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Structural characterization of palladium-platinum particles in natural-gas-oxidation catalyst – Ex-situ and preliminary in-situ thermal aging studies

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Natural gas (NG) is a potential sustainable energy source for vehicles because exhaust emissions from NG engines are much lower than those from e.g. diesel engines. Worldwide, there are more than 17 million NG-powered vehicles and recently a total amount of NG vehicles (NGVs) has increased exponentially [1]. Exhaust gases of NGVs contain, however, unburned methane which is a potential greenhouse gas and ozone precursor. EU emission standards have regulated CH_4 emissions from new NG-heavy-duty vehicles since 2000 [2]. To fulfill all the time tightening regulations and to achieve a clean atmosphere, a strong effort to further develop efficient and resistant catalysts for NGVs is required. Supported palladium catalysts are known to be active for methane combustion. However, their deactivation, caused by poisoning and thermal aging, is a problem. It is well-known that methane oxidation activity of the Pd-catalysts decreases e.g. when PdO composes to metallic and when PdO particles sinter at elevated temperatures. The aim of this work was to study the structural changes of noble metal particles in the PtPd/γ-Al_2O_3 natural-gas-oxidation catalyst at elevated temperatures. Changes compared to the fresh catalyst were studied ex-situ by various characterization methods. Changes were studied also in-situ by environmental transmission electron microscope (ETEM).

The ex-situ thermal aging treatments were carried out at various temperatures between 400−1100ºC for 5 hours in oxidative (80% N_2 + 20% O_2) and in reductive (95.5% N_2 + 0.5% O_2) atmospheres. Before and after the treatments, the catalyst was characterized by X-ray diffractometer (XRD) and analytical transmission electron microscope (TEM). Specific surface area, pore size, and pore volume as well as surface characteristics by X-ray photoelectron spectroscope (XPS) were determined for the fresh and selected heat-treated catalysts. The in-situ studies were carried out with ETEM by heating the fresh catalyst sample from room temperature up to 900ºC.

The fresh catalyst consists of small (<5 nm) and well-distributed PtPd (1:4 wt%) particles in the oxide form on the γ-Al_2O_3 support (Figs. 1 and 2) with high specific surface area. Thermal aging treatments caused significant structural changes in the catalyst, however, critical temperature levels were above the normal exhaust gas temperature (<500°C) of the NG-oxidation catalyst [3]. According to the ex-situ studies in the oxidative atmosphere, the first changes in the noble metal particles were detected after the thermal aging treatment at 700ºC (Fig. 1). Slightly grown particles formed and they seemed to have a PdPt core and a PdO shell, also small PdO particles were still detected (Fig. 2). In addition, specific surface area of the catalyst decreased slightly. Phase transformation of γ-Al_2O_3 to δ- and/or θ-Al_2O_3 was detected after the treatment at 800ºC (Fig. 1). More changes after the treatment at 1000ºC were observed (Figs. 1 and 2); core-shell noble metal particles had grown still, however, also small metallic PdPt particles were detected. The γ-Al_2O_3 support was changed to δ- and/or θ-Al_2O_3 and also α-Al_2O_3 was observed. Specific surface area was significantly decreased compared to the fresh catalyst. In the treatment at 1100ºC, large bimetallic PtPd particles with a thin PdO shell formed, in addition, the support transformed mainly to α-Al_2O_3 (Figs. 1 and 2). Specific surface area and total pore volume collapsed. In the in-situ studies, structural changes in the catalyst sample could be followed in the real time. However based on our preliminary studies, it is very challenging. In the high vacuum, γ-Al_2O_3 was very beam and temperature sensitive. γ-Al_2O_3 could be stabilized by drying the sample in the ETEM at 130ºC in high vacuum for few minutes. However, the problem was evaporation of Pd at temperatures above 700ºC (300 Pa O_2). Thus, the size of the particles reduced instead of sintering and mainly Pt was detected in the particles (Fig. 3).

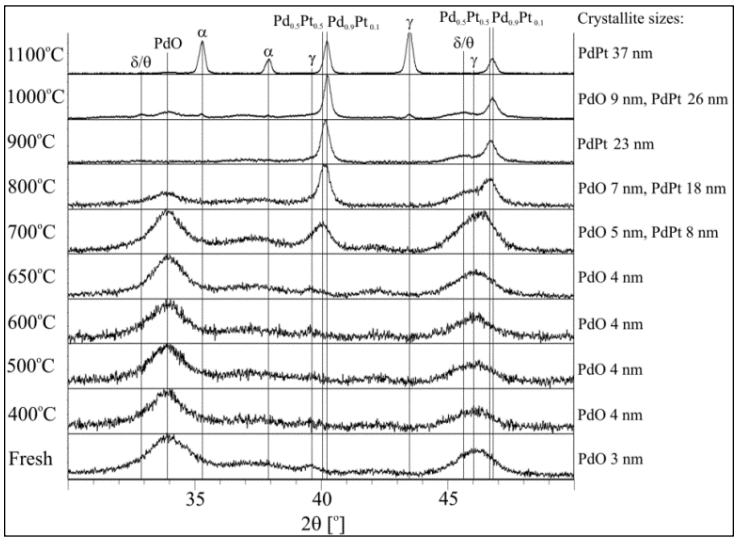

Figure 1. XRD patterns and average crystallite sizes of the noble metal particles for the fresh and heat-treated catalysts

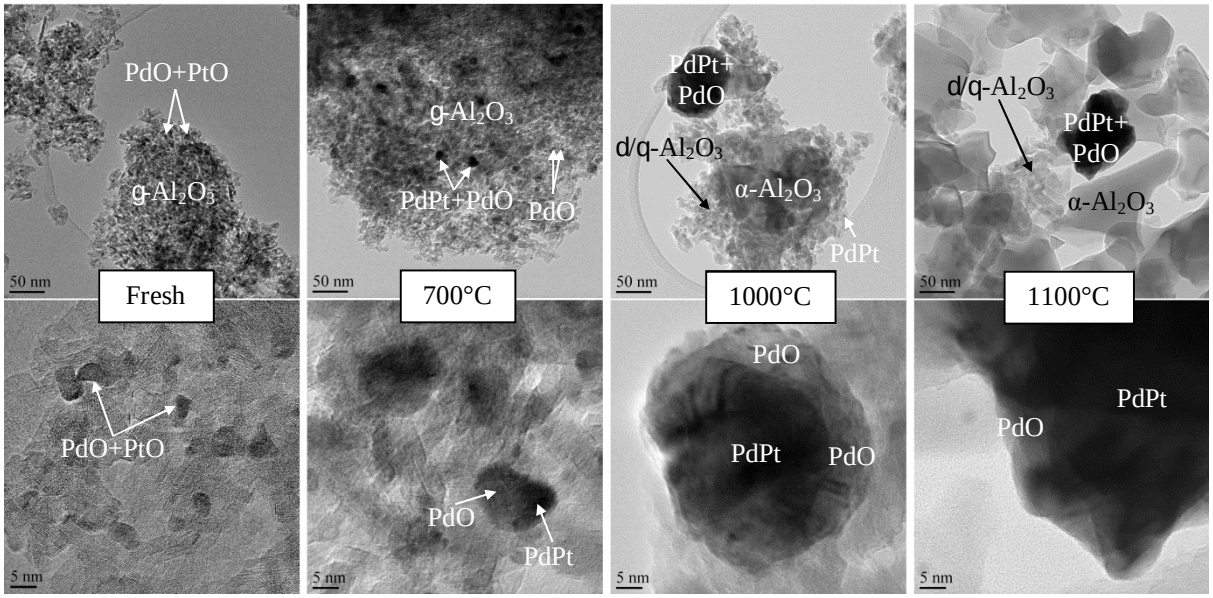

Figure 2. TEM images of the fresh catalyst and the catalyst after thermal aging at selected temperatures

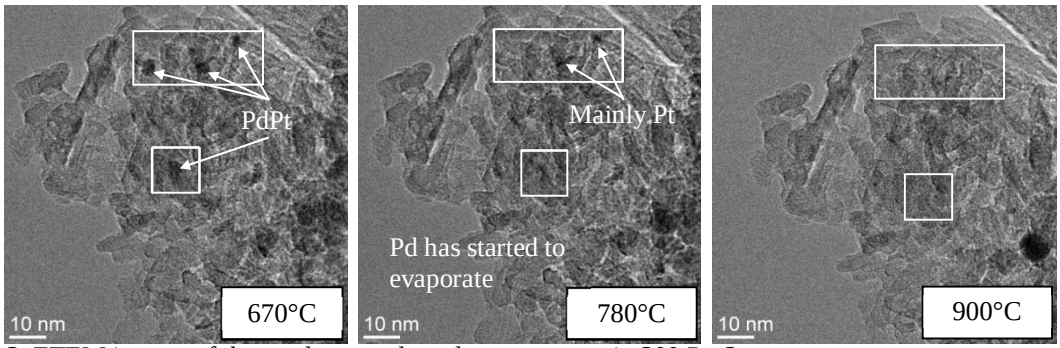

Figure 3. ETEM images of the catalyst at selected temperatures in 300 Pa O_2

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