Deactivation correlations over Pd/Rh monoliths: the role of gas phase composition

U. Lassi\textsuperscript{a, *}, M. Hietikko\textsuperscript{b}, K. Rahkamaa-Tolonen\textsuperscript{a}, K. Kallinen\textsuperscript{c}, A. Savimäki\textsuperscript{c}, M. Härkönem\textsuperscript{c}, R. Laitinen\textsuperscript{b}, and R.L. Keiski\textsuperscript{a}

\textsuperscript{a}Department of Process and Environmental Engineering, University of Oulu, P.O. Box 4300, FIN-90014 Oulu, Finland
\textsuperscript{b}Department of Chemistry, University of Oulu, P.O. Box 3000, FIN-90014 Oulu, Finland
\textsuperscript{c}Ecocat Oy, Catalyst Research, P.O. Box 71, FIN-90101 Oulu, Finland

Deactivation of Pd/Rh monoliths is considered. Based on the results of different characterization techniques, a deactivation correlation between laboratory scale ageing, engine bench ageing, and vehicle ageing is proposed.

KEY WORDS: ageing; deactivation; palladium; rhodium; three-way-catalyst.

1. Introduction

Successful commercial automotive three-way exhaust gas catalysts have to meet the requirements for high thermal stability and catalytic activity. Therefore, the understanding of deactivation correlations is an important issue in their design and preparation. Engine bench ageing is the best way to study deactivation phenomena, but due to the restrictions of cost and time, there is a need for an improved laboratory scale ageing cycle that reliably reproduces the ageing-induced changes in the catalyst.

In the present research, ageing-induced changes on Pd/Rh exhaust gas catalysts are studied using several surface characterization techniques. In particular, the effect of the gas phase composition on the catalytic activity and ageing-induced physical and chemical changes in the bulk washcoat are considered. It is important to establish the role of hydrothermal ageing in deactivation, since the exhaust gas mixture always contains ca. 10 vol% of water [1] and water vapour is known to be a sintering agent for many metal oxides [2,3]. Results of laboratory scale ageings are compared with those for the engine bench and vehicle-aged catalysts, and the deactivation correlation is presented.

2. Experimental

2.1. Catalysts and ageing procedures

The catalysts used in the experiments were designed to meet Euro IV emission limits and contained palladium and rhodium supported on modified $\gamma$-Al$_2$O$_3$. In addition to $\gamma$-Al$_2$O$_3$, the washcoat also contained CeO$_2$, La$_2$O$_3$ and Ce$_3$Zr$_{1-x}$O$_2$ mixed oxides as stabilizers and promoters. Catalysts were prepared by mixing the washcoat materials with precursor salts as a water slurry and by coating the thin Fe-Cr-Al foil to produce a layered washcoat structure. The catalysts were dried at 100–150 °C and calcined at 300–550 °C. The dried and calcined catalysts are referred to as “fresh” in the following text.

Catalysts were aged to simulate the high temperature conditions in the exhaust gas streams. Laboratory ageings were carried out at temperatures of 800–1200 °C in reducing ($5\%$ H$_2$/$N_2$) and oxidizing (air) atmospheres in the presence of 10 vol% H$_2$O. The engine bench ageing was carried out in the exhaust gas stream of a V8 engine for 40 h. The engine ageing procedure involved stoichiometric (10 min, 1050–1060 °C, $\lambda = 1.00$) and rich (50 min, 1030 °C, $\lambda = 0.98–0.99$) air-to-fuel ratios. The vehicle ageing was accomplished under European driving conditions of 100,000 km. All the catalysts were identical in chemical composition and thus only the changes induced by ageings were considered.

2.2. Catalyst characterization and activity tests

Several surface characterization techniques were utilized in this study. The total surface areas ($m^2/g$) were determined from N$_2$ adsorption isotherms according to a standard BET method by using a Couler Omnisorp 360CX, after outgassing the catalysts overnight in vacuum at 140 °C. X-ray diffraction (XRD) was used to determine the solid–solid phase transitions in the bulk washcoat and to evaluate their effect on the catalytic activity and surface areas after the ageings. X-ray diffractograms were recorded directly from the catalyst foils on a Siemens D5000 diffractometer employing nickel-filtered Cu K$_x$ radiation ($\lambda = 1.5406$ Å, 40 kV, 30 mA) at 0.02° intervals in the range $2\theta \leq 20 \leq 75$° with 1 s count accumulation per step. Diffraction patterns were assigned using the PDF database supplied by International Centre for Diffraction Data [4].
NO-TPD (temperature-programmed desorption) measurements for fresh and aged catalysts were carried out in a quartz chamber at temperatures 30–800 °C with a linear heating rate of 30 °C/min. In the pretreatment stage, the catalysts were evacuated for 2 h and then reduced under a H₂ flow for 10 min at 500 °C, followed by 15 min at 550 °C and the adsorption of 5% NO/Ar onto the surface of the catalyst at room temperature for 10 min. Pressure in the reactor chamber was below 10⁻⁴ mbar (down to 10⁻⁷ mbar) during the vacuum measurements. The product gas flow was analyzed by a quadrupole mass spectrometer.

Catalytic activities were determined by laboratory scale light-off measurements in lean and rich conditions (see table 1) by using the reduction of NO by CO as a model reaction. The catalysts were monoliths with a cylindrical shape having a diameter of 8 mm and a length of 28 mm. In the pretreatment stage, catalysts were reduced at 500 °C for 10 min, followed by 15 min at 550 °C. The total gas flow in the measurements was 1 dm³/min corresponding to a feed gas space velocity (GHSV) of 43,000 h⁻¹. The temperature of the catalyst was increased from room temperature to 400 °C with a heating rate of 20 °C/min. The gas concentrations were determined using a multi-component FTIR gas analyzer.

3. Results and discussion

3.1. Loss in surface area

The specific surface areas and pore volumes after 3 h of hydrothermal ageing are presented in table 2. The corresponding BET values for the fresh, engine-bench aged, and vehicle-aged catalysts were 69, 22, and 16 m²/g, respectively. The BET results indicated the ageing-induced structural changes in the bulk washcoat of the catalysts, which were verified by XRD. Catalyst surface areas and pore volumes strongly decreased as a function of ageing temperature in all ageing atmospheres. The loss in surface area was associated with an increase in pore size [5].

The presence of water vapour has an accelerating effect in the deactivation process, since the hydrothermally aged catalysts had lost approximately 20% of the initial surface area at the lowest ageing temperature of 800 °C. However, no significant differences in BET values after the reducing and oxidizing hydrothermal ageings were observed. By contrast, the catalyst surface areas remained unchanged in the dry reducing gas at 800 °C [5] indicating a regenerative effect on the deactivation. This is consistent with the observations of Piras et al. [6], who reported that ceria was totally ineffective as a stabilizing agent for Al₂O₃ under the oxidizing conditions at 1200 °C, while its effects were enhanced under the reducing conditions. The stabilizing effects of CeO₂ are associated with its reactions with the γ-Al₂O₃ washcoat, as discussed below. The high temperature deactivation of ceria and zirconia based catalysts probably depends on the surface area of ceria or on poor contact between the precious metals and ceria in aged catalysts [7]. The decrease in surface areas was also associated with the changes in the structures of oxides, such as the increased crystallite size of ceria as a result of sintering, which is consistent with the results obtained in this research. The temperature region of 800–1000 °C is critical for the thermal deactivation of the catalyst [7].

3.2. Loss in catalytic activity

Catalytic activities were determined after hydrothermal ageings in lean and rich conditions. The detailed light-off temperatures of CO and NO are presented in table 3. Catalyst light-off temperatures increased as a function of ageing temperature. The activity of the catalyst remained higher if ageing was carried out in the reducing gas phase. The aged catalysts were deactivated, which was observed as ageing-induced physical and chemical changes in the bulk washcoat and as a loss in surface area.