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Catalysts for Methane Oxidation in the Presence of SO₂

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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 green-house 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/(g_{cat}·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 concentration measured by the micro GC was used to calculate the CH₄ conversion.

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.

Results and Discussion

During the tests, CO₂ was the only product which indicates complete oxidation of CH₄ under the reaction conditions. The activity of 1 wt. % Rh/ZSM-5 and 1 wt. % Pd/ZSM-5, measured in the presence of 5 vol. % H₂O but absence of SO₂ in the temperature range of 250-550 °C, is shown in Figure 1. (a) It indicates that Rh has comparable activity as Pd, which is generally acknowledged as the most active catalyst for CH₄ oxidation [2], when distributed on same support, ZSM-5. Figure 1. (b) shows the conversion of CH₄ over 2 wt.% Rh/ZSM-5 and 2 wt.% Pd/ZSM-5 both during heating up and cooling down in the presence of 20 ppm SO₂. The temperature for reaching 10 % (T₁₀), 50 % (T₅₀), and 90 % (T₉₀) conversion of CH₄ over the catalysts are summarized in Table 1. In the presence of 20 ppm SO₂, 2 wt. %

Rh/ZSM-5 is more active than 2 wt. % Pd/ZSM-5 with a temperature for 50 % conversion 37 °C lower than that for 2 wt. % Pd/ZSM-5. The deactivation in the subsequent two runs for 2 wt. % Rh/ZSM-5 catalyst was less significant than for 2 wt. % Pd/ZSM-5 catalyst, with T₅₀ shifted by 5 °C for Rh and 17 °C for Pd. This indicates stronger SO₂ tolerance of Rh than Pd under the same condition. 15 h time on stream tests at 450 and 500 °C for the Rh and Pd catalysts in the presence of SO₂ also show higher SO₂ tolerance of Rh.

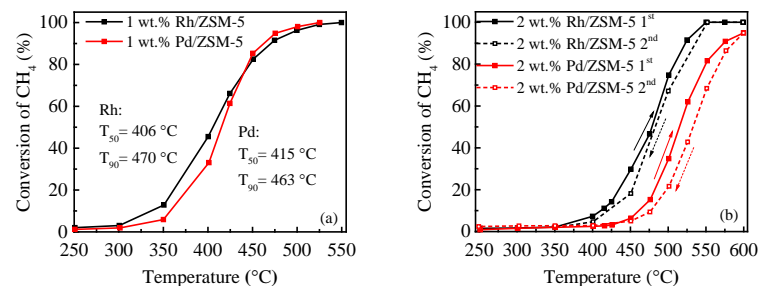


Figure 1. Conversion of CH₄ over 1 wt.% Rh/ZSM-5 and 1 wt.% Pd/ZSM-5 in the absence of SO₂ (a), Conversion of CH₄ over 2 wt.% Rh/ZSM-5 and 2 wt.% Pd/ZSM-5 in the presence of SO₂ (b). 2500 ppm CH₄, 10 vol. % O₂, 5 vol.% H₂O, 20 ppm SO₂ when present, in N₂, GHSV= 150, 000 ml/(g_{cat}·h).

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

Catalysts	SO ₂ presence	T ₅₀ (°C)		T ₉₀ (°C)	
		Heating	Cooling	Heating	Cooling
1 wt.% Pd/ZSM-5	/	415	/	463	/
1 wt.% Rh/ZSM-5	/	406	/	470	/
2 wt.% Pd/ZSM-5	20 ppm	515	532	573	586
2 wt.% Rh/ZSM-5	20 ppm	478	483	523	536

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

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