Activity and aging of a Pd/Pt-Al_2O_3-catalyst for methane oxidation

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Introduction

Lean burn gas engines are widely used in various applications like ships, trucks or combined heating and power plants. They provide a lot of advantages and partly outperform traditional Diesel engines. Besides their ability to use natural gas or biogas as fuel, they also emit a very small amount of particulate matter. However, gas engines suffer from a methane-slippage, which is the main component of natural gas. Due to its strong greenhouse activity and consequently tightening environmental legislation, effective catalytic converters are necessary to guarantee an economic and ecologic use of gas engines [1].

Pt-Pd catalysts are presently considered to be one of the most active systems for total oxidation of methane [2]. They demonstrate high specific activity and thermal stability, which is improved by Pd doping [3]. On the other hand, catalytic activity of Pt-Pd-catalysts strongly depends on the gas mixture, e.g. the activity is suppressed in the presence of water (unavoidable in the exhaust gas) [4]. Furthermore the long-term activity under steady state conditions is a major problem and the deactivation mechanism caused by different gas components is not fully understood. Therefore, the present study aims in a first step at the identification of typical gas components which contribute to catalyst deactivation and also at gaining more insight into their effects on catalyst properties.

Materials and Methods

Catalytic experiments were performed with a non commercial Pd-Pt/Al_2O_3 model catalyst provided by Heraeus Precious Metals GmbH & Co. KG, Germany. Light-Off-measurements (170 – 480 °C) were conducted at laboratory reactors under different gas compositions, containing N_2, 12% H_2O, 10% O_2, 6% CO_2, 3200ppm CH_4 and also 500ppm CO, 150ppm NO_x, other HC (225ppm) and 2.5-4ppm SO_2. Additionally, steady state activity tests were performed at 450 °C for 100 h to investigate the long-term activity of the catalyst under different gas compositions. For detecting the reaction products a MKS FTIR instrument was used. The fresh and aged catalysts were characterized using BET, CO-chemisorption, XRD, TEM + EDX and XAS. In situ and ex situ XAS measurements were conducted at the Pt-L3-edge at the XAS beamline (ANKA, Karlsruhe, Germany) and at the Pd-K-edge at SNBL beamline (ESRF, Grenoble, France). Furthermore reactivation experiments (e.g. reduction of aged samples with hydrogen) were performed to see if the deactivation process could be inverted.

Results and Discussion

Regarding the long-term activity, it was found that the gas composition has a dramatic effect. Figure 1 shows the methane conversion at 450 °C over 100 hours. Under lean conditions only containing N_2, H_2O, O_2, CO_2 and CH_4 (a) the catalyst significantly loses its activity, whereas the addition of small amounts of CO, NO and NO_2 (b) leads to a high long term activity. However, SO_2 (c and d) is observed to cause a rapid aging of the catalyst.

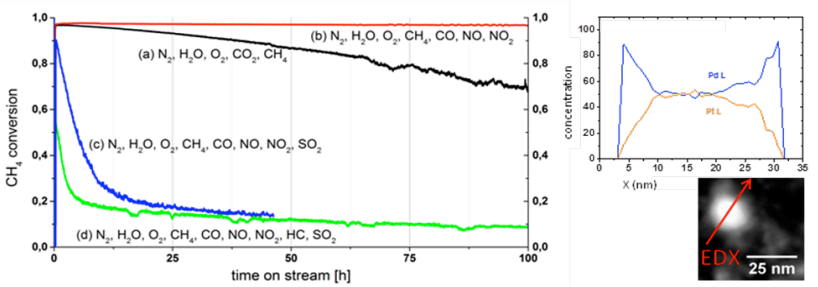

Figure 1. Long-term activity test of a Pd-Pt/Al_2O_3 catalyst at 450 °C under different gas compositions (left, a-d). TEM + EDX of aged catalyst (right).

XRD revealed no phase changes and also the specific surface area stays the same for fresh and aged samples. From the CO-Chemisorption data on fresh and aged catalysts SO_2 was observed to lead to a blockage of active metal sites. TEM measurements combined with EDX showed alloyed Pd-Pt-particles and Pd-only particles for the fresh sample. For the one aged under lean conditions (N_2, H_2O, O_2, CO_2, CH_4) furthermore some core shell particles with a higher Pd concentration in the shell were found. During in-situ XAS measurements (Light-Off) under N_2, H_2O, O_2, CO_2, CH_4 it was found that Pd is mostly in its oxidized state (which is supposed to be the more active one [5]) up to high temperature (750 °C) while Pt is both in a reduced and an oxidized state.

Complete reactivation of a sample aged under atmosphere (a) was reached by reduction with H_2 at 400 °C while sulfur poisoned samples remained deactivated. Furthermore the addition of NO/NO_2 and also the reduction of methane concentration led to a reactivation during catalyst aging under N_2, H_2O, O_2 and CH_4.

Significance

The influence of the gas compositions on the activity of a noble metal based catalyst for methane oxidation is shown. The results also reveal possibilities to enhance the long-term stability and in particular to reactivate a methane oxidation catalyst.

References

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