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Accelerated deactivation studies of the natural-gas oxidation catalyst—Verifying the role of sulfur and elevated temperature in catalyst aging

Mari Honkanen[a,*], Marja Kärkkäinen[b], Tanja Kolli[b], Olli Heikkinen[c], Ville Viitanen[c], Lunjie Zeng[d], Hua Jiang[c], Kauko Kallinen[e], Mika Huuhtanen[b], Riitta L. Keiski[b], Jouko Lahtinen[c], Eva Olsson[d], Minnamari Vippola[a]

[a] *Department of Materials Science, Tampere University of Technology, P.O. Box 589, 33101 Tampere, Finland*
[b] *Environmental and Chemical Engineering, Faculty of Technology, University of Oulu, P.O. Box 4300, 90014 Oulu, Finland*
[c] *Department of Applied Physics, Aalto University, P.O. Box 14100, 00076 Aalto, Finland*
[d] *Department of Applied Physics, Chalmers University of Technology, 41296 Gothenburg, Sweden*
[e] *Dinex Ecocat Oy, Typpitie 1, 90620 Oulu, Finland*

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ABSTRACT

Accelerated deactivation, caused by thermal aging (TA) and/or sulfur + water poisoning (SW), of the PtPd/γ-Al_2O_3 natural-gas oxidation catalyst was studied. Thermal aging and poisoning treatments were performed separately and with varied combinations and comprehensive characterization of the catalyst was carried out after each step. The fresh catalyst has small, oxidized PtPd particles (<5 nm) uniformly distributed in the γ-alumina washcoat. After the SW-treatment, a small amount of bulk aluminum sulfate was observed near the slightly grown noble metal particles. During the thermal aging, γ-alumina changed to δ-/θ- and α-alumina. In addition, total decomposition of oxidized Pt and partly decomposition of oxidized Pd occurred resulting in the formation of the grown noble metal particles with a bimetallic PtPd core and a polycrystalline PdO shell. Also few, small (~5 nm) bimetallic PtPd particles were still detected. In the TA + SW-treated catalyst with grown noble metal particles, a small amount of bulk aluminum sulfate was detected and it was randomly distributed over the noble metal particles and washcoat. The activity in the terms of methane conversion over the TA-, SW-, and SW + TA-treated catalysts was similar but it was decreased compared to the fresh catalyst. The activity of the TA + SW-treated catalyst was drastically decreased compared to the fresh catalyst due to significant morphological changes and aluminum sulfate formation.

1. Introduction

Natural gas (NG) is a potential sustainable energy source for vehicles and engines as its environmental impacts are smaller than those of e.g., crude oil-based fuels. For example exhaust emissions of the natural gas vehicles (NGVs) are much lower than those in the diesel vehicles. However, exhaust gases of NGVs contain unburned methane and carbon monoxide, a potential greenhouse gases, and thus catalytic oxidation converters are needed [1,2]. Supported palladium catalysts are widely known to be active for methane combustion and it is agreed that PdO is the active phase while metallic palladium is much less active. Pd ↔ PdO transformation is reversible and according to Farrauto et al. [3], decomposition temperature of PdO to Pd in the PdO/Al_2O_3 catalyst is ~800 °C and reformation temperature of Pd to PdO during cooling is ~600 °C. Hysteresis in the reformation is due to strongly bound oxygen on the Pd surface inhibiting bulk oxidation [4]. Many other factors, such as gas phase composition and pressure, type of support, additives and contaminants, and pretreatment conditions, have also effects on the Pd ↔ PdO transformation [5]. In addition, several studies have reported that the activity and stability of Pd catalysts in methane combustion can be improved by adding Pt into the catalyst to decelerate sintering of Pd and PdO, e.g., [6–9].

Deactivation of the catalyst, caused by poisoning and thermal aging, is a problem also in the natural gas applications. Poisoning is

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[*] Corresponding author.
E-mail addresses: mari.honkanen@tut.fi (M. Honkanen), marja.karkkainen@oulu.fi (M. Kärkkäinen), tanja.kolli@oulu.fi (T. Kolli), olli.heikkinen@aalto.fi (O. Heikkinen), ville.j.viitanen@gmail.com (V. Viitanen), lunjie@chalmers.se (L. Zeng), hua.jiang@aalto.fi (H. Jiang), kki@dinex.fi (K. Kallinen), mika.huuhtanen@oulu.fi (M. Huuhtanen), riitta.keiski@oulu.fi (R.L. Keiski), jouko.lahtinen@aalto.fi (J. Lahtinen), eva.olsson@chalmers.se (E. Olsson), minnamari.vippola@tut.fi (M. Vippola).

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due to adsorption of impurities, e.g., S, P, Zn, Ca, and Mg, present in the exhaust gases, on the catalytic active sites. Poisons can also react with the active sites followed by formation of non-active compounds [10]. Sulfur is known to be one of the most important components for deactivation of the Pd catalysts for methane oxidation [11] and only a small amount of SO_2 significantly decreases catalyst activity by blocking the active noble metal sites by sulfur compounds [12]. It is known that sulfur in the NGV exhaust gas originates from odorants and lubricating oils and from gas itself. Under the typical natural-gas engine conditions, with large excess of air and with an oxidation catalyst, sulfur will be oxidized to SO_2 and SO_3. Above 300 °C, a catalyst has enough activity for the oxidation of SO_2 to SO_3 [10]. Metallic Pt on the PtPd catalysts is found to be active to adsorb sulfur compounds. Therefore, the presence of metallic Pt prevents adsorption of sulfur on the Pd surface sites which are then available for methane oxidation [13]. Also the catalyst washcoat affects sulfur poisoning. For example Pd/Al_2O_3 catalysts deactivate less than Pd/SiO_2 catalysts due to adsorption of SO_x also on the Al_2O_3 washcoat material [11]. According to Mowery and McCormick [14], when SO_2 and water exist, the sulfation of the PdO/Al_2O_3 catalyst happens by oxidation of SO_2 to SO_3 on PdO and further SO_3 over PdO can form $PdSO_4$ or can migrate to Al_2O_3 forming $Al_2(SO_4)_3$. The sulfation is reversible and SO_x from the catalyst surface easily desorbs already below 400 °C and more stable washcoat sulfates decompose above 700 °C [15]. SO_2 can affect also the acidity of the Al_2O_3 support. Konsolakis et al. [16] noticed that the fresh $Pd/\gamma\text{-}Al_2O_3$ catalyst has only Lewis acid sites but SO_2 treatment increases significantly Brönsted acid sites on the $\gamma\text{-}Al_2O_3$ support. According to Wischert et al. [17], the reactivity of $\gamma\text{-}Al_2O_3$ towards methane is due to the highly reactive Lewis acid-base pairs (Al,O) enabling low-energy pathways for the dissociation of C—H bond in methane.

Thermal deactivation of a catalyst is reported to be caused by: (a) loss of active surface area due to crystallite growth of the noble metal particles and due to pore collapse on crystallites of the active phase, (b) loss of support area due to collapse of the washcoat and/or (c) chemical transformations of active catalytic phases to non-active phases. In general, sintering occurs at elevated temperatures (>500 °C) and is accelerated by water vapor [18]; the driving force for sintering is to minimize surface energy and it is reduced with the transport, growth, and coalescence of the particles [10].

Two mechanisms for sintering of catalyst nanoparticles have been proposed: particle migration followed by coalescence (PMC) and Ostwald ripening (OR). In the particle migration, sintering occurs by migration of the whole crystallites along the support surface and coalescence of the crystallites forms larger particles. OR is migration of single metal atoms or molecular species from small particles to large ones; larger particles grow at the expense of smaller particles [10,18–21]. Hansen et al. [19] studied the mechanism of the catalyst nanoparticle sintering mainly by in situ transmission electron microscopy. They noticed that the early stage of the sintering is dominated by OR and surface area increases rapidly caused by the disappearance of the smallest particles. In the further stage, grown particles coalesce when they are close to each other. Sintering becomes slower when particles grow and the distance between them increases [19]. Many factors e.g., temperature, atmosphere, metal type, support, and impurities affect the rate of noble metal sintering. The sintering rate increases exponentially with elevated temperature and metals sinter faster in oxygen than in hydrogen atmosphere [18]. Generally, sintering of the noble metal clusters is accelerated by the presence of gases; Parkinson et al. [22] reported that existence of carbon monoxide induced coalescence of Pd atoms in the Pd/Fe_3O_4 system and that formed Pd-carbonyl species were responsible for increased Pd mobility. Water vapor has also been found to accelerate sintering. In reducing atmosphere, the stability of the metal crystallites typically decreases with decreasing noble metal melting temperature. In oxidizing atmosphere, stability depends on the volatility of metal oxides and on the noble metal–support interactions [18]. In addition, the position of the noble metal particles affects the rate of sintering; a valley position is much more stable than an on-top position [21]. Pores in the support hinder the mobility of the metal crystallites; especially if pore diameters are about same size as the crystallites [18]. Impurities affect the sintering rate, for example sulfur increases mobility of the metal atoms [18,23,24] while for example calcium is found to decrease it [18].

In the case of the catalysts with an alumina washcoat, phase transformations of the support may occur; γ-alumina with high specific surface area can change to δ-alumina and finally via θ-alumina to stable α-alumina [10]. Phase transformation results in sintering or grain growth followed by a decrease in the surface area [25]. According to Wischert et al. [17], the phase transformation of $\gamma\text{-}Al_2O_3$ to $\theta\text{-}Al_2O_3$ causes the reconstruction of the surface resulting in decrease of highly reactive sites for methane.

In the real vehicle aging conditions, deactivation process is a complex phenomenon and e.g., both thermal aging and poisoning exist. In our earlier study [26], the natural-gas heavy-duty-vehicle-aged (160,000 km) $PtPd/\gamma\text{-}Al_2O_3$-based catalyst was studied. Significant morphological changes and chemical poisoning were detected compared to the fresh catalyst and this has led to drastic deactivation in methane conversion. It was difficult to conclude which changes were caused by thermal aging and which by chemical poisoning. Thus, detailed studying of deactivation phenomena in the vehicle-aged catalysts was found very challenging. Sulfur poisoning of the oxidation catalysts is widely studied, e.g., [10,11,13–15,18]. In this study, sulfur poisoning and thermal aging were studied separately and with varied combinations enabling detailed analysis of the role of sulfur in the catalyst and effects of thermal aging before or after sulfur poisoning. This kind of in-depth knowledge gained is crucial in the development of efficient exhaust emission reduction systems for NGVs.

2. Experimental

2.1. Catalyst material

The studied material was a PtPd (1:4 wt-%) catalyst supported on γ-alumina washcoat on the metallic monolith. The studied catalyst was manufactured and designed by Dinex Ecocat Oy for lean-burn natural gas applications. Total metal loading in the catalyst was 8.8 g/dm^3 and the catalyst was calcined at 550 °C for 4 h. The catalyst was studied as fresh and after various chemical and thermal laboratory-scale accelerated deactivation treatments.

2.2. Laboratory-scale accelerated deactivation treatments

Laboratory-scale sulfur + water treatment (SW) and thermal aging (TA) treatment were carried out to find out detailed knowledge about deactivation phenomena of the $PtPd/\gamma\text{-}Al_2O_3$ oxidation catalyst for natural-gas applications. SW-treatment was performed in the following conditions: 100 ppm SO_2, 10 vol-% H_2O, 10 vol-% air, balanced with N_2. The quartz tube reactor was heated from room temperature to 400 °C in a nitrogen and air flow with the heating rate of 10 °C/min. After 5 h of the SW-treatment, the reactor was cooled down to the room temperature in nitrogen and air flow. The gas hourly space velocity (GHSV) was 20,000 h^{-1} during the treatment. Thermal aging was carried out in the tube reactor under synthetic air (80% N_2 + 20% O_2) at 1000 °C for 5 h. The used temperature was above the normal operation temperature of the catalysts but it was chosen to mimic an accelerated thermal aging and thus the long-term behavior of the catalyst. Temperature for