Calcination temperature effect on silica supported Pt catalyst for low temperature ethylene oxidation

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Introduction
Ethylene is a plant maturation hormone released from fruits and vegetables. Trace amount of ethylene can accelerate their aging even at low temperature. In order to avoid food loss during storage and transport, complete and continuous elimination of ethylene at low temperature is an important issue. Despite several reports of heterogeneous catalysts [1], none of them were applicable for practical use. Our group has successfully reported complete oxidation of trace amount of ethylene at 0 °C using a mesoporous silica supported metal catalyst [2]. In this study, we studied the effect of hydrophobicity of mesoporous silica support on the activity of supported Pt catalyst for ethylene oxidation.

\[
\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}
\]

Experimental
We used mesoporous silica (SBA-15) [3] and nonporous SiO\(_2\) (AEROSIL-380, Evonik) as silica supports. Calcination of SBA-15 and SiO\(_2\) at different temperatures (700, 800 and 900 °C) for 16 h was conducted to control hydrophobicity of their surfaces. Pt nanoparticle on the supports can be formed by an impregnation of Pt cations (1 wt%) with an aqueous (NO\(_2\))\(_2\)·(NH\(_3\))\(_2\)Pt·HNO\(_3\) solution, followed by thermal reduction of the Pt cation-loaded samples under H\(_2\) flow. The resulting catalysts were denoted Pt/SBA-15(cal. temp.) or Pt/SiO\(_2\) (cal. temp.). Ethylene oxidation at 0 °C was performed in a stainless steel fixed-bed reactor under an atmospheric pressure at a space velocity of 1500 mL h\(^{-1}\) g\(^{-1}\). Ethylene conversion and CO\(_2\) yield were estimated at a steady state (300 min).

Table 1. Structural properties and catalytic activities of supported Pt catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(\text{S}_{\text{BET}}^a)</th>
<th>(\text{Volume}^b)</th>
<th>(\text{D}_{\text{pt}}^c)</th>
<th>Conv.(^d) (%)</th>
<th>Yield(^e) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/SBA-15</td>
<td>867 (\text{m}^2\text{g}^{-1})</td>
<td>1.04 (\text{mLg}^{-1})</td>
<td>3.9 (\text{nm})</td>
<td>28 (%)</td>
<td>13 (%)</td>
</tr>
<tr>
<td>Pt/SBA-15(700)</td>
<td>723 (\text{m}^2\text{g}^{-1})</td>
<td>0.89 (\text{mLg}^{-1})</td>
<td>3.3 (\text{nm})</td>
<td>51 (%)</td>
<td>18 (%)</td>
</tr>
<tr>
<td>Pt/SBA-15(800)</td>
<td>572 (\text{m}^2\text{g}^{-1})</td>
<td>0.76 (\text{mLg}^{-1})</td>
<td>5.0 (\text{nm})</td>
<td>45 (%)</td>
<td>28 (%)</td>
</tr>
<tr>
<td>Pt/SBA-15(900)</td>
<td>252 (\text{m}^2\text{g}^{-1})</td>
<td>0.30 (\text{mLg}^{-1})</td>
<td>4.1 (\text{nm})</td>
<td>31 (%)</td>
<td>15 (%)</td>
</tr>
<tr>
<td>Pt/SiO(_2)</td>
<td>392 (\text{m}^2\text{g}^{-1})</td>
<td>0.39 (\text{mLg}^{-1})</td>
<td>2.4 (\text{nm})</td>
<td>30 (%)</td>
<td>11 (%)</td>
</tr>
<tr>
<td>Pt/SiO(_2) (700)</td>
<td>325 (\text{m}^2\text{g}^{-1})</td>
<td>0.32 (\text{mLg}^{-1})</td>
<td>2.7 (\text{nm})</td>
<td>35 (%)</td>
<td>16 (%)</td>
</tr>
<tr>
<td>Pt/SiO(_2) (800)</td>
<td>313 (\text{m}^2\text{g}^{-1})</td>
<td>0.32 (\text{mLg}^{-1})</td>
<td>2.7 (\text{nm})</td>
<td>35 (%)</td>
<td>17 (%)</td>
</tr>
<tr>
<td>Pt/SiO(_2) (900)</td>
<td>240 (\text{m}^2\text{g}^{-1})</td>
<td>0.26 (\text{mLg}^{-1})</td>
<td>2.7 (\text{nm})</td>
<td>37 (%)</td>
<td>18 (%)</td>
</tr>
</tbody>
</table>

\(^a\)BET surface area, \(^b\)Mesopore volume estimated by BJH theory, \(^c\)Average diameter of Pt nanoparticles evaluated by CO-pulse titration, \(^d\)Ethylene conversion, \(^e\)CO\(_2\) yield

Results and Discussion
Table 1 summarizes structural properties and catalytic activities of supported Pt catalysts with different calcination temperatures. In the case of mesoporous silica, calcination treatment gave a positive effect on both the conversion and the yield despite no large difference in average diameter of Pt nanoparticle (3.0-5.0 nm) among these catalysts. Pt/SBA-15(800) showed high ethylene conversion (45%) and CO\(_2\) yield (28%). H\(_2\)O adsorption experiment indicated that hydrophobicity of SBA-15 continuously increases with the increase in calcination temperature. Hydrophobic environment is highly beneficial to enhance desorption of evolved water from catalyst surface, leading possibly to high activity in ethylene oxidation. However, calcination at 900 °C accompanied degradation of original mesoporous structure and decreased largely BET surface area and mesopore volume, which suggested that most of Pt particles would be embedded outside of mesopores.

Catalytic activity of Pt/SiO\(_2\) was comparable to that of Pt/SBA-15. While calcination treatment of SiO\(_2\) at high temperature also increased hydrophobicity of its surface, there was no significant change in original catalytic activity of Pt nanoparticle embedded on hydrophobic SiO\(_2\). In these cases, Pt nanoparticles are simply distributed on flat and hydrophobic SiO\(_2\) surface, which results in no positive influence on ethylene oxidation. In conclusion, high catalytic activity of Pt/SBA-15(800) could therefore be explained by the stabilization of Pt nanoparticles within hydrophobic mesopores preventing deactivation with water.

References