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Thermal and chemical aging of model three-way catalyst Pd/Al_2O_3 and its impact on the conversion of CNG vehicle exhaust

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ABSTRACT

Thermal and chemical aging induced physical and chemical modifications in the model three-way catalyst Pd/Al_2O_3 for compressed natural gas vehicles exhaust were studied. The fresh catalyst Pd/Al/F (calcined at 500 °C for 4 h) was subjected to either thermal (Pd/Al/700) or chemical (poisoned with phosphorous (P), *X*P/Pd/Al; $X = 1.8$ or 7.5 wt%) aging under air flow at 700 °C for 5 h. The catalysts were analyzed by N_2-physisorption, CO-chemisorption, high angular annular dark-field scanning transmission electron microscopic (HAADF-STEM), X-ray diffraction (XRD), solid state ^{31}P MAS NMR, H_2-temperature programmed reduction (H_2-TPR) and in situ X-ray absorption near edge structure spectroscopy (XANES) during H_2-TPR. Characterization results reveal that thermal aging leads to merely physical modifications such as decreased surface area of the support and palladium (Pd) dispersion in Pd/Al/700. Whereas, chemical aging causes both severe physical and chemical modifications in *X*P/Pd/Al: (i) physical modifications are clogging of support pores and fouling of Pd nanoparticles with P as evident from N_2-physisorption, CO-chemisorption and HAADF-STEM and (ii) chemical alterations are the conversion of support aluminum oxide into aluminum phosphate as evident from solid state ^{31}P MAS NMR, and decreased reducibility of PdO_x species as evident from H_2-TPR and in situ XANES. Consequently, chemical aging is more detrimental than thermal aging for three-way catalytic (TWC) performance as evident from the activity data. Undoubtedly, P (chemical aging) profoundly decreases the TWC efficiency. On the other hand, mere thermal aging considerably decreases CO and CH_4 oxidation efficiency, but interestingly improves the NO reduction efficiency.

1. Introduction

Automotive exhaust gas comprising of carbon monoxide (CO), nitrogen oxides (NO_x) and unburned hydrocarbons (HC) contribute to global warming, ozone layer depletion, acid rain and environmental toxicity [1–3]. Additionally, new fuel concepts like compressed natural gas (CNG) consisting of mainly methane (a more potent greenhouse gas and difficult to combust than any other hydrocarbon) post new challenges [4–6]. CNG is preferred over gasoline due to its abundance, low price and importantly, CO_2 produced per unit of energy generated is much lower [5–7]. The three-way catalysts (TWC) play a key role in meeting todays stringent legislations for emissions [8–14]. However, TWC deactivate rapidly due to thermal and chemical aging on CNG fuelled vehicles than on gasoline powered ones [5,14]. Thermal aging is a result of high temperature surges in the catalytic converters. Chemical aging is due to phosphorous (P), zinc (Zn), magnesium (Mg), calcium (Ca) or sulphur (S) originating from either engine oil additives (e.g. zinc dialkyldithiophosphate (ZDDP)) or fuel contaminants (e.g. S) [2,5,13].

As such, very few studies on deactivation of TWC ($Pd/Rh/CeZrO_2/Al_2O_3$ and $Pt/Rh/CeZrO_2/Al_2O_3$) aged on CNG fuelled vehicles are reported [14,15]. Studies on $Pd/Rh/CeZrO_2/Al_2O_3$ conclude that chemical aging (P content was between 2.25 and 0.5 wt%) is not as important as thermal aging [15]. Similarly, the report on $Pt/Rh/CeZrO_2/Al_2O_3$ concludes that P and Ca accumulate only on the surface and they do not poison noble metals [14]. Some of us recently reported a TWC aged on a bi-fuel passenger car (90% CNG and 10% gasoline operation) for 35,000 km (corresponding to approximately 800 operating h) [5]. The results show significant amount of methane slip while CNG operation over the catalysts aged between 2500 and 35,000 km. In

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contrast, the slip of total unburned hydrocarbons during gasoline operation is roughly the same over the period and was minimal. This fuel sensitive behavior of the catalyst was not completely understood, especially the role of P that was detected in the wash coat.

Differently, studies on real TWC converters aged on gasoline fuelled vehicles have shown that thermal aging results in the loss of surface area of the support $CeZrO_2/Al_2O_3$ (wash coat) and of the active metals (i.e., sintering of Rh, Pd and/or Pt) [13]. Whereas, chemical aging with P leads to fouling and clogging of the wash coat pores and to modified composition of the support by the formation of $CePO_4$ and $AlPO_4$ phases as well as formation of an over-layer of glassy Zn phosphate and Ca phosphate on the wash coat surface. It was concluded that Ce in $CePO_4$ does not involve in the redox cycle (Ce^{3+}/Ce^{4+}) as in CeO_2 and hence it seriously deteriorates the oxygen storage capacity (OSC) of the support $CeZrO_2$ [16,17]. However, the effect of $AlPO_4$ on TWC properties is not known [16–18]. It should be mentioned that the interaction between the noble metals and P was ruled out as a definite deactivation mechanism [19]. From the literature review it appears that, in general, the effect of P on noble metals is not completely understood and, there is no consensus on which aging process (thermal or chemical) causes the most damage to TWC efficiency [14–19].

This work aims to understand the deactivation process of TWC converter for CNG vehicles reported in [5]. To this end, model TWC powders were subjected to thermal and chemical aging followed by detailed characterization and activity studies. In this study, we report namely Pd/Al_2O_3. The results demonstrate that chemical aging is indeed more detrimental than thermal aging, as the former causes both severe physical and chemical modifications to the catalyst while the latter induces merely physical alterations. Small amounts of P (1.8 wt%) is enough to diminish the TWC efficiency.

2. Materials and methods

2.1. Materials

Pd/Al_2O_3 powder (1.6 wt% Pd) was provided by Umicore AG. The catalyst was calcined in air at 500 °C for 4 h (henceforth referred as Pd/Al/F). To study the influence of phosphorous (P), one of the chemical contaminants originating from engine oil additives, on the three-way catalytic performance, the fresh catalyst powder was impregnated with two different amounts of P from the aqueous $(NH_4)_3PO_4$ solution. The resulting catalysts were dried at 120 °C over-night and then treated in a muffle furnace in air at 700 °C for 5 h (*X*P/Pd/Al; *X* = P wt%) to promote reaction between P and Al_2O_3. This process is called chemical aging. For comparative purposes, the fresh catalyst was also thermally aged (without P) in a muffle furnace flowing air at 700 °C for 5 h (Pd/Al/700). Physico-chemical properties of the catalysts are presented in Table 1.

2.2. Methods

Inductively coupled plasma optical emission spectroscopy (*ICP-OES*): The Pd and P contents in the catalysts were determined (an average of two values) by ICP-OES (Varian VistaPro). 30 mg catalyst was dissolved in 4 ml aqua regia using a microwave system (MLS 1200 mega). The resulting solution was made up to 10 ml with ultrapure (18.2 mΩ cm, Millipore) water. Standards for external calibration were prepared from single element standards in ICP quality® (Merck).

N_2 physisorption: Nitrogen adsorption and desorption isotherms at −196 °C were obtained on a Micromeritics ASAP 2020c instrument. Prior to the experiments, the samples were pretreated at 350 °C for 2 h. The total surface area of the catalysts was determined by the Brunauer–Emmett–Teller (BET) method [20]. The total pore volume of the catalysts was determined from the desorption branch of the isotherm using the Barrett–Joyner–Halender (BJH) model [21].

CO chemisorption: Experiments were performed on a Micromeritics ASAP 2020c instrument. Catalysts were evacuated at 200 °C for 1 h and reduced in hydrogen at 300 °C for 2 h. After which CO chemisorption was carried out at 35 °C. A Pd to CO stoichiometry of 1:1 was used for data evaluation [22].

Transmission electron microscopy: High angular annular dark-field scanning transmission electron microscopic (HAADF-STEM) images were taken by a JEOL FS2200-FEG at 200 kV and in column omega filter. The catalysts were dispersed in double-deionized water and dropped on carbon-film-coated copper grids and dried in air. Approximately 50 Pd particles were measured for determination of an average particle size (Table 1).

X-ray diffraction (*XRD*): The powder XRD patterns of the catalysts were obtained on a PANalytical X'Pert PRO θ–2θ scan system (Johansson monochromator and a X'Celerator linear detector) using Cu Kα_1 (1.5406 Å, 45 kV and 40 mA). XRD data were collected in the range of 10–80° (2θ) using a step size of 0.0167° and a step time of 50 s.

Solid state ^{31}P MAS NMR: Single pulse experiments were performed at room temperature on a Bruker Avance 400 NMR spectrometer using a 2.5 mm CP/MAS probe at spinning rates of 25,000 Hz. The ^{31}P chemical shifts were referenced to an external sample of solid triphenylphosphine oxide at 27.0 ppm.

Temperature programmed reduction with hydrogen (*H_2-TPR*): Experiments were performed on a Quantachrome CHEMBET-3000 instrument to study the effect of P on the reducibility of PdO*x* species. The quartz reactor was loaded with 100 mg of catalyst (sieve fraction of 150–200 μm) and a K-type thermocouple was inserted into the middle of the catalyst bed to measure temperature. H_2-TPR experiments were performed by introducing 5 vol.% H_2 in N_2 (25 ml min^{-1}) with a temperature ramp of 5 °C min^{-1}. The H_2 uptake during the reduction process was measured with thermal conductivity detector (TCD). The H_2O formed during the reduction was prevented from passing through the detector by adsorption onto a molecular sieve.

In situ *X-ray absorption near edge structure* (*XANES*): Data were collected in transmission mode at the Swiss-Norwegian Beam Line (SNBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble. Spectra were obtained at the Pd K edge (24.35 keV) using a double crystal Si(1 1 1) monochromator. Ion chamber detectors were used to determine intensities of the incident (I_o) and transmitted (I_1) X-rays. In situ XANES spectra were recorded (between room temperature and 200 °C) during the temperature programmed reduction with hydrogen (H_2) to study the reducibility of PdO_x species in the catalysts. To this end, a micro-reactor setup similar to that well documented in [6,23] was employed. Briefly, the setup comprises of a quartz capillary micro-reactor equipped with an air blower (serving as an oven), temperature programmer and a gas-feeding system with mass-flow controllers (Brooks). The capillary micro-reactor (3.0 mm diameter and 6 cm length) was loaded with 30 mg of catalyst, firmly packed between two plugs of quartz wool and fixed on to the oven. The air temperature between the capillary and the oven is considered as the catalyst bed temperature. The Athena software was used for XANES analysis [24]. The XANES data were energy calibrated, background subtracted and normalized. Pd metal foil and PdO were used as model compounds.

Three-way catalytic tests: Activity tests were performed in a quartz tubular reactor (6 mm internal diameter and 40 cm length). The reactor was loaded with catalyst (100 mg and sieve fraction of 150–200 mm) which was diluted with quartz particles of the same size in a 1:1 volume ratio and firmly packed between two plugs of quartz wool. A thermocouple was inserted into the