Supporting Information

Dual-dehydrogenation-promoted catalytic oxidation of formaldehyde on alkali-treated Pt clusters at room temperature

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Preparation of catalysts

All reagents were of analytical grade and were used without further purification.

Preparation of sample I: 0.4 g of P25 was dispersed in 20 mL of deionized water under magnetic stirring for 30 min. Then 0.8 mL of H₂PtCl₆ (2.56 mmol L⁻¹) aqueous solution was added to the suspension under magnetic stirring for another 30 min. Next, 5 mL of NaBH₄ (0.02 mol L⁻¹) aqueous solution was quickly added to the suspension under magnetic stirring for 60 min. After reduction, the suspension was separated by centrifugation. The obtained precipitate was washed three times with deionized water and finally dried under vacuum at 80 °C for 6 h.

Preparation of sample II: 0.15 g of sample I was dispersed in 20 mL of deionized water under magnetic stirring for 30 min. Then 5 mL of NaOH (1 mol L⁻¹) aqueous solution was added to the suspension under magnetic stirring for 60 min. Next, the suspension was separated by centrifugation. The obtained precipitate was washed three times with deionized water and finally dried under vacuum at 80 °C for 6 h.

Preparation of sample III: 0.15 g of sample I was dispersed in 20 mL of deionized water under magnetic stirring for 30 min. Then 5 mL of Na₂CO₃ (0.5 mol L⁻¹) aqueous solution was added to the suspension under magnetic stirring for 60 min. Next, the suspension was separated by centrifugation. The obtained precipitate was
washed three times with deionized water and finally dried under vacuum at 80 °C for 6 h.

**Preparation of sample IV:** 0.4 g of P25 was dispersed in 20 mL of deionized water under magnetic stirring for 30 min. Then 0.8 mL of H₂PtCl₆ (2.56 mmol L⁻¹) was added to the suspension under magnetic stirring for another 30 min. After that, 5 mL of the mixed aqueous solution of NaBH₄ (0.02 mol L⁻¹) and NaOH (1 mol L⁻¹) was quickly added to the suspension under magnetic stirring for 60 min. After reduction, the suspension was separated by centrifugation. The obtained precipitate was washed three times with deionized water and finally dried under vacuum at 80 °C for 6 h.

**Preparation of sample V:** 0.3 g of sample IV was dispersed in 40 mL of deionized water under magnetic stirring for 30 min. Then 10 mL of NaCl (0.5 mol L⁻¹) aqueous solution was added to the suspension under magnetic stirring for 60 min. Next, the suspension solution was separated by centrifugation. The obtained precipitate was washed three times with deionized water and finally dried under vacuum at 80 °C for 6 h.

**Preparation of sample VI:** 0.15 g of sample V was dispersed in 20 mL of deionized water under magnetic stirring for 30 min. Then 5 mL of NaOH (1 mol L⁻¹) aqueous solution was added to the suspension under magnetic stirring for 60 min. Next, the suspension solution was separated by centrifugation. The obtained precipitate was washed three times with deionized water and finally dried under vacuum at 80 °C for 6 h.
Table S1. Atomic ratios of Ti, O, Na, Pt and Cl for the Sample I, II, III, IV, V and VI

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti</th>
<th>O</th>
<th>Na</th>
<th>Pt</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>31.06</td>
<td>62.20</td>
<td>5.47</td>
<td>0.22</td>
<td>1.05</td>
</tr>
<tr>
<td>II</td>
<td>31.41</td>
<td>61.90</td>
<td>6.14</td>
<td>0.23</td>
<td>0.32</td>
</tr>
<tr>
<td>III</td>
<td>30.42</td>
<td>62.19</td>
<td>6.89</td>
<td>0.24</td>
<td>0.26</td>
</tr>
<tr>
<td>IV</td>
<td>30.12</td>
<td>62.51</td>
<td>6.94</td>
<td>0.22</td>
<td>0.21</td>
</tr>
<tr>
<td>V</td>
<td>31.79</td>
<td>62.42</td>
<td>5.30</td>
<td>0.22</td>
<td>0.28</td>
</tr>
<tr>
<td>VI</td>
<td>30.98</td>
<td>62.20</td>
<td>6.34</td>
<td>0.24</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Fig. S1 Optimized geometrical structures of Pt$_{43}$ cluster. The exchange-correlation function used in all DFT calculations was described by the Perdew-Burke-Ernzerhof (PBE) of the Generalized Gradient Approximation (GGA). The interaction between ionic core and valence electrons was treated by the ultrasoft pseudo-potential. The cutoff energy of 350 eV, the Monkhorst-Pack k-point mesh of $1 \times 1 \times 1$ and self-consistent field tolerance of $2.0 \times 10^{-6}$ eV per atom were used to conduct the geometry optimization calculations for various Pt clusters. Pt$_{43}$ cluster was optimized in 20 Å $\times$ 20 Å $\times$ 25 Å box. The convergence thresholds of the geometry optimization calculations were $2.0 \times 10^{-5}$ eV per atom for energy, 0.1 GPa for stress, 0.05 eV Å$^{-1}$ for force and 0.002 Å for displacement. The higher cutoff energy and the wider Monkhorst-Pack k-point mesh were tested. The obtained results indicate that the variations were smaller than 0.01 Å in the displacement and 0.01 eV in the free energy, indicating high accuracy of the performed calculations.
Fig. S2 Optimized free radical and molecular structures: (a) O$_2$, (b) HCHO, (c) CO, (d) H$_2$O$_2$, (e) H$_2$O, (f) ·CHO, (g) CO$_2$, (h) ·COOH and (i) H$_2$CO$_3$. The numbers in each panel represent the bond lengths. The green, gray and red spheres represent H, C and O atoms, respectively. All molecules are optimized in a cube with the side length of 10 Å. The cutoff energy of 350 eV for the plane-wave basis set, the Monkhorst-Pack k-point mesh of 1 × 1 × 1 and the self-consistent field tolerance of 2.0 × 10$^{-6}$ eV per atom were adopted to conduct the geometry optimization calculations. The convergence thresholds for energy, stress, force and displacement in the optimization calculations were 2.0 × 10$^{-5}$ eV per atom, 0.1 GPa, 0.05 eV Å$^{-1}$ and 0.002 Å, respectively. The higher cutoff energy and the wider Monkhorst-Pack k-point mesh were also tested. The obtained results indicate that the variations were smaller than 0.01 Å in the displacement and 0.01 eV in the free energy, indicating high accuracy of the performed calculations.
Fig. S3 CO$_2$ concentration as a function of the reaction time for samples I, II, III, IV, V and VI.

Fig. S4 High-resolution XPS spectra of samples I, II, III, IV, V and VI. (a) Ti 2p, (b) O 1s, (c) Na 1s and (d) Pt 4f regions.
**Fig. S5** HRTEM images of sample I (a) and sample IV (b).

**Fig. S6** Adsorption of HCHO molecule on Pt cluster. HCHO molecule cannot be stably chemisorbed on Pt cluster.
Fig. S7 Adsorption of HCHO molecule on {101}, {100} and {001} surfaces of anatase TiO$_2$. The $2 \times 2$, $2 \times 1$ and $2 \times 2$ supercells consisting of four unit layers were used to simulate the {101}, {100} and {001} surfaces of anatase TiO$_2$, respectively. A 15 Å vacuum slab was introduced to eliminate the interaction between adjacent O$_2$ molecules. The cutoff energy of 400 eV and the Monkhorst-Pack k-point mesh of $4 \times 4 \times 1$ were adopted to conduct the geometry optimization calculations. The tolerances of energy, force, stress and displacement in the optimized calculation were $2.0 \times 10^{-5}$ eV per atom, 0.05 eV Å$^{-1}$, 0.1 GPa and 0.002 Å, respectively. During the geometry optimization calculations, the positions of all atoms were optimized except for those in the bottom unit layer. Moreover, the more unit layers, the thicker vacuum slab, the higher cutoff energy, the larger supercell and the wider Monkhorst-Pack k-point mesh were tested, respectively. The obtained results suggested that the variations were smaller than 0.01 Å in displacement and 0.02 eV in energy, indicating high accuracy of present calculations.
**Fig. S8** Interaction between HCHO molecule and surface O₂ species on Pt cluster. The two-coordination O atom in surface O₂ species cannot independently dehydrogenate HCHO molecule.

**Fig. S9** Interaction between HCHO molecule and –OH group on Pt cluster. The –OH group on Pt cluster cannot dehydrogenate HCHO molecule, indicating its low oxidizing activity.
**Fig. S10** Interaction between CO molecule and –OH group on Pt cluster. The C atom of CO molecule cannot be bonded to the O atom of the –OH group on Pt cluster.

**Fig. S11** Interaction between CO molecule and –O group on Pt cluster. The oxidizing activity of –O group on Pt cluster is also low, which can not dehydrogenate HCHO molecule.
Fig. S12 Interaction between HCHO molecule and –OH groups on Pt cluster. Any one of the two –OH groups cannot independently oxidize HCHO molecule.
Fig. S13 Interaction between HCHO molecule and Cl\(^{-}\) ion adsorbed on Pt cluster. The –OH group cannot cooperate with the adsorbed Cl\(^{-}\) ion to dually dehydrogenate HCHO molecule.