Controlled Synthesis of Nanoscale Pd-CeO\textsubscript{2} Structures and Their Corresponding Influence on Catalytic Performance

Chenhao Du,\textsuperscript{a} Guanzhong Lu\textsuperscript{a, *}

\textsuperscript{a}Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai, 200237, P. R. China.

*Email: gzhlue@ecust.edu.cn

Abstract: We applied two different methods to obtain nanoscale Pd-ceria structures. In one sample core-shell like Pd-CeO\textsubscript{2} was obtained to maximize the Pd-ceria interface. In other sample, CeO\textsubscript{2} nanocrystals merely decorated on Pd NPs. Through CO oxidation and CH\textsubscript{4} combustion, we demonstrated that the Pd-CeO\textsubscript{2} interface contributed to the low-temperature CO oxidation process while had detrimental effect on low-temperature CH\textsubscript{4} combustion. For CH\textsubscript{4} combustion we believed PdO was the active component, minor CeO\textsubscript{2} decoration had little influence on the CH\textsubscript{4} combustion activity. The experiment results deepen the understanding of the nature of active sites and provide guidance on designing novel nanocatalysts.

Keywords: Pd-CeO\textsubscript{2}, nanostructure, CH\textsubscript{4} combustion, CO oxidation

1. Introduction (11-point boldface)

In the past decade, the concept of ‘nanocatalyst’, with the emphasis on the controlled fabrication of active sites at nanoscale level, has emerged and developed rapidly\textsuperscript{1}. In this Abstract, we introduced new methods to obtain different ‘dispersible’ Pd-ceria nanostructures by using nanoparticles as ‘artificial atoms’. The catalytic performances in CO oxidation and methane combustion reactions were evaluated and the influence of specific surface nanostructure was observed.

2. Results and discussion

Two model samples (denoted as MS-1 and MS-2) were prepared. In MS-1 we used 2.5nm Pd nanoparticles as starting building block and the CeO\textsubscript{2} nanoparticles were functionalized via an amino-assisted approach at room temperature, forming a core-shell like structure (Fig 1a). In MS-2 4.5nm Pd nanoparticles were used, and CeO\textsubscript{2} nanocrystals were introduced by thermal decomposition method (Fig 1c).

Both sample were supported on Al\textsubscript{2}O\textsubscript{3} and calcined at 550 °C. In MS-1, small Pd nanoparticles were mostly encapsulated in CeO\textsubscript{2} nanoparticles while in MS-2 CeO\textsubscript{2} nanocrystals were scattered randomly, with PdO nanoparticles were the dominate species (Figure1b&d). In both samples the size of the Pd NPs could be well maintained and the schematic illustration of MS-1&MS-2 was given in Scheme 1.

Figure 1. TEM images of as-prepared MS-1(a), MS-2 (c) and the corresponding supported samples: MS-1/Al\textsubscript{2}O\textsubscript{3} (b), MS-2/Al\textsubscript{2}O\textsubscript{3} (d). The white arrows in (a) indicate the Pd NPs.

Scheme 1. Schematic illustration of MS-1 and MS-2 supported on Al\textsubscript{2}O\textsubscript{3} and calcined at 550 °C.
We applied these two model catalysts in CO oxidation reaction and methane combustion reaction. The detailed results are shown in Table 1. The experiment results clearly demonstrated that the specific nanostructure prominently influenced the catalytic performances. For CO oxidation the better activity of MS-1 could be attributed to the more Pd-CeO₂ interface area; which showed lower catalytic methane combustion compared with the PdO species.

Table 1. Catalytic activities of MS-1 and MS-2 in CO oxidation and CH₄ combustion reactions

<table>
<thead>
<tr>
<th>Samples (Reaction)</th>
<th>E_a (KJ/mol)</th>
<th>TOF (*10⁻³)</th>
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</thead>
<tbody>
<tr>
<td>MS-1 (CO oxidation)</td>
<td>47.0</td>
<td>5.86 (38 °C)</td>
</tr>
<tr>
<td>MS-2 (CO oxidation)</td>
<td>65.1</td>
<td>5.37 (80 °C)</td>
</tr>
<tr>
<td>MS-1 (CH₄ combustion)</td>
<td>87.4</td>
<td>2.85 (300 °C)</td>
</tr>
<tr>
<td>MS-2 (CH₄ combustion)</td>
<td>99.7</td>
<td>7.38 (300 °C)</td>
</tr>
</tbody>
</table>

3. Conclusions
In this Abstract we have successfully prepared two different types of Pd-CeO₂ nanostructures and supported them on Al₂O₃. Two model reactions, CO oxidation and CH₄ reaction were applied to evaluate the catalytic activities of the nanocatalysts. From the structure and catalytic activity relationship we can observe that the Pd-CeO₂ interface could contribute to the CO oxidation process while PdO with minor ceria decoration would improve the CH₄ combustion reaction.

References