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Rh/ZSM-5 as a Sulfur Tolerant Catalyst for Methane Oxidation

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Introduction

Natural gas can be an alternative fuel for ships in coastal zones to minimize the emissions of CO₂, NO_x, and particulates from diesel engines. However, unburnt methane can slip from the engine, causing another emission problem. CH₄ is a green-house gas with an atmospheric potential of 26-28 times that of CO₂ [1] and it need to be mitigated from the exhaust gas. Converting CH₄ to CO₂ and H₂O catalytically in the after treatment system can be promising. However, 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. Pd based catalysts are the most active in the absence of H₂O and SO₂[2], but they deactivate severely by SO₂ even at low ppm levels. In this contribution, it is investigated if Rh catalysts on a suitable carrier material can be developed to tolerate the exhaust gas conditions above. Here Rh/ZSM-5 was prepared and tested under simulated engine exhaust gas conditions with both H₂O and SO₂ present. The influence of operating temperature and SO₂ concentration were studied.

Materials and Methods

The 2 wt.% Rh/ZSM-5 (Zeolyst, Si:Al = 280) catalyst was prepared by the Incipient Wetness Impregnation (IWI) method followed by calcination in air at 600 °C for 6 h. A fixed-bed quartz reactor was used to test the performance of the catalyst 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/(g_{cat}·h). The reaction gas consisted of 2500 ppm CH₄, 10 vol. % O₂, 5 vol. % H₂O and 1-20 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 measured CH₄ concentration was used to calculate CH₄ conversion. The fresh and spent catalysts were characterized by TEM and CO-DRIFTS.

The fresh catalyst was tested at 450, 475 and 500 °C. Initially, a 15 h test was done in the absence of SO₂, and then 1 ppm SO₂ was introduced to the reaction stream until the conversion of CH₄ became stable. Then the SO₂ concentration was raised in steps to 2, 5, 10, and 20 ppm SO₂ awaiting steady state at each SO₂ concentration level. Based on these data, a Temkin isotherm was used to find the adsorption heat of SO₂ on the 2 wt.% Rh/ZSM-5 catalyst with the assumption that the fraction of remaining activity correspond to the fraction of sites not covered by SO₂.

Results and Discussions

The conversion of CH₄ was stable at 450, 475, and 500 °C in the absence of SO₂ (Figure 1). By addition of 1 ppm SO₂, the conversion of CH₄ decreased significantly at the three operating temperatures. The stabilized conversion after around 50 h in the presence of 1 ppm SO₂ could be improved significantly (from 27 % to 79%) by elevating the operating temperature from 450 to 500 °C. As the SO₂ concentration was increased to 2, 5, 10, and 20 ppm SO₂, the conversion of CH₄ further decreased. It indicates that it is possible to get stable conversion in the presence of H₂O and SO₂ on the 2 wt.% Rh/ZSM-5 catalyst. The CH₄ removal efficiency can be significantly improved by elevating the operating temperature and lowering the SO₂ concentration to a low level. The SO₂ concentration in the real natural gas engine condition is 1-2 ppm, thus a high CH₄ removal efficiency can be achieved around 500 °C, which is achievable in a real engine system.

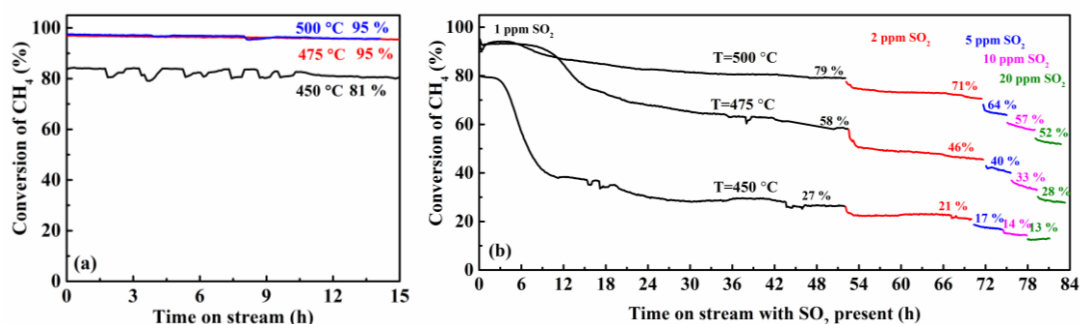


Figure 1. Conversion of CH₄ on 2 wt.% Rh/ZSM-5 catalyst in long-term stability test in the absence of SO₂ (a) and presence (b) of 1-20 ppm SO₂ at 450, 475, and 500 °C.

2500 ppm CH₄, 10 vol.% O₂, 5 vol.% H₂O, 1-20 ppm SO₂ when present, balanced with N₂, GHSV= 150,000 ml/(g_{cat}·h)

References

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