The Role of Modifiers in Multi-component Au/MgO Catalysts Designed for Preferential Oxidation of CO

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Introduction

Pt-based electrocatalysts of fuel cells can be easily poisoned by CO traces, which makes purification of hydrogen gas streams produced in reformers mandatory. Preferential oxidation of CO (PROX) for CO removal would provide a low cost technology. Supported gold catalysts exhibit prominent activity in CO oxidation. Gold catalysts modified with different transition metals proved to have high activity in CO oxidation, which can be due to formation of metal ion – gold nanocluster ensemble sites [1].

In our recent work Pb, V and Sm proved to be the most promising modifiers of multicomponent Au/MgO catalysts [2]. In this contribution the role of different components will be clarified and a schematic model of the active sites will be proposed.

Materials and Methods

Multicomponent catalysts have been prepared by means of homogeneous precipitation of nitrate precursors using urea as precipitating agent. Catalytic properties have been studied in a 16 channel flow through reactor. Catalysts were investigated in detail by different spectroscopic techniques (XPS, FTIR, UV-vis) and HRTEM.

Results and Discussion

In order to elucidate the role of major components (Pb, V and Sm) the best multi-component catalyst has been compared to mono-, bi- and tri-metallic compositions. Kinetic data shown in Table 1 reveal synergistic effect of V and Sm. The addition of these two modifiers together increases significantly the rate of CO oxidation. Upon addition of Pb hydrogen oxidation is strongly suppressed resulting in a significant selectivity improvement.

Comparing particle size distribution of modified and unmodified catalysts it has been evidenced that average particle size increases upon addition of modifiers. In XRD spectra it was also proved that gold is more crystalline in unmodified catalysts. Therefore, it can be supposed that some of the modifiers are soluble in gold and dilution of gold by them results in larger particle size and simultaneously lower crystallinity. XPS results and UV-vis spectra revealed that Pb is alloyed with Au.

Interestingly, in FTIR spectra only very weak CO adsorption could be observed. It is presumable that during the preparation by homogeneous precipitation a part of the magnesia is dissolved at boiling and after the precipitation step, when the slurry is cooled down to RT, crystallization of MgO takes place. As its solubility is higher than that of gold hydroxides, first gold containing precipitates appear upon cooling, which are then covered by magnesia layer.

Table 1. Reaction kinetic results over various catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>k₁</th>
<th>k₂</th>
<th>k₁/k₂</th>
<th>Conversion, %</th>
<th>Selectivity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>7.9</td>
<td>1.4</td>
<td>5.5</td>
<td>40.8</td>
<td>72.0</td>
</tr>
<tr>
<td>AuPb</td>
<td>7.5</td>
<td>1.2</td>
<td>6.3</td>
<td>41.8</td>
<td>72.7</td>
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<tr>
<td>AuV</td>
<td>5.3</td>
<td>1.6</td>
<td>3.4</td>
<td>32.0</td>
<td>63.9</td>
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<tr>
<td>AuSm</td>
<td>6.8</td>
<td>1.5</td>
<td>4.4</td>
<td>40.9</td>
<td>64.8</td>
</tr>
<tr>
<td>AuPbV</td>
<td>6.7</td>
<td>1.3</td>
<td>5.0</td>
<td>42.1</td>
<td>66.6</td>
</tr>
<tr>
<td>AuPbVSm</td>
<td>11.7</td>
<td>0.7</td>
<td>16.4</td>
<td>64.0</td>
<td>75.3</td>
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<tr>
<td>AuVSm</td>
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<td>7.2</td>
<td>2.2</td>
<td>78.1</td>
<td>41.5</td>
</tr>
<tr>
<td>AuPbVSm</td>
<td>19.5</td>
<td>4.6</td>
<td>4.2</td>
<td>90.5</td>
<td>50.7</td>
</tr>
</tbody>
</table>

Components in wt % : Au–2.6, Pb–3.5, V–2.4, Sm–2.7. Reaction temperature: 80 °C, P₀₂= 1.0 kPa; P₇H₂=1.0 kPa; P₇CO=60 kPa; He balance; Flow rate=30 ml/min; catalyst = 30 mg; k₁, k₂ are rate constants of CO and hydrogen oxidation, respectively.

Figure 1A depicts schematic view of multicomponent catalysts. It has to be mentioned that in HRTEM image shown in Figure 1B characteristic fringe spacing of Au (111) is slightly higher than that of published in the related art, which can be due to alloying of Au with Pb. The image on Figure 1B reveals a rounded gold particle with blurred contours. It indicates that surface of gold nanoparticles is partially covered by MgO, leading to the disappearance of surface anisotropy of Au. Figure 1B clearly shows the atomic closeness between the gold nanoparticle and Sm₂O₃ island.

Figure 1. Model of multi-component Au/MgO catalysts (A) and HRTEM evidence (B)

Significance

Multicomponent catalysts designed combinatorially for PROX with compositions unknown earlier showed remarkable activity, long term stability and high selectivity. Synergetic effect of different components on the catalytic performance has been observed which is due to alloying of gold with Pb and modification of the nano-environment of gold by Sm and V oxides.

References