Preparing SnO\textsubscript{2} nano-rod supports for Pd for toluene combustion: insight into the Pd valence state distribution and its effect on the activity

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Abstract: Pure SnO\textsubscript{2} nano-rods and nano-rods promoted by the secondary metal cations in the lattice matrix have been synthesized by a hydrothermal method, and used to support Pd to prepare catalysts for toluene combustion. It has been revealed that in comparison with regular SnO\textsubscript{2} powder support, a much higher ratio of metallic Pd\textsuperscript{0} can be formed and stabilized on the surfaces of all the nano-rod supports, thus improving the toluene combustion activity significantly. The information reported in this paper could give people some novel insight on how to develop low content noble metal catalysts for environment protection catalysis.

Keywords: SnO\textsubscript{2} nano-rod, Pd valence state distribution, Toluene combustion.

1. Introduction

Over past decades, it has been revealed that the morphologies of nanoparticles play critical roles to determine their catalytic properties.\textsuperscript{1} For example, for the catalytic oxidation of 1,2-dichloroethane and ethyl acetate, CeO\textsubscript{2} nano-rods exhibited the best activity among all of the prepared morphologies.\textsuperscript{2} High surface areas, clearly defined and exposed crystal planes are key factors accounting for the enhanced catalytic performance. In another case, Xie and co-workers have found that CoO\textsubscript{2} nano-rods show excellent activity for CO oxidation due to the presence of abundant active Co\textsuperscript{3+} cations on (110) facets.\textsuperscript{3} Our previous work has also substantiated that SnO\textsubscript{2} nano-rod shows the similar reaction behaviors to noble metal catalysts for CO oxidation, which displays much higher activity than regular SnO\textsubscript{2} nano particles.\textsuperscript{4} As a continued work, pure and modified SnO\textsubscript{2} nano-rods have been synthesized to support Pd for toluene combustion in this study, with the target to achieve better supports to reduce the amount of noble metals.

2. Experimental

Pure and modified SnO\textsubscript{2} nano-rod supports, denoted as SnO\textsubscript{2}-R, Sn\textsubscript{99}In\textsubscript{1}-R, Sn\textsubscript{99}Cr\textsubscript{1}-R, Sn\textsubscript{99}Al\textsubscript{1}-R, Sn\textsubscript{99}W\textsubscript{1}-R and Sn\textsubscript{99}Co\textsubscript{1}-R, have been synthesized with a hydrothermal method. The Sn/M molar ratios of the modified supports are controlled at 99/1. Before supporting the Pd active component, the supports were calcined at 450 °C in air atmosphere for 4 h. After a certain amount of Pd was loaded onto the supports, the samples were dried and calcined again at 450 °C in air atmosphere for 4 h to get the final catalysts. The catalysts were tested for toluene deep oxidation with a space velocity of 20000 mL/(g \cdot h), and characterized by XRD, SEM, TEM, XPS, N\textsubscript{2} adsorption-desorption, O\textsubscript{2}-TPD and H\textsubscript{2}-TPR.

3. Results and discussion

As shown by the typical SEM image embedded in Figure 1, well-ordered nano-rods with very low surface areas (Table 1) have been successfully obtained for all the samples. Figure 1(A) proves that after loading the same amount of Pd, all the SnO\textsubscript{2} nano-rod supports (SnO\textsubscript{2}-R) display much higher activity than the regular SnO\textsubscript{2} powder particles (SnO\textsubscript{2}-P). As displayed in Figure 1(B), the temperature for 95% toluene conversion over 0.1%Pd/SnO\textsubscript{2}-R is 250 °C, but that over 0.1%Pd/SnO\textsubscript{2}-P is 100 °C higher, testifying SnO\textsubscript{2} nano-rods are far better supports than SnO\textsubscript{2} powder particles.

Aiming to further improve the reaction activity of the catalysts, different metal cations have been employed to modify the lattice matrix of pure SnO\textsubscript{2} nano-rod and then used to support 1% Pd for toluene combustion. Figure 2 shows that Pd supported on all the modified SnO\textsubscript{2} nano-rod supports shows significantly improved overall activity than 1%Pd/SnO\textsubscript{2}-R and 1%Pd/SnO\textsubscript{2}-P. 1%Pd-Sn\textsubscript{99}Co\textsubscript{1}-R and 1%Pd-
Sn₉₉Cr₁₋R displays the highest activity among all the catalysts. XPS results have testified that in comparison with the 1%Pd/SnO₂-P prepared with regular SnO₂ powder support, the surface metallic Pd⁰ ratios of the catalysts prepared with SnO₂ nano-rod supports are much higher except for 1%Pd-Sn₉₉Cr₁₋R. Furthermore, all the catalysts prepared with modified SnO₂ nano-rod supports displays higher O_ads/O_lat ratios than both 1%Pd/SnO₂-R and 1%Pd/SnO₂-P, indicating the formation of more surface active oxygen species. It is concluded that the concerted interaction between metallic Pd⁰ sites and surface active oxygen species are the major factors deciding the activity of the catalysts.

![Figure 1. Toluene deep oxidation on the catalysts.](image)

(A) Toluene conversion vs Temperature

(B) T_1₀%T_5₀%T_9₅% of the catalysts.

(a) 0.1%Pd/SnO₂-P, (b) 0.1%Pd/SnO₂-R, (c) 0.5%Pd/SnO₂-P, (d) 0.5%Pd/SnO₂-R, (e) 0.01%Pd/SnO₂-R, (f) 0.05%Pd/SnO₂-R

![Figure 2. Toluene deep oxidation on the catalysts.](image)

Table 1. The physicochemical properties of the catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_{BET} (m²/g)</th>
<th>O_ads/O_lat</th>
<th>Pd⁰/(Pd⁴+Pd³⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%Pd-SnO₂-P</td>
<td>54</td>
<td>0.36</td>
<td>0.34</td>
</tr>
<tr>
<td>1%Pd-SnO₂-R</td>
<td>1</td>
<td>0.34</td>
<td>0.67</td>
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<tr>
<td>1%Pd-Sn₉₉Al₁₋R</td>
<td>1</td>
<td>0.53</td>
<td>0.57</td>
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<tr>
<td>1%Pd-Sn₉₉Cr₁₋R</td>
<td>1</td>
<td>0.60</td>
<td>0.43</td>
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<tr>
<td>1%Pd-Sn₉₉Co₁₋R</td>
<td>1</td>
<td>0.62</td>
<td>0.49</td>
</tr>
<tr>
<td>1%Pd-Sn₉₉In₁₋R</td>
<td>1</td>
<td>0.49</td>
<td>0.63</td>
</tr>
<tr>
<td>1%Pd-Sn₉₉W₁₋R</td>
<td>1</td>
<td>0.52</td>
<td>0.62</td>
</tr>
</tbody>
</table>

4. Conclusions

In this work, it has been revealed that SnO₂ nano-rods, either modified or un-modified, are better supports than regular SnO₂ powder for Pd for toluene combustion. On all the nano-rod supports, higher ratio of metallic Pd⁰ has been formed. Furthermore, on the surface of all the modified nano-rod supports, more abundant active oxygen species is present. These are believed to be the major factors to improve the activity of the catalysts.

References