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Supporting Information

Single-layered Platinum Nanocage: A Highly Selective and Efficient Catalyst for Fuel Cell

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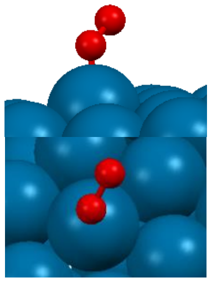
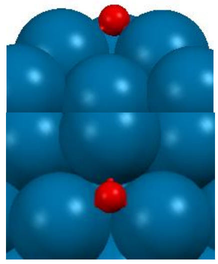
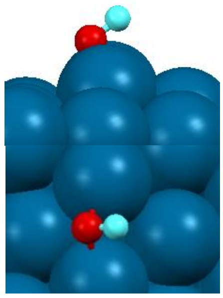
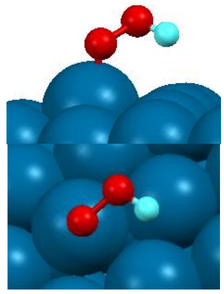
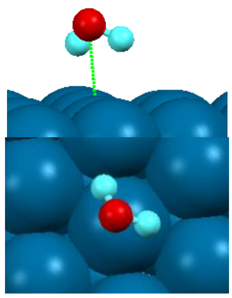
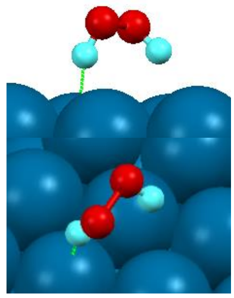
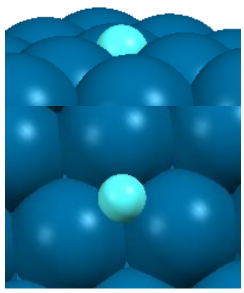
S1: Adsorption site of the most stable adsorbates on the (111) facet of the Pt_{66} nanocage

Adsorbate	Optimized structure	Adsorbate	Optimized structure
$*O_2$		$*O$	
$*OH$		$*OOH$	
$*H_2O$		$*H_2O_2$	
$*H$			

S2: Microkinetic Analysis

A microkinetic analysis is developed from the DFT calculated values to give more insight into the coverage, reaction rate and the selectivity of different products. Elementary steps considered in the microkinetic model are summarized as following.

O_2 (g) + * → O_2*

½ H_2 (g) + * → H*

$O_2* + * \xrightarrow{k_1} 2O*$

$O_2* + H* \xrightarrow{k_2} OOH* + *$

$OOH* + * \xrightarrow{k_3} O* + OH*$

$O* + H* \xrightarrow{k_4} OH* + *$

$OOH* + H* \xrightarrow{k_5} H_2O_2* + *$

$H_2O_2* + * \xrightarrow{k_6} OH* + OH*$

$OH* + H* \xrightarrow{k_7} H_2O* + *$

The adsorption of O_2 and H_2 are highly exothermic and the process are assumed to be in equilibrium and are expected to be strongly adsorbed. The equilibrium constants are calculated using the following equation $K_{eq} = \exp[-(\Delta E_{ads}-T\Delta S)/k_BT]$, where ΔE_{ads} is the adsorption energy of O_2 and H_2, and ΔS is the entropy change of O_2 and H_2 upon adsorption, k_B is the Boltzmann's Constant and T is the temperature in Kelvin. The gas phase entropy is obtained from NIST database.[1] The other steps are described by forward and backward reaction rate. Rate constants are calculated using the following equation.

$$k_{i/-i} = \left(\frac{k_B T}{h}\right)\left(\frac{q_F}{q_I}\right) e^{-\Delta G^{\ddagger}/k_B T}$$

Where k_B is the Boltzmann constant, T is the temperature, h is the Plank constant. Here q_I and q_F are the vibrational partition functions for the initial and final state structures and $\Delta G^{\ddagger}$ is the

Gibbs free energy barrier for the initial and final state of the elementary reaction. The vibrational partition functions were calculated using the following equation:

$$q = \sum_i \frac{1}{1 - e^{-h\nu_i/k_B T}}$$

where υ_i are the vibrational frequencies.

The backward reactions are not considered for all the exothermic forward reactions assuming the exothermic reactions are irreversible. The site balance of intermediate species included in the reaction is written in terms of coverage.

$\Theta_{O2} + \Theta_{OOH} + \Theta_{O} + \Theta_{OH} + \Theta_{H2O} + \Theta_{H2O2} + \Theta_{*} = 1$

The coverage of O_2 and H_2 are obtained by the following equations.

$\Theta_{O2} = p_{O2} K_{O2} \Theta_*$

$\Theta_{H} = p_{H2}^{1/2} K_{H2} \Theta_*$

The coverage of the other species is obtained by considering the steady-state approximation, where the rate of formation and rate of consumption of each species are assumed to be equal:

$d\Theta_O/dt = 2k_1\Theta_{O2}\Theta_* - k_4\Theta_O\Theta_H + k_3\Theta_{OOH}\Theta_* = 0$ (S1)

$d\Theta_{OOH}/dt = k_2\Theta_{O2}\Theta_H - k_3\Theta_{OOH}\Theta_* - k_5\Theta_H\Theta_{OOH} = 0$ (S2)

$d\Theta_{OH}/dt = k_4\Theta_O\Theta_H + k_3\Theta_{OOH}\Theta_* - k_7\Theta_{OH}\Theta_H + 2k_6\Theta_{H2O2}\Theta_* = 0$ (S3)

$d\Theta_{H2O2}/dt = k_5\Theta_H\Theta_{OOH} - k_6\Theta_{H2O2}\Theta_* = 0$ (S4)

$d\Theta_{H2O}/dt = k_7\Theta_{OH}\Theta_H = 0$ (S5)

Now, adding the S1 and S3, we get

$2k_1\Theta_{O2}\Theta_* + 2k_3\Theta_{OOH}\Theta_* - k_7\Theta_{OH}\Theta_H + 2k_6\Theta_{H2O2}\Theta_* = 0$

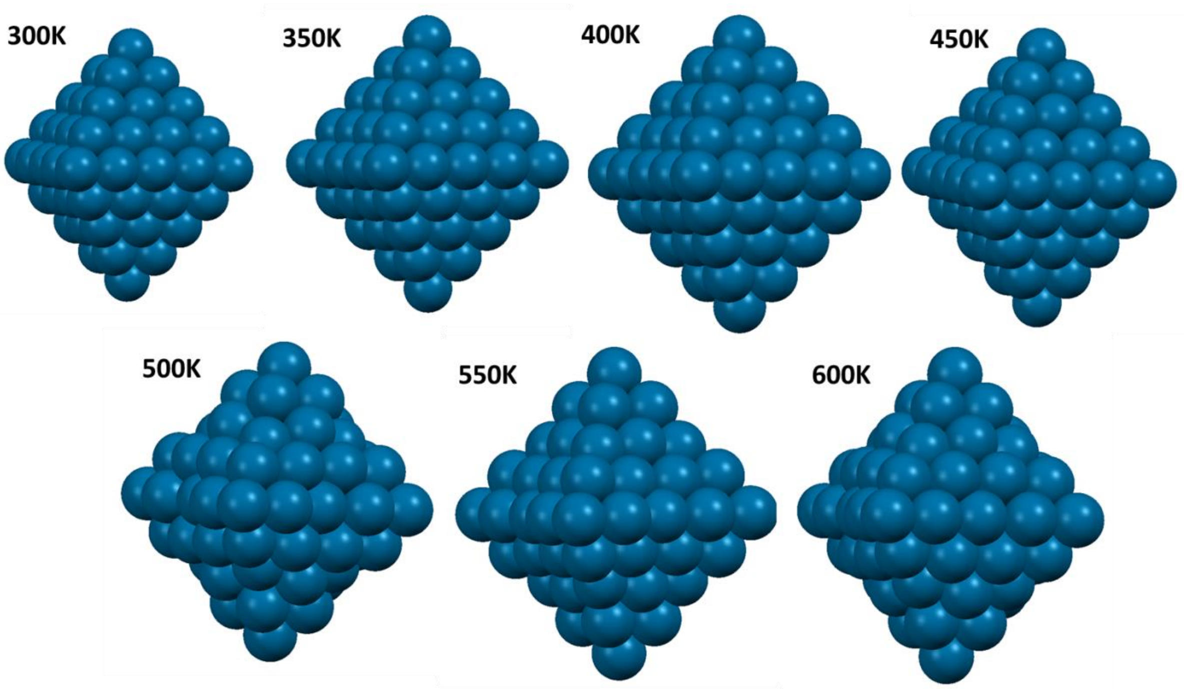
Using the value of Θ_{H2O2} in the above equation, we get

$\Theta_{OH} = \frac{2k_1\Theta_{O2}\Theta_* + (2k_3\Theta_* + 2k_5\Theta_H)\Theta_{OOH}}{k_7\Theta_H}$

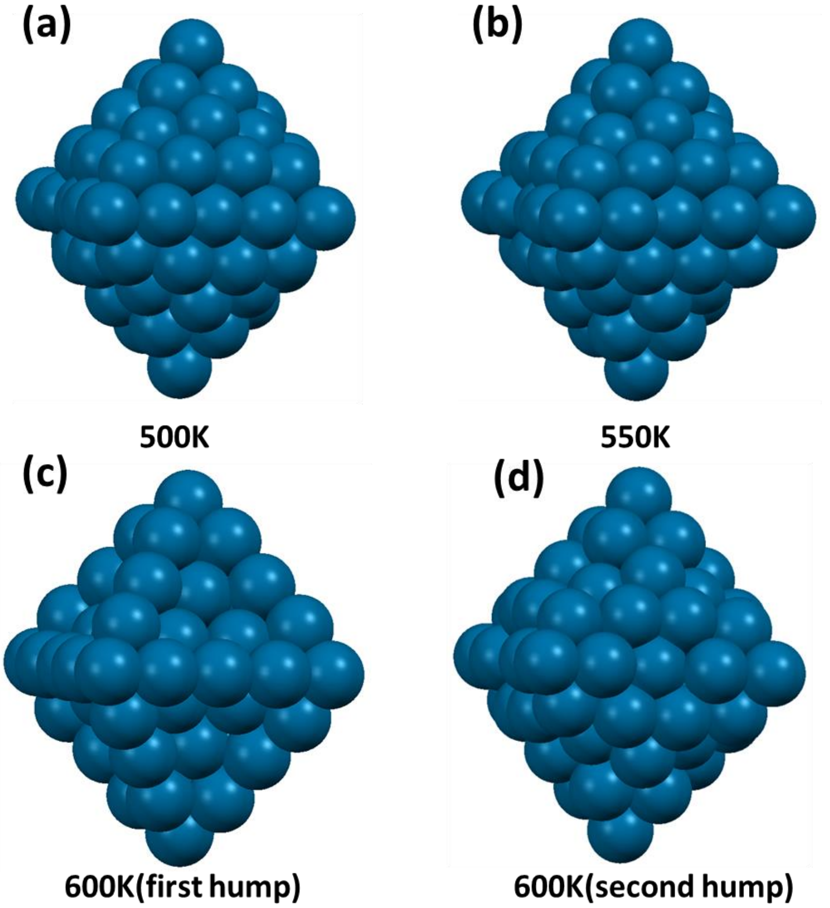
Now, using the value of Θ_{H2O2} and Θ_{OH}

$$\frac{d\Theta_{H2O2}/dt}{d\Theta_{H2O}/dt} = \frac{2k_5\Theta_H}{2k_1\Theta_{O2}\Theta* + 2k_3\Theta* + 2k_5\Theta_H}$$

S3: Snapshots of the nanocage after the simulation at different temperatures



S4: Snapshots of the nanocage during the simulation at different temperatures



S5: Values of phonon frequencies

1 f	216.397269	cm-1
2 f	216.390613	cm-1
3 f	216.386107	cm-1
4 f	212.498069	cm-1
5 f	212.492794	cm-1
6 f	211.898624	cm-1
7 f	211.893677	cm-1
8 f	211.885754	cm-1
9 f	207.194281	cm-1
10 f	206.298681	cm-1
11 f	206.288807	cm-1
12 f	206.288406	cm-1
13 f	204.809370	cm-1
14 f	204.024513	cm-1
15 f	203.140960	cm-1
16 f	203.139597	cm-1
17 f	203.139471	cm-1
18 f	202.342601	cm-1
19 f	202.342100	cm-1
20 f	202.341279	cm-1
21 f	199.064115	cm-1
22 f	199.055852	cm-1
23 f	199.036579	cm-1
24 f	198.946030	cm-1
25 f	198.940236	cm-1
26 f	196.898465	cm-1

27 f	196.875841	cm-1
28 f	191.696890	cm-1
29 f	191.563261	cm-1
30 f	191.534444	cm-1
31 f	191.533104	cm-1
32 f	191.357522	cm-1
33 f	191.348837	cm-1
34 f	191.344277	cm-1
35 f	186.567979	cm-1
36 f	186.559462	cm-1
37 f	186.541792	cm-1
38 f	174.351973	cm-1
39 f	174.326767	cm-1
40 f	174.325227	cm-1
41 f	170.056933	cm-1
42 f	169.145360	cm-1
43 f	169.134252	cm-1
44 f	169.100871	cm-1
45 f	167.585393	cm-1
46 f	167.578682	cm-1
47 f	159.796396	cm-1
48 f	159.748679	cm-1
49 f	159.745521	cm-1
50 f	158.597013	cm-1
51 f	158.591112	cm-1
52 f	158.296059	cm-1
53 f	158.293344	cm-1

54 f 158.272506 cm-1

55 f 156.429550 cm-1

56 f 156.429417 cm-1

57 f 156.414640 cm-1

58 f 155.370191 cm-1

59 f 155.355359 cm-1

60 f 155.352346 cm-1

61 f 154.650994 cm-1

62 f 154.633116 cm-1

63 f 154.630503 cm-1

64 f 154.448433 cm-1

65 f 153.554207 cm-1

66 f 153.553562 cm-1

67 f 153.539671 cm-1

68 f 153.099550 cm-1

69 f 153.095081 cm-1

70 f 153.088415 cm-1

71 f 145.224251 cm-1

72 f 145.222899 cm-1

73 f 145.213292 cm-1

74 f 141.044103 cm-1

75 f 141.036874 cm-1

76 f 141.032107 cm-1

77 f 140.349207 cm-1

78 f 139.358300 cm-1

79 f 139.341066 cm-1

80 f 136.801158 cm-1

81 f	135.126733	cm-1
82 f	135.118000	cm-1
83 f	135.116471	cm-1
84 f	132.469803	cm-1
85 f	132.453610	cm-1
86 f	126.792780	cm-1
87 f	126.785384	cm-1
88 f	126.748204	cm-1
89 f	124.572329	cm-1
90 f	124.539914	cm-1
91 f	124.530342	cm-1
92 f	124.519404	cm-1
93 f	124.517932	cm-1
94 f	124.490562	cm-1
95 f	120.283321	cm-1
96 f	120.231270	cm-1
97 f	120.230184	cm-1
98 f	119.687426	cm-1
99 f	119.686831	cm-1
100 f	119.664871	cm-1
101 f	118.705245	cm-1
102 f	118.701471	cm-1
103 f	118.672999	cm-1
104 f	117.977674	cm-1
105 f	117.475657	cm-1
106 f	117.474674	cm-1
107 f	117.449522	cm-1

108 f	116.303550	cm-1
109 f	116.293997	cm-1
110 f	115.712217	cm-1
111 f	115.636521	cm-1
112 f	115.622368	cm-1
113 f	115.620605	cm-1
114 f	114.215915	cm-1
115 f	114.204048	cm-1
116 f	114.203932	cm-1
117 f	105.390923	cm-1
118 f	105.336583	cm-1
119 f	105.336224	cm-1
120 f	103.255597	cm-1
121 f	103.214325	cm-1
122 f	103.213635	cm-1
123 f	102.576424	cm-1
124 f	102.562288	cm-1
125 f	102.547928	cm-1
126 f	101.481127	cm-1
127 f	101.415193	cm-1
128 f	99.480960	cm-1
129 f	99.466128	cm-1
130 f	99.418246	cm-1
131 f	98.463143	cm-1
132 f	98.462015	cm-1
133 f	98.430052	cm-1
134 f	97.955717	cm-1

135 f	97.949681	cm-1
136 f	95.669067	cm-1
137 f	95.651752	cm-1
138 f	93.736848	cm-1
139 f	93.670527	cm-1
140 f	93.669284	cm-1
141 f	90.275764	cm-1
142 f	90.275181	cm-1
143 f	90.239315	cm-1
144 f	89.500314	cm-1
145 f	89.451227	cm-1
146 f	89.449778	cm-1
147 f	88.557440	cm-1
148 f	88.509162	cm-1
149 f	87.971942	cm-1
150 f	85.719509	cm-1
151 f	85.656995	cm-1
152 f	85.650446	cm-1
153 f	81.352762	cm-1
154 f	81.350543	cm-1
155 f	81.314130	cm-1
156 f	80.957805	cm-1
157 f	77.653238	cm-1
158 f	77.635871	cm-1
159 f	77.634017	cm-1
160 f	76.391176	cm-1
161 f	74.473961	cm-1

162 f 74.467352 cm-1

163 f 73.787004 cm-1

164 f 73.758942 cm-1

165 f 73.757655 cm-1

166 f 72.693832 cm-1

167 f 72.684093 cm-1

168 f 72.670422 cm-1

169 f 72.591312 cm-1

170 f 68.986312 cm-1

171 f 68.981394 cm-1

172 f 68.942350 cm-1

173 f 65.527997 cm-1

174 f 65.454709 cm-1

175 f 65.453659 cm-1

176 f 64.642665 cm-1

177 f 64.640316 cm-1

178 f 64.598151 cm-1

179 f 58.743402 cm-1

180 f 58.669549 cm-1

181 f 52.802558 cm-1

182 f 52.766415 cm-1

183 f 52.761236 cm-1

184 f 52.697560 cm-1

185 f 49.057866 cm-1

186 f 49.056609 cm-1

187 f 49.021709 cm-1

188 f 34.243464 cm-1

189 f	34.126837	cm-1
190 f	34.124727	cm-1
191 f	16.613894	cm-1
192 f	16.602548	cm-1
193 f	16.397284	cm-1
194 f/i	17.026834	cm-1
195 f/i	17.039677	cm-1
196 f/i	17.043370	cm-1
197 f/i	35.377571	cm-1
198 f/i	35.394129	cm-1