Supporting information

Reconstruction of Rh nanoparticles in methanol oxidation reaction

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C) and D) show TEM images of nanomaterials with different particle sizes. E) illustrates a histogram of particle ratios against particle size (nm). The x-axis represents particle size (nm), and the y-axis represents the particle ratio. The chart indicates a peak around 4 nm, suggesting a concentration of particles at this size.
Fig. S1 TEM images and size distributions of Rh-ncs obtained by varying the precursor concentration: (a) 1.25mM; (b) 2.5mM; (c) 5mM; (d) 10mM; (e) 20mM; (f) 40mM, respectively.

Fig. S2 XPS spectra recorded of different types of Rh-ncs/SiO₂ catalysts. (a) fresh 2.4 nm Rh-ncs/SiO₂, (b) fresh 5.9 nm Rh-ncs/SiO₂, (c) 5.9 nm Rh-ncs/SiO₂ that was used at 453 K, (d) 5.9 nm Rh-ncs/SiO₂ that was used with temperature-programmed ramp up to 503 K, (e) 5.9 nm Rh-ncs/SiO₂ was calcined at 503 K.
Fig. S3 TEM images of Rh-ncs/SiO$_2$ catalysts with the average side length of 5.9 nm under various treatments. (a) before reaction; (b) after the reaction at 473 K; The average particle size of figure B is 6.5 nm.

Fig. S4 Two-dimensional diagram of (100) and (111) facets in Rh-ncs.

area (100)=$6(a^2+2\sqrt{2}ac+c^2)$, area (111)=$2\sqrt{3}a^2$. 

<table>
<thead>
<tr>
<th>Catalyst (5.9 nm)</th>
<th>Side length (a.u.)</th>
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<tbody>
<tr>
<td></td>
<td>normalized length ratio</td>
</tr>
<tr>
<td>fresh catalyst</td>
<td>0.37</td>
</tr>
<tr>
<td>used catalyst (453 K)</td>
<td>0.58</td>
</tr>
<tr>
<td>used catalyst (473 K)</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Fig. S5 HR-TEM images and the interplanar spacing of 5wt% Rh/SiO$_2$-imp catalyst.
Fig. S6 The activity and selectivity of two Rh-ncs/SiO₂ catalysts (A, B, with the average side length of 2.4 nm, C, D, with the average side length of 5.9 nm) in the methanol oxidation reaction at 453 K for A, C, and 473 K for B, D. Oxygen content was about 25% and balanced with N₂.

Fig. S7 ODH activity of two Rh-ncs/SiO₂ catalysts. The reaction condition was as the same as upper figure. (The irreversible nature of the oxidative conversion of CH₃OH to HCHO requires one oxidative CH₃OH dehydrogenation (ODH) event for each HCHO, DMM, and MF molecule formed. ODH rates rigorously reflect the intrinsic oxidation reactivity of active domains, without contributions from methanol molecules consumed because of various secondary reactions.)
Fig. S8 The interplanar spacing of Rh ncs in HR-TEM images (Figure 6).

Fig. S9 Stability of impregnation-derived Rh/SiO$_2$ catalyst.