Catalysts for Methane Oxidation in the Presence of SO2

Zhang, Yu; Christensen, Jakob Munkholt; Glarborg, Peter; Jensen, Anker Degn

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Catalysts for Methane Oxidation in the Presence of SO2:

Yu Zhang1, Jakob Munkholt Christensen*, Peter Glarborg1, and Anker Degen Jensen1
1DTU Chemical Engineering, Technical University of Denmark (DTU), Kgs. Lyngby, DK-2800, Denmark
* jmc@kt.dtu.dk

Introduction

Natural gas is an interesting fuel for ships in coastal zones, where high sulfur marine fuels cannot be used. However, slip of unburnt methane from the engine poses another emission problem, as CH4 is a greenhouse gas with an atmospheric potential 26-28 times that of CO2 [1] and it should be mitigated from the exhaust gas. Catalytic oxidation of CH4 to CO2 and H2O in the after treatment system can be a promising solution, but an efficient catalyst that remains sufficiently active under real exhaust gas conditions (350-550 °C, 5-10 vol.% H2O and 1-2 ppm SO2) is still being sought with the inhibition from SO2 being a major issue.

In this contribution, Rh and Pd were studied as promising active materials distributed on three different supports, i.e. zeolite (ZSM-5), silica, and alumina.

Materials and Methods

The catalysts were prepared by Incipient Wetness Impregnation (IWI) followed by calcination in air at 600 °C for 6 h. A fixed-bed quartz reactor was used to test the performance of the catalysts under different conditions. In each experiment, 0.12 g catalyst was diluted with 1.08 g sand. The gas hourly space velocity (GHSV) was kept at 150,000 ml/(gcat.h). The reaction gas consisted of 2500 ppm CH4, 10 vol. % O2, 5 vol. % H2O and 20 ppm SO2 when present, balancing with N2. The exit gas was analyzed with an online IR gas analyzer to monitor CO2, CO, O2, and SO2 concentrations, and a Micro GC for CH4 concentration. The CH4 conversion at 1-2 ppm SO2) is still being sought with the inhibition from SO2 being a major issue.

Results and Discussion

The prepared catalysts were tested both in the absence of SO2 and in the presence of 20 ppm SO2 in the temperature range of 250-600 °C to compare the activity. The conversion of CH4 at each temperature was measured at steady state for 40 min. The long-term SO2 resistance of the catalysts were also measured by running in 20 ppm SO2 at 450 and 500 °C for 15 h. XRD, TEM, STEM, and CO-DRIFTS measurements were used to analyze the fresh and spent catalysts to verify the type of active site and the change of active site after SO2 poisoning.

Table 1. T10, T50, and T90 of catalysts in the presence of absence of 20 ppm SO2

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>SO2 presence</th>
<th>T50 (°C)</th>
<th>T90(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heating</td>
<td>Cooling</td>
<td>Heating</td>
</tr>
<tr>
<td>1 wt.% Pd/ZSM-5</td>
<td>/</td>
<td>406</td>
<td>/</td>
</tr>
<tr>
<td>1 wt.% Rh/ZSM-5</td>
<td>/</td>
<td>415</td>
<td>/</td>
</tr>
<tr>
<td>2 wt.% Pd/ZSM-5</td>
<td>20 ppm</td>
<td>478</td>
<td>483</td>
</tr>
<tr>
<td>2 wt.% Rh/ZSM-5</td>
<td>20 ppm</td>
<td>515</td>
<td>532</td>
</tr>
</tbody>
</table>

The interaction of CO with Rh active sites was measured by CO-DRIFTS and it verified the presence of both single-atom Rh sites and nano-particle Rh on ZSM-5 support [3]. The role of the single site and nano-particle site during oxidation of CH4 under both absence and presence of SO2 conditions need to be further studied.

Significance

This work has led to the design of a new catalyst Rh-ZSM-5 for CH4 removal under simulated engine exhaust gas conditions with good oxidation activity and sulfur tolerance.

References