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 CO_2, NO_X, and particulates from diesel engines. However, unburnt methane can slip from the engine, causing another emission problem. CH_4 is a green-house gas with an atmospheric potential of 26-28 times that of CO_2 [1] and it need to be mitigated from the exhaust gas. Converting CH_4 to CO_2 and H_2O 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.% H_2O and 1-2 ppm SO_2) is still being sought. Pd based catalysts are the most active in the absence of H_2O and SO_2[2], but they deactivate severely by SO_2 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 H_2O and SO_2 present. The influence of operating temperature and SO_2 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 CH_4, 10 vol. % O_2, 5 vol. % H_2O and 1-20 ppm SO_2 when present, balancing with N_2. The exit gas was analyzed with an online IR gas analyzer to monitor CO_2, CO, O_2, and SO_2 concentrations, and a Micro GC for CH_4 concentration. The measured CH_4 concentration was used to calculate CH_4 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 SO_2, and then 1 ppm SO_2 was introduced to the reaction stream until the conversion of CH_4 became stable. Then the SO_2 concentration was raised in steps to 2, 5, 10, and 20 ppm SO_2 awaiting steady state at each SO_2 concentration level. Based on these data, a Temkin isotherm was used to find the adsorption heat of SO_2 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 SO_2.

Results and Discussions

The conversion of CH_4 was stable at 450, 475, and 500 °C in the absence of SO_2 (Figure 1). By addition of 1 ppm SO_2, the conversion of CH_4 decreased significantly at the three operating temperatures. The stabilized conversion after around 50 h in the presence of 1 ppm SO_2 could be improved significantly (from 27 % to 79%) by elevating the operating temperature from 450 to 500 °C. As the SO_2 concentration was increased to 2, 5, 10, and 20 ppm SO_2, the conversion of CH_4 further decreased. It indicates that it is possible to get stable conversion in the presence of H_2O and SO_2 on the 2 wt.% Rh/ZSM-5 catalyst. The CH_4 removal efficiency can be significantly improved by elevating the operating temperature and lowering the SO_2 concentration to a low level. The SO_2 concentration in the real natural gas engine condition is 1-2 ppm, thus a high CH_4 removal efficiency can be achieved around 500 °C, which is achievable in a real engine system.
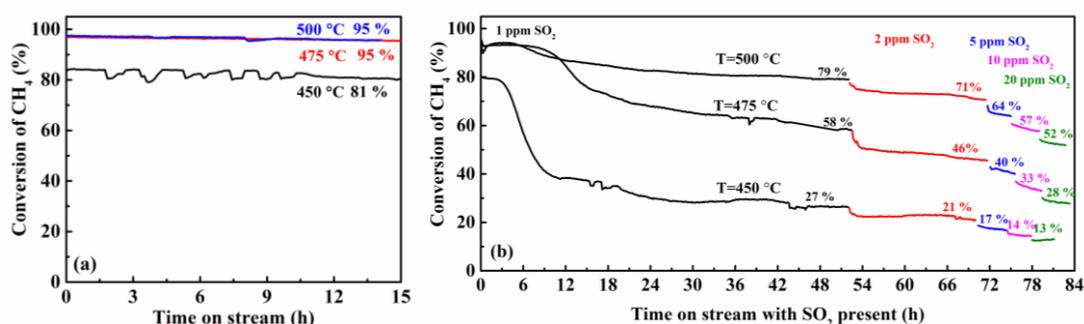

Figure 1. Conversion of CH_4 on 2 wt.% Rh/ZSM-5 catalyst in long-term stability test in the absence of SO_2 (a) and presence (b) of 1-20 ppm SO_2 at 450, 475, and 500 °C. 2500 ppm CH_4, 10 vol.% O_2, 5 vol.% H_2O, 1-20 ppm SO_2 when present, balanced with N_2, GHSV= 150,000 ml/(g$_{cat}$·h)

References
[1] Chai, X., David, J.T., and Devinder, M. Prog. Energy Combust. Sci. 33, 56 (2016).
[2] Yang, L., Jian, M., and Wende, H. ACS Catal. 8127 6 (2016).