_{init}$	$\#_{final}$	E_{init} (eV)	E_{final} (eV)	E_{TS} (eV)	barrier (eV)	k_{450K} (1/s)	k_{700K} (1/s)	Notes
5	2	0.2688	0.0727	0.4793	0.2105	5.65×10^{10}	3.93×10^{11}	Region II
2	5	0.0727	0.2688	0.4793	0.4066	1.84×10^{9}	7.80×10^{10}	Region II
3	1	0.2263	0.0000	0.2266	0.0004	1.06×10^{13}	1.07×10^{13}	Region I
1	3	0.0000	0.2263	0.2266	0.2266	3.37×10^{10}	2.72×10^{11}	Region I
6	3	0.2871	0.2263	0.2921	0.0050	4.23×10^{12}	4.43×10^{12}	Region I
3	6	0.2263	0.2871	0.2921	0.0658	1.17×10^{12}	2.15×10^{12}	Region I
15	1	0.4426	0.0000	0.7465	0.3040	5.10×10^{9}	8.39×10^{10}	RB I
1	15	0.0000	0.4426	0.7465	0.7465	9.96×10^{4}	9.65×10^{7}	RB I
17	6	0.5257	0.2871	1.1356	0.6099	1.02×10^{7}	2.79×10^{9}	RB I
6	17	0.2871	0.5257	1.1356	0.8486	2.39×10^{4}	5.92×10^{7}	RB I
17	13	0.5257	0.4038	1.3375	0.8118	1.84×10^{5}	3.25×10^{8}	
13	17	0.4038	0.5257	1.3375	0.9337	5.05×10^{3}	2.74×10^{7}	
15	6	0.4426	0.2871	0.7726	0.3300	1.70×10^{10}	3.55×10^{11}	RB I
6	15	0.2871	0.4426	0.7726	0.4855	3.95×10^{8}	3.45×10^{10}	RB I
8	2	0.3837	0.0727	0.5914	0.2077	2.18×10^{12}	1.47×10^{13}	Region II
2	8	0.0727	0.3837	0.5914	0.5186	1.37×10^{9}	1.62×10^{11}	Region II
14	11	0.4316	0.3999	0.5944	0.1628	1.09×10^{11}	4.90×10^{11}	Region II
11	14	0.3999	0.4316	0.5944	0.1944	1.70×10^{11}	1.02×10^{12}	Region II
18	5	0.5404	0.2688	0.5556	0.0152	6.68×10^{12}	7.68×10^{12}	Region II
5	18	0.2688	0.5404	0.5556	0.2868	1.06×10^{10}	1.48×10^{11}	Region II
19	8	0.5409	0.3837	0.8237	0.2828	3.95×10^{9}	5.34×10^{10}	Region II
8	19	0.3837	0.5409	0.8237	0.4401	2.97×10^{8}	1.71×10^{10}	Region II
19	13	0.5409	0.4038	1.2646	0.7236	1.81×10^{5}	1.42×10^{8}	RB II
13	19	0.4038	0.5409	1.2646	0.8608	1.27×10^{4}	3.51×10^{7}	RB II
20	2	0.5468	0.0727	1.1528	0.6060	5.55×10^{6}	1.47×10^{9}	Region II
2	20	0.0727	0.5468	1.1528	1.0801	7.30×10^{1}	1.53×10^{6}	Region II
19	18	0.5409	0.5404	0.8142	0.2732	4.63×10^{10}	5.74×10^{11}	Region II
18	19	0.5404	0.5409	0.8142	0.2737	4.23×10^{10}	5.26×10^{11}	Region II
22	13	0.5706	0.4038	1.2564	0.6859	1.55×10^{3}	8.61×10^{5}	
13	22	0.4038	0.5706	1.2564	0.8527	4.77×10^{3}	1.23×10^{7}	
22	15	0.5706	0.4426	1.3274	0.7569	4.37×10^{2}	4.66×10^{5}	
15	22	0.4426	0.5706	1.3274	0.8849	5.18×10^{3}	1.79×10^{7}	
11	7	0.3999	0.2974	0.6603	0.2604	2.92×10^{10}	3.21×10^{11}	Region II
7	11	0.2974	0.3999	0.6603	0.3630	1.81×10^{9}	5.12×10^{10}	Region II
24	13	0.5821	0.4038	1.6471	1.0650	1.24×10^{2}	2.26×10^{6}	RB I
13	24	0.4038	0.5821	1.6471	1.2433	2.34×10^{0}	2.20×10^{5}	RB I
9	2	0.3900	0.0727	0.8441	0.4541	5.23×10^{7}	3.43×10^{9}	Region II
2	9	0.0727	0.3900	0.8441	0.7714	4.37×10^{5}	5.32×10^{8}	Region II
23	8	0.5771	0.3837	0.6578	0.0807	8.40×10^{12}	1.77×10^{13}	Region II
8	23	0.3837	0.5771	0.6578	0.2742	1.30×10^{11}	1.63×10^{12}	Region II
11	9	0.3999	0.3900	0.5823	0.1824	1.26×10^{11}	6.76×10^{11}	Region II
9	11	0.3900	0.3999	0.5823	0.1923	2.11×10^{10}	1.24×10^{11}	Region II
14	21	0.4316	0.5524	0.5873	0.1557	7.55×10^{10}	3.17×10^{11}	Region II
21	14	0.5524	0.4316	0.5873	0.0348	1.85×10^{10}	2.55×10^{10}	Region II
9	8	0.3900	0.3837	1.1946	0.8045	2.60×10^{4}	4.30×10^{7}	Region II
8	9	0.3837	0.3900	1.1946	0.8109	3.47×10^{5}	6.07×10^{8}	Region II

10	9	0.3909	0.3900	0.4603	0.0694	5.78×10^{12}	1.09×10^{13}	Region II
9	10	0.3900	0.3909	0.4603	0.0702	1.85×10^{12}	3.52×10^{12}	Region II
14	12	0.4316	0.4010	0.5832	0.1517	8.67×10^{10}	3.51×10^{11}	Region II
12	14	0.4010	0.4316	0.5832	0.1823	5.32×10^{10}	2.85×10^{11}	Region II
10	8	0.3909	0.3837	1.1956	0.8047	8.64×10^{4}	1.43×10^{8}	Region II
8	10	0.3837	0.3909	1.1956	0.8119	3.67×10^{5}	6.49×10^{8}	Region II
21	8	0.5524	0.3837	0.9699	0.4175	1.82×10^{7}	8.53×10^{8}	Region II
8	21	0.3837	0.5524	0.9699	0.5863	2.57×10^{8}	5.69×10^{10}	Region II
14	9	0.4316	0.3900	0.5844	0.1528	1.06×10^{11}	4.32×10^{11}	Region II
9	14	0.3900	0.4316	0.5844	0.1943	2.75×10^{10}	1.64×10^{11}	Region II
20	26	0.5468	0.6783	0.9186	0.3718	3.14×10^{9}	9.64×10^{10}	Region II
26	20	0.6783	0.5468	0.9186	0.2404	3.61×10^{10}	3.30×10^{11}	Region II
9	12	0.3900	0.4010	0.4040	0.0140	1.12×10^{12}	1.28×10^{12}	Region II
12	9	0.4010	0.3900	0.4040	0.0031	2.65×10^{12}	2.73×10^{12}	Region II
15	28	0.4426	0.7824	0.8373	0.3947	4.45×10^{9}	1.69×10^{11}	
28	15	0.7824	0.4426	0.8373	0.0549	7.28×10^{12}	1.21×10^{13}	
17	27	0.5257	0.6863	0.9394	0.4136	1.79×10^{9}	8.08×10^{10}	
27	17	0.6863	0.5257	0.9394	0.2531	2.37×10^{10}	2.44×10^{11}	
22	19	0.5706	0.5409	1.0961	0.5255	1.18×10^{5}	1.49×10^{7}	RB II
19	22	0.5409	0.5706	1.0961	0.5551	5.17×10^{6}	8.59×10^{8}	RB II
30	13	0.8941	0.4038	1.1341	0.2400	8.51×10^{10}	7.76×10^{11}	
13	30	0.4038	0.8941	1.1341	0.7303	6.41×10^{5}	5.35×10^{8}	
20	4	0.5468	0.2495	1.1956	0.6488	2.77×10^{6}	1.09×10^{9}	Region II
4	20	0.2495	0.5468	1.1956	0.9461	1.91×10^{2}	1.16×10^{6}	Region II
4	29	0.2495	0.8094	1.0266	0.7771	1.57×10^{5}	2.01×10^{8}	RB II
29	4	0.8094	0.2495	1.0266	0.2172	9.18×10^{11}	6.79×10^{12}	RB II
4	2	0.2495	0.0727	0.2669	0.0175	1.47×10^{13}	1.72×10^{13}	Region II
2	4	0.0727	0.2495	0.2669	0.1942	3.56×10^{12}	2.13×10^{13}	Region II
25	30	0.6314	0.8941	1.0873	0.4559	3.10×10^{8}	2.07×10^{10}	
30	25	0.8941	0.6314	1.0873	0.1931	6.67×10^{10}	3.95×10^{11}	
26	8	0.6783	0.3837	0.7479	0.0696	1.17×10^{12}	2.22×10^{12}	Region II
8	26	0.3837	0.6783	0.7479	0.3643	2.13×10^{9}	6.10×10^{10}	Region II
27	11	0.6863	0.3999	0.8956	0.2093	3.98×10^{10}	2.74×10^{11}	RB II
11	27	0.3999	0.6863	0.8956	0.4957	3.97×10^{7}	3.82×10^{9}	RB II
30	24	0.8941	0.5821	1.9287	1.0346	5.56×10^{2}	7.65×10^{6}	RB I
24	30	0.5821	0.8941	1.9287	1.3466	2.62×10^{-1}	6.36×10^{4}	RB I
16	3	0.4679	0.2263	0.5098	0.0419	4.13×10^{11}	6.07×10^{11}	Region I
3	16	0.2263	0.4679	0.5098	0.2836	8.96×10^{9}	1.22×10^{11}	Region I
25	6	0.6314	0.2871	0.8157	0.1843	2.93×10^{11}	1.60×10^{12}	RB I
6	25	0.2871	0.6314	0.8157	0.5286	4.79×10^{7}	6.24×10^{9}	RB I
24	16	0.5821	0.4679	0.6053	0.0232	8.89×10^{12}	1.10×10^{13}	Region I
16	24	0.4679	0.5821	0.6053	0.1374	2.12×10^{11}	7.50×10^{11}	Region I
17	15	0.5257	0.4426	1.0643	0.5386	1.08×10^{8}	1.55×10^{10}	
15	17	0.4426	0.5257	1.0643	0.6217	1.15×10^{7}	3.52×10^{9}	
28	13	0.7824	0.4038	0.8558	0.0734	1.18×10^{12}	2.33×10^{12}	
13	28	0.4038	0.7824	0.8558	0.4521	1.88×10^{8}	1.21×10^{10}	
7	5	0.2974	0.2688	0.3197	0.0223	3.83×10^{12}	4.70×10^{12}	Region II

5	7	0.2688	0.2974	0.3197	0.0509	2.64×10^{12}	4.22×10^{12}	Region II
23	2	0.5771	0.0727	0.6283	0.0512	1.82×10^{12}	2.92×10^{12}	Region II
2	23	0.0727	0.5771	0.6283	0.5556	1.62×10^{7}	2.70×10^{9}	Region II

Table S3. The barrier heights and HTST rate constants of all direct paths between isomers in Table S1. The columns are index of the initial isomer, index of the final isomer, energy of initial isomer, energy of final isomer, energy of transition state, barrier height, rate constant at 450 K, rate constant at 700 K, and notes respectively. The notes indicate whether it is a transition inside one region ("Region I" or "Region II"), or a transition at region boundary (RB) ("RB I" or "RB II"), or other types (empty). Note that this table includes not only the transition shown in MST (Figure 3), but also other direct paths in the original isomerization graph (Figure S1). The extra paths are not part of MEP, and their barrier energies and rate constants can be high. The HTST rate constants are calculated according to Eq. (2).

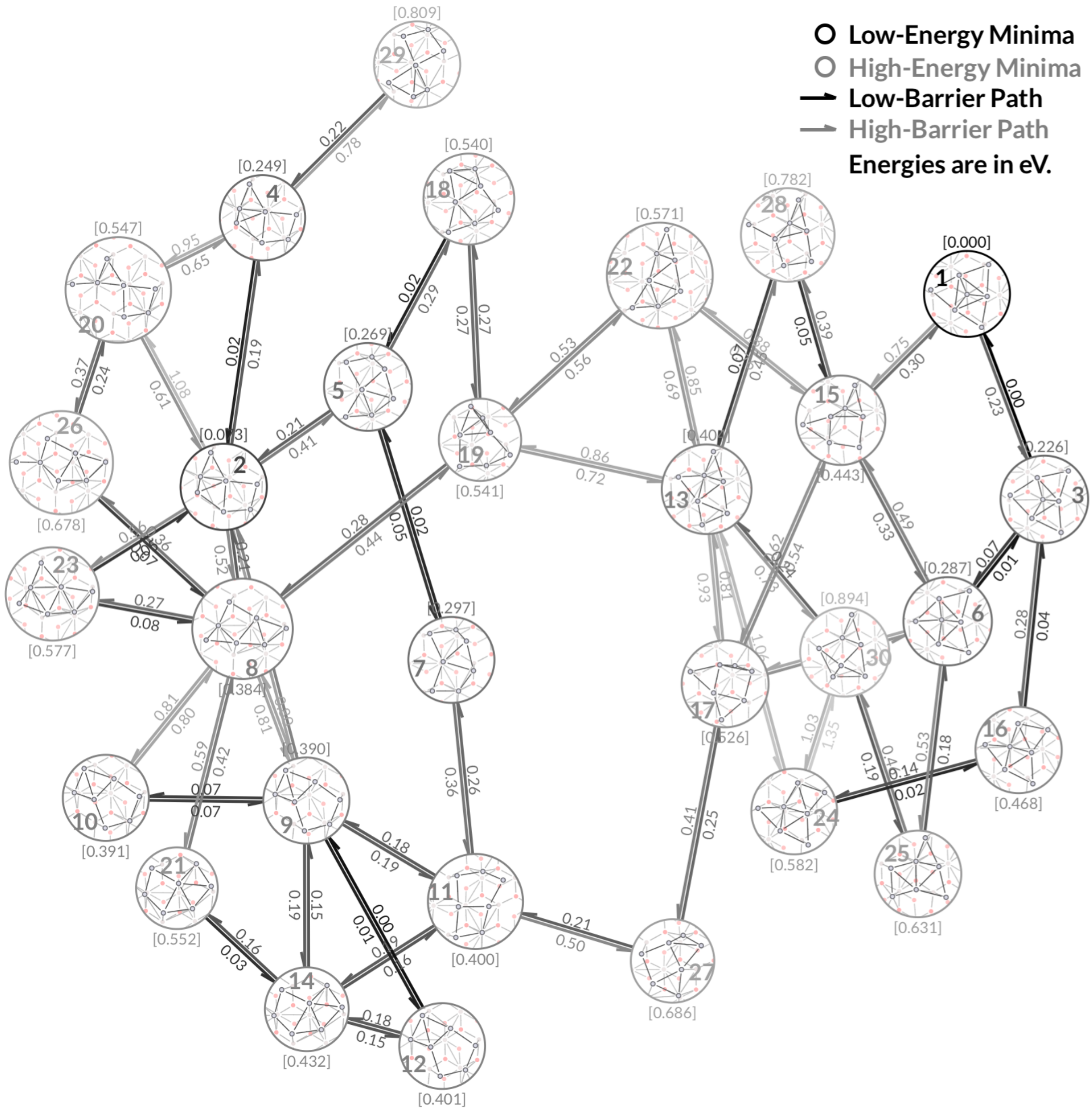


Figure S1. The Pt_7 on Al_2O_3 isomerization graph, including all direct NEB paths between low-energy isomers, shown as 48 edges in the graph. The notations are the same as Figure 3. The rate constants for each edge is listed in Table S2. Figure 3 is a subgraph of this graph, contains all vertices and only edges that are part of MEP.

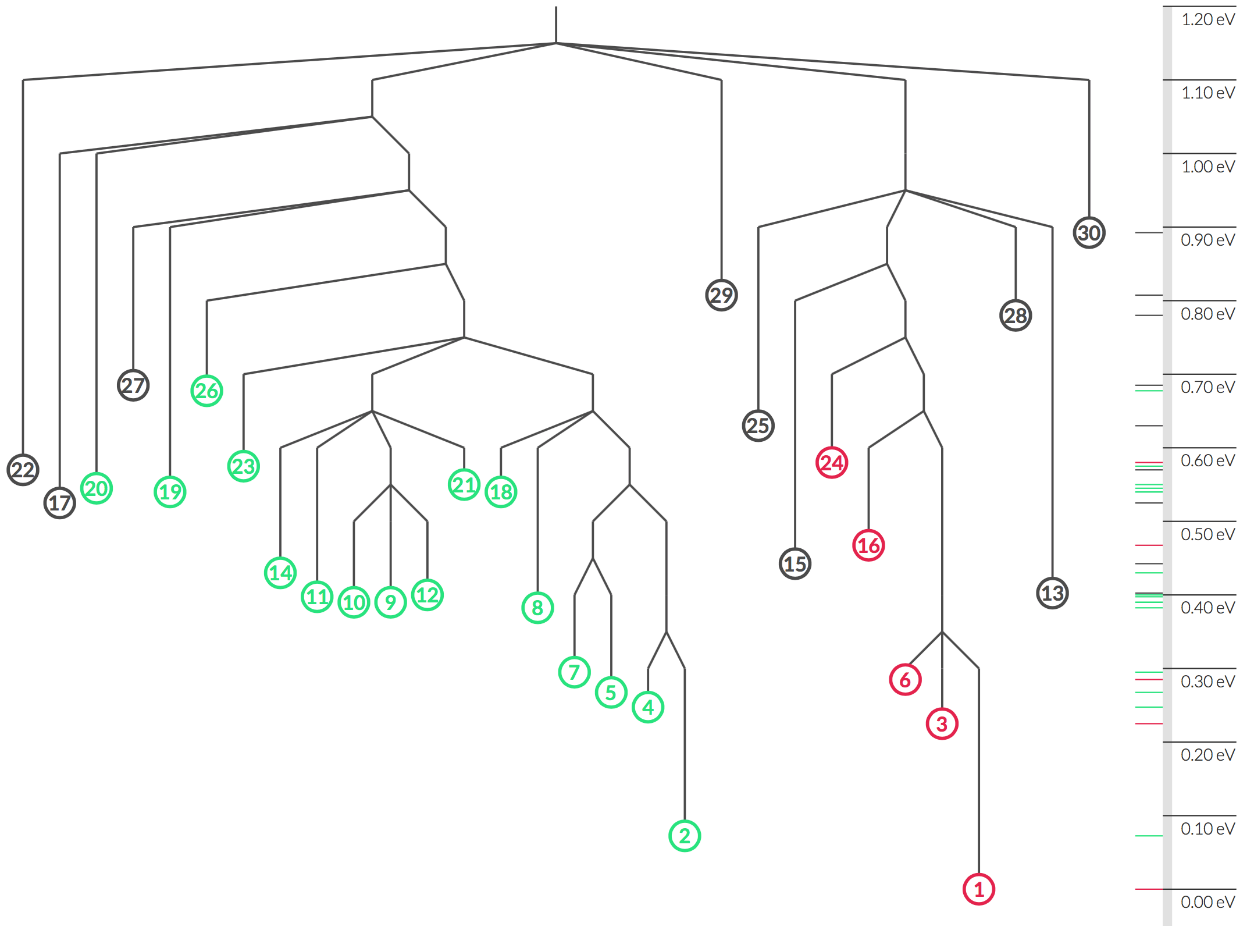


Figure S2. The disconnectivity graph of Al_2O_3 supported Pt_7 cluster isomers, showing connectivity between low-energy isomers. Isomers that are considered within region I and region II in 700 K are labeled as red and green, respectively. The energy (relative to global minimum) scale are shown as the vertical bar to the right.

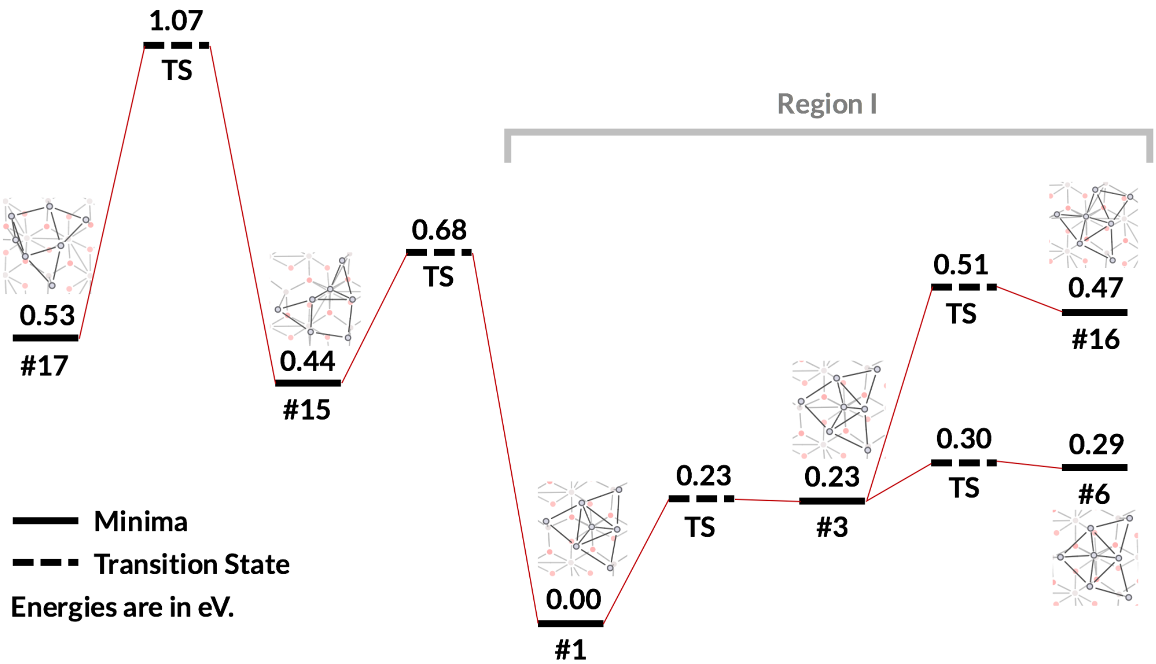


Figure S3. The isomerization MEP among isomers in region I and some adjacent isomers. The high barrier energy between isomer #1 and 15 makes the transition outwards region I difficult at catalytic relevant temperature.

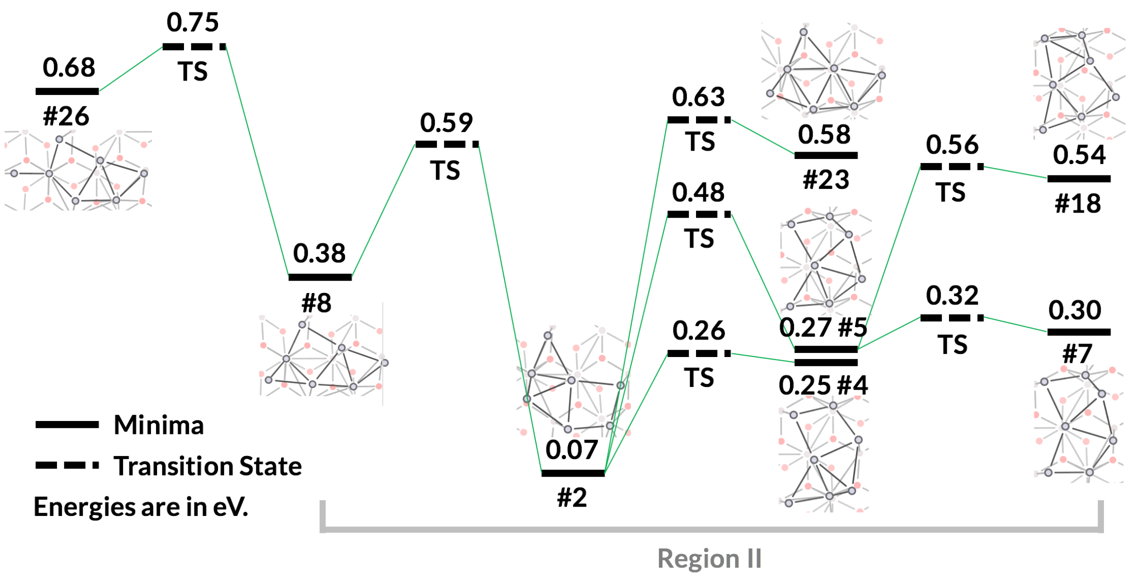


Figure S4. The isomerization MEP among isomers in region I and some adjacent isomers. The high energy of transition state between isomer #8 and #26 makes the transition outwards region II difficult at catalytic relevant temperature.

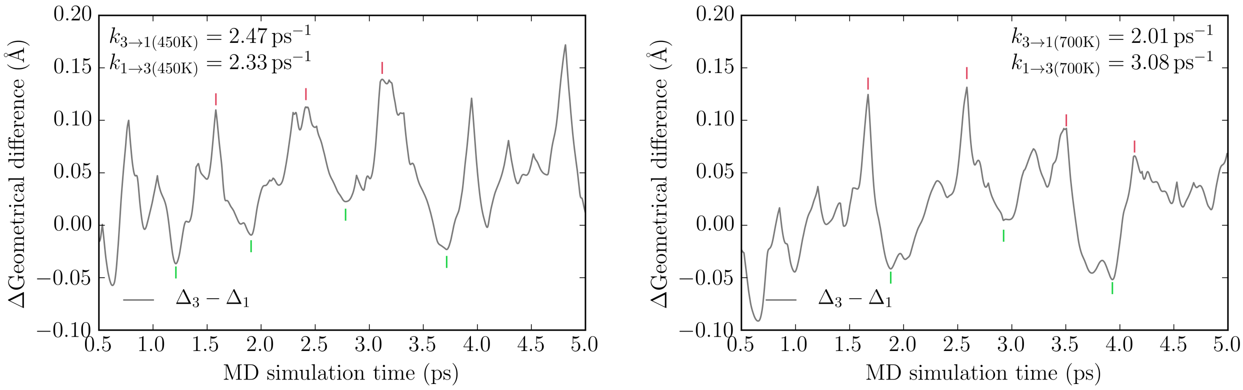


Figure S5. The difference between geometrical differences measured from isomers #3 and #1 based on MD trajectories starting from isomer #1 simulated at (a, left) 450 K and (b, right) 700 K. The maxima (labeled by red vertical lines) correspond to instants when the MD geometry is closest to isomer #1 and farthest to isomer #3, and the minima (labeled by green vertical lines) correspond to instants when the MD geometry is closest to isomer #3 and farthest to isomer #1. The rate constants are estimated by the inverse of average time span between adjacent maxima and minima.

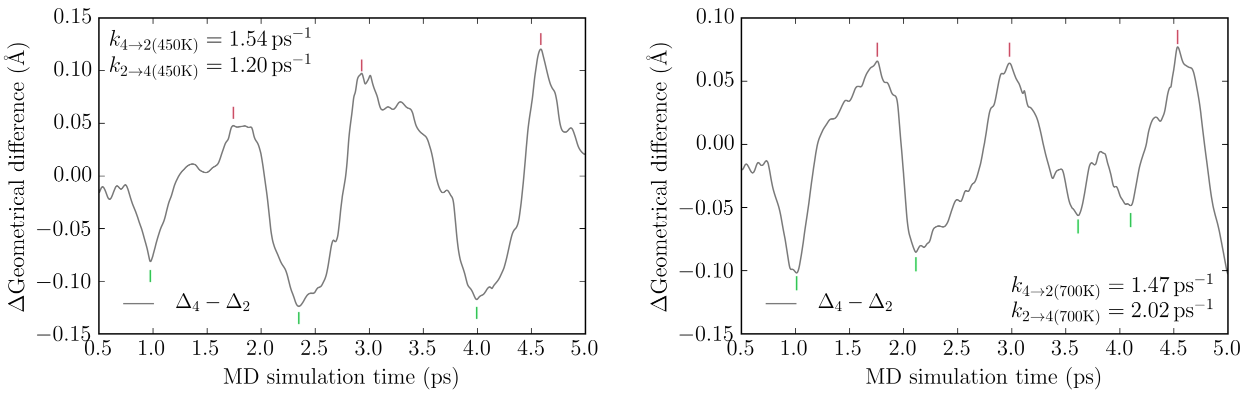


Figure S6. The difference between geometrical differences measured from isomers #4 and #2 based on MD trajectories starting from isomer #2 simulated at (a, left) 450 K and (b, right) 700 K. The maxima (labeled by red vertical lines) correspond to instants when the MD geometry is closest to isomer #2 and farthest to isomer #4, and the minima (labeled by green vertical lines) correspond to instants when the MD geometry is closest to isomer #4 and farthest to isomer #2. The rate constants are estimated by the inverse of average time span between adjacent maxima and minima.

Computational Details:

A 15 Angstrom vacuum gap along surface *z* axis has been added to avoid image interactions. The energy cutoff of basis set expansion is set to 400 eV. The dipole correction is enabled for NEB and frequency (finite difference method) calculations. For path optimization, 5 images are used between a pair of isomers. The normal NEB is performed first. Then for those converged paths without any intermediates, climbing-image NEB (CI-NEB) is used to find the transition state geometry and the corresponding transition state energy. If the path contains intermediates, the isomers corresponding to the intermediates are identified. Eventually the path between any two isomers can be decomposed to one or multiple direct paths. We found 48 such direct paths which are listed in Table S3. Among these paths, 29 direct paths are part of minimal energy paths, which are shown in Figure 3.