Complete Methane Oxidation on Palladium Model Catalyst
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Introduction
Catalytic combustion of methane in excess O₂ over Pd catalysts is used to reduce NOx formation for the generation of energy in gas turbines and to reduce methane emissions in the exhaust of gas-powered engines[1]. To design better catalytic combustion systems, the following questions need to be answered: (1) what is the turnover rate at various temperatures and palladium phases; (2) what is the mechanism for activity change during catalyst phase transition at high temperature; (3) what is the reason for catalyst deactivation. It is the objective of this contribution to answer these questions.
The catalyst in this research was a polycrystalline palladium foil. The catalyst could be transferred from the reactor to an ultrahigh vacuum analysis chamber without exposure to the atmosphere[2, 3]. The advantages of this system are the absence of internal mass and heat transfer, complete accessibility of the active surface by analytical techniques and absence of support effects.

Results and Discussion
The first task was to measure the rate per unit of surface area of active phase. We had to develop a method to measure the PdO surface area, which consisted of exchanging superficial ¹⁶O with ¹⁸O using ¹⁸O₂ [2]. The reaction orders and activation energies were found to be a function of temperature and the palladium chemical state (Table 1). Considering the change in the surface area of the active component was important in deriving the correct rates. The kinetic results show that palladium oxide is more active at temperatures below 750°C; but palladium metal is more active at temperatures above 750°C (Fig. 1).

<table>
<thead>
<tr>
<th>Temp. Range (K)</th>
<th>Pd Phase</th>
<th>Ea (kJ mol⁻¹)</th>
<th>Temp. Range (K)</th>
<th>Pd Phase</th>
<th>Reaction Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>568-623</td>
<td>PdO</td>
<td>125</td>
<td>598</td>
<td>PdO</td>
<td>0.7 0.2 -0.9</td>
</tr>
<tr>
<td>783-873</td>
<td>PdO</td>
<td>26</td>
<td>863</td>
<td>PdO</td>
<td>0.6 0 0</td>
</tr>
<tr>
<td>933-1003</td>
<td>Pd metal</td>
<td>118</td>
<td>973</td>
<td>Pd metal</td>
<td>0.7 0 0</td>
</tr>
</tbody>
</table>
When the sample was heated above the decomposition temperature of PdO and decomposed to Pd, the rate decreased substantially. The lower rate was attributed to a combination of surface area reduction and a different reaction mechanism. When the reaction temperature was subsequently decreased to allow for the formation of PdO, the sample showed hysteresis in the catalytic conversion (Fig. 2). The reactivity was regained (and PdO formed) only when the reaction temperature was decreased substantially below the point where PdO should be formed. The reactivity could also be regained without decreasing the reaction temperature by increasing the O₂ pressure in the reactant mixture. Thus, we concluded that the hysteresis was caused by a low concentration of oxygen on the Pd surface preventing the formation of the bulk oxide.

Catalyst deactivation was observed in some samples and it was assigned to an oxide of silicon covering the surface of the foil (Fig. 3). The presence of water at reaction temperature was necessary to allow the spreading of silicon oxide onto the catalyst surface.

Reference