Zr掺杂对PdO/Ce$_{1-x}$Pd$_x$O$_{2-\delta}$催化剂CO和CH$_4$催化氧化的影响

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Effects of Zr Addition on CO and CH$_4$ Catalytic Oxidation over PdO/Ce$_{1-x}$Pd$_x$O$_{2-\delta}$ Catalyst

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Table S1  Pd contents, difference in value of Pd contents in catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd Content (w/%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$\triangle C_{Pd}$ (w/%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdO/CP</td>
<td>1.70</td>
<td>0.20&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>CP</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>PdO/CPZ</td>
<td>1.65</td>
<td>0.28&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>CPZ</td>
<td>1.37</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> determined by XRF technique;  
<sup>b</sup> difference in value of Pd contents in PdO/CP and CP catalysts, PdO/CPZ and CPZ catalysts;  
<sup>c</sup> $\triangle C_{Pd} = 1.70 - 1.50 = 0.20$ (wt. %)  
<sup>d</sup> $\triangle C_{Pd} = 1.65 - 1.37 = 0.28$ (wt. %)
Part I The calculation of TOF of PdO species on the surface of PdO/CP and PdO/CPZ catalysts for CO oxidation.

Table S2. Flow rate of CO, CO conversion, amount of CO molecules chemisorbed on the PdO/CP and PdO/CPZ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$F_{CO}$ (μmol·s$^{-1}$) $^a$</th>
<th>$X_{CO}$/% $^b$</th>
<th>$V_{CO}$ (mL·g$^{-1}$) $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdO/CP</td>
<td>0.3</td>
<td>5.5</td>
<td>2.1</td>
</tr>
<tr>
<td>PdO/CPZ</td>
<td>0.3</td>
<td>19.4</td>
<td>2.9</td>
</tr>
</tbody>
</table>

$^a$ flow rate of CO; $^b$ CO conversion at 80 °C; $^c$ amount of CO chemisorbed on the PdO/CP and PdO/CPZ catalysts.

The amount of PdO/CP and PdO/CPZ catalysts used in CO oxidation is 200 mg. Assuming the amount of CO molecules chemisorbed on the PdO/CP and PdO/CPZ catalyst are $N_1$ and $N_2$, correspondingly.

$$N_1 = \frac{0.42 \times 10^{-3} \text{ L}}{22.4 \text{ L/mmol}} = 1.86 \times 10^{-5} \text{ mol}$$

$$N_2 = \frac{0.58 \times 10^{-3} \text{ L}}{22.4 \text{ L/mmol}} = 2.59 \times 10^{-5} \text{ mol}$$

Assuming the TOF of PdO on the surface of PdO/CP for CO oxidation is $\text{TOF}_{\text{PdO}}$, the TOF of PdO on the surface of PdO/CPZ for CO oxidation is $\text{TOF}_{\text{PdO-2}}$.

$$\text{TOF}_{\text{PdO}} = \frac{F_{CO} \times X_{CO}}{N_1} = \frac{0.3 \times 10^{-6} \text{ mol/s} \times 5.5\%}{1.86 \times 10^{-5} \text{ mol}} = 0.09 \times 10^{-2} \text{ (s$^{-1}$)}$$

$$\text{TOF}_{\text{PdO-2}} = \frac{F_{CO} \times X_{CO}}{N_2} = \frac{0.3 \times 10^{-6} \text{ mol/s} \times 19.4\%}{2.59 \times 10^{-5} \text{ mol}} = 0.22 \times 10^{-2} \text{ (s$^{-1}$)}$$
Part II  The calculation of TOF of Pd\(^{\text{II+}}\) cations in the CP and CPZ catalysts for CH\(_4\) oxidation.

Table S3  Flow rate of CH\(_4\), CH\(_4\) conversion, crystal size and cell parameter of CeO\(_2\), Pd content in the CP and CPZ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(F_{\text{CH}_4}) ((\mu)mol/s) (^a)</th>
<th>(X_{\text{CH}_4}) (%) (^b)</th>
<th>Crystal size of CeO(_2) (nm)</th>
<th>Cell parameter of CeO(_2) (nm)</th>
<th>Pd Content (wt. %) (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>0.15</td>
<td>15.2</td>
<td>18.3</td>
<td>0.5407</td>
<td>1.50</td>
</tr>
<tr>
<td>CPZ</td>
<td>0.15</td>
<td>10.7</td>
<td>12.9</td>
<td>0.5405</td>
<td>1.37</td>
</tr>
</tbody>
</table>

\(^a\) Flow rate of CH\(_4\) in \(\mu\)mol/s\(^{-1}\); \(^b\) CH\(_4\) conversion at 350 °C; \(^c\) Pd content in CP or CPZ solid solution

Scheme S1  Cube and Crystal particle and unit cell of CeO\(_2\), and ball-and-stick model.

Picture S1 Crystal particle of CeO\(_2\).

Picture S2 One side (top side) of a CeO\(_2\) cube (denoted as side a).

Picture S3 Ball-and-stick model of one side of a CeO\(_2\) cube.

Picture S4 Unit cell of CeO\(_2\) (denoted as cube abc).
Picture S5 Ball-and-stick model of a unit cell of CeO$_2$.

In a CeO$_2$ crystal particle, there are three kinds of unit cell as showed in scheme S2. The yellow unit cell in the central exposed only one side (top side), the green unit cell on the edge exposed two sides (top and right sides), and the pink unit cell in the corner exposed three sides (top, front and right sides).

![Scheme S2](image)

**Scheme S2**  Unit cell of CeO$_2$ expose different number of side.

**For CP catalyst:**

CeO$_2$ is face-centered cubic structure and a crystal particle contained many unit cell of CeO$_2$. For CP solid solution, the crystal size of CeO$_2$ is 18.3 nm, and the cell parameter of CeO$_2$ is 0.5407 nm. Assuming the number of unit cell in a CeO$_2$ crystal particle is $N_1$,

$$N_1 =\left(\frac{18.3}{0.5407}\right)^3 = 33.8^3 \approx 34^3 = 39304$$

The number of unit cell of CeO$_2$ exposed one side is $n_{11}$,  
\[ n_{11} = (34 - 2)^2 \times 6 = 6144 \]

The number of unit cell of CeO$_2$ exposed two sides is $n_{12}$,  
\[ n_{12} = (34 - 2) \times 4 \times 2 + 4 \times (34 - 2) = 384 \]

The number of unit cell of CeO$_2$ exposed three sides is $n_{13}$,  
\[ n_{13} = 8 \]

The number of unit cell of CeO$_2$ exposed zero side is $n_{10}$,  
\[ n_{10} = 39304 - 6144 - 384 - 8 = 32768 \]

The number of sides of unit cell exposed on the surface of a CeO$_2$ crystal particle
is $S_{11}$, and the number of total sides of unit cell in a CeO$_2$ crystal particle is $S_{12}$.

$$S_{11} = n_{11} \times 1 + n_{12} \times 2 + n_{13} \times 3 = 6144 \times 1 + 384 \times 2 + 8 \times 3 = 6936$$

$$S_{12} = (34 \times 34 \times 34 + 34 \times 34) \times 3 = 121320$$

The percentage of the exposed sides in the total sides in a CeO$_2$ crystal particle $R_1$,

$$R_1 = \frac{S_{11}}{S_{12}} \times 100\% = \frac{6936}{121320} \times 100\% = 5.71\%$$

The content of Pd in CP solid solution $K_1 = \frac{0.2 \, \text{g} \times 1.5\%}{106.4 \, \text{g/mol}} = 2.82 \times 10^{-5} \, \text{mol}$

Assuming the Pd$^{n+}$ cations dispersed in CP solid solution uniformly. In fact, only the Pd$^{n+}$ cations exposed on the surface of CeO$_2$ crystal particle contributed to the CH$_4$ oxidation. It should be noted that a CeO$_2$ crystal particle is selected as object of study in the calculation of $R_1$, and this value is also applicable to the whole CP solid solution.

$$\text{TOF}_{\text{Pd}^{n+}} = \frac{F_{\text{CH}_4} \times X_{\text{CH}_4}}{K_1 \times R_1} = \frac{1.488 \times 10^{-7} \, \text{mol/s} \times 15.2\%}{2.82 \times 10^{-5} \, \text{mol} \times 5.71\%} = 0.014 \, \text{s}^{-1}$$

**For CPZ catalyst:**

The crystal size of CeO$_2$ is 12.9 nm, and the cell parameter of CeO$_2$ 0.5405 nm.

Assuming the number of unit cell in a CeO$_2$ crystal particle is $N_2$,

$$N_2 = \left( \frac{12.9}{0.5405} \right)^3 \approx 24^3 = 13824$$

The number of unit cell of CeO$_2$ exposed one side is $n_{21}$, $n_{21} = (24 - 2)^2 \times 6 = 2904$

The number of unit cell of CeO$_2$ exposed two sides is $n_{22}$,

$$n_{22} = (24 - 2) \times 4 \times 2 + 4 \times (24 - 2) = 264$$

The number of unit cell of CeO$_2$ exposed three sides is $n_{23}$, $n_{23} = 8$,

The number of unit cell of CeO$_2$ exposed zero side is $n_{20}$, 


The number of sides of unit cell exposed on the surface of a CeO$_2$ crystal particle is $S_{21}$, and the number of total sides of unit cell in a CeO$_2$ crystal particle is $S_{22}$.

\[ S_{21} = n_{21} \times 1 + n_{22} \times 2 + n_{23} \times 3 = 2904 \times 1 + 264 \times 2 + 8 \times 3 = 3456 \]

\[ S_{22} = (24 \times 24 \times 24 + 24 \times 24) \times 3 = 43200 \]

The percentage of the exposed sides in the total sides in a CeO$_2$ crystal particle $R_2$,

\[ R_2 = \frac{S_{21}}{S_{22}} \times 100\% = \frac{3456}{43200} \times 100\% = 8\% \]

The content of Pd in CPZ solid solution $K_2 = \frac{0.2 \text{ g} \times 1.37\%}{106.4 \text{ g/mol}} = 2.58 \times 10^{-5} \text{ mol}$

Assuming the Pd$^{n+}$ cations dispersed in CPZ solid solution uniformly. In fact, only the Pd$^{n+}$ cations exposed on the surface of CeO$_2$ crystal particle contributed to the CH$_4$ oxidation. It must be noted that a CeO$_2$ crystal particle is selected as object of study in the calculation of $R_2$, and this value is also applicable to the whole CPZ solid solution.

\[ \text{TOF}_{\text{Pd}} = \frac{F_{\text{CH}_4} \times X_{\text{CH}_4}}{K_2 \times R_2} = \frac{1.488 \times 10^{-7} \text{ mol/s} \times 10.7\%}{2.58 \times 10^{-5} \text{ mol} \times 8\%} = 0.008 \text{ s}^{-1} \]