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Methodology development for laboratory-scale exhaust gas catalyst studies on phosphorus poisoning

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Abstract

Deactivation of powdery automotive exhaust gas catalyst components (Rh or Pt loaded cerium–zirconium mixed oxides) was studied in laboratory-scale by developing two different chemical ageing procedures: incipient wetness impregnation with an aqueous salt solution of $(NH_4)_2HPO_4$ and the adding of the $(NH_4)_2HPO_4$ salt solution into the samples from a gaseous phase. Vehicle-aged commercial exhaust gas catalysts were used as a reference material for phosphorus poisoning. Phosphorus contamination in the poisoned samples was detected with X-ray fluorescence spectroscopy (XRF). Scanning electron microscope equipped with energy dispersive spectrometer (SEM–EDS) as well as XRF were used to analyze contaminants in the reference catalysts. Poison compounds formed on the catalytic surface of both laboratory-scale aged samples and vehicle-aged reference catalysts were identified with X-ray diffraction spectroscopy (XRD). The poisoning induced changes in the catalytic activities and characteristic surface areas of the samples were studied with activity tests and BET measurements, respectively. By both ageing methods, phosphorus could be added to the samples repeatedly, time-savingly, affordably, and safely, and the same phosphorus compounds formed under real driving conditions were detected. These methods are therefore considered to be potential ageing procedures when studying accelerated chemical poisoning of powdery automotive exhaust catalyst components in laboratory-scale.

Keywords: Exhaust gas catalysis; Deactivation; Poisoning; Phosphorus

1. Introduction

Deactivation of automotive exhaust gas catalysts is a combination of several ageing phenomena. The most important deactivation mechanisms are thermal ageing and contamination. Considerable amounts of phosphorus, zinc, calcium, and magnesium, which are typical impurities in lubrication oils, are normally observed on the catalyst surface after years of driving [1]. Phosphorus is usually concentrated at the forward-most section of monolithic converters. In the front section of converters, decreasing of catalytic activity and changes in characteristics, such as loss of surface area, have been associated with extensive phosphorus deposition [2,3]. Phosphorus contamination has been detected in aged catalysts as a phosphate-containing overlayer (a mixture of Zn, Ca, and Mg phosphates on the washcoat) or as phosphate compounds formed directly with the washcoat components (aluminium and cerium phosphates) [4–9].

Vehicle-ageing and engine-ageing procedures are widely used in studying poisoning phenomena of exhaust gas catalysts. However, these methods are often relatively expensive and slow. In addition, studying the effects of single deactivation mechanisms on the total decrease of the catalytic activity may be complicated. The mechanism of phosphorus poisoning is not completely known, and therefore studies carried out with simplified model components are required. The main objective of this study was to develop a methodology for accelerated chemical deactivation studies that can be carried out in a controlled way, time-savingly, affordably, and safely in laboratory-scale. In this research, the deactivation of automotive catalysts caused by phosphorus poisoning was studied by developing two different chemical ageing procedures in laboratory-scale. In addition, two vehicle-aged commercial catalysts, a three-way catalyst (TWC) and a diesel catalyst, were used as a reference material. Poisoning induced changes in the catalyst samples were studied by comparing the catalytic activities and BET surface areas of the fresh catalyst powders with the ones of the phosphorus treated samples. SEM–EDS and XRF were used to analyze contaminants in the reference catalysts, and phosphorus content of

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the laboratory-scale aged samples was determined with XRF. XRD was used to identify contaminants on the catalytic surfaces of the poisoned samples and the vehicle-aged reference catalysts.

2. Experimental

2.1. Catalyst samples

The study included two sets of catalyst samples: Rh (2 wt%) or Pt (1.5 wt%) containing Zr–CeO_2 (Ce rich) and Ce–ZrO_2 (Zr rich) mixed oxide powders (used as oxygen storage capacity (OSC) material). Two vehicle-aged metallic catalyst monoliths provided by Ecocat Oy were used as industrial reference catalysts for poisoning: a Rh/Pd/Al_2O_3/La_2O_3/OSC catalyst (aged for 100,000 km in a petrol-driven vehicle) for Rh loaded samples, and a Pt/Al_2O_3/La_2O_3/OSC (aged for 80,000 km in a diesel-driven vehicle) for Pt loaded samples. The monoliths were divided into different test zones in the axial (front and rear) direction in order to evaluate the position-dependent role of poisons on the catalytic activity. As mentioned above [2,3], the role of chemical deactivation is most significant in the forward-most section of monolithic converters. Therefore, the front zones of the commercial catalysts were used as a reference material in XRD studies carried out for the powdery samples after the phosphorus treatments.

2.2. Ageing procedures

Two different methods were utilized for the phosphorus ageing. In the first stage of the methodology development, the test series consisted of Rh loaded catalyst powders representing components used in TWC applications. The samples were impregnated with an aqueous salt solution of $(NH_4)_2HPO_4$ followed by calcination in air at 500 °C. The final phosphorus content of the samples was 1 wt% [10]. In the other poison treatment, the ageing procedure was further developed to better correspond to the extreme conditions in a catalytic converter during real driving. Phosphorus was added to a sample under continuous air flow and in a high temperature aiming to simulate poisoning in hydrothermal ageing conditions. The gas phase poisoning was carried out for a test series consisting of Pt loaded catalyst powders that represented components used in diesel catalyst applications. The ageing was performed by feeding aqueous salt solution of $(NH_4)_2HPO_4$ with a peristaltic pump into a quartz tube in which the catalyst powder (1.5 g) was placed in a furnace. The $(NH_4)_2HPO_4$ content of the solution was 0.13 mol/l and the feeding rate was 0.1 ml/min. The treatment was performed in an air flow of 0.25 l/min at 700 °C with the ageing time of 4 h.

2.3. Activity measurements

Activity measurements were carried out by using laboratory-scale light-off experiments in order to study the poisoning induced changes between the fresh and aged catalyst powder samples. Catalytic activities were determined in lean reaction conditions by using model reactions. The test gas mixture for the Rh loaded mixed oxides was used to simulate lean petrol exhaust gas conditions and consisted of 1000 ppm NO and 800 ppm CO. A test gas mixture containing 1000 ppm NO, 1000 ppm C_3H_6, and 10 vol% O_2 was used for the Pt loaded mixed oxides in order to simulate diesel exhaust gas conditions. Both gas mixtures were balanced with N_2. Before the measurements, the Rh loaded mixed oxides were reduced in a 500 ml/min hydrogen flow at 500 °C for 10 min, followed by 15 min at 550 °C. Pt loaded mixed oxides were oxidized in a 50 ml/min air flow at 500 °C for 20 min. The measurements were carried out at atmospheric pressure in a tubular furnace with a quartz reactor. The powder samples (0.25 g) were mixed with quartz sand and placed in the reactor tube with a support of quartz wool. The gas flow was controlled by mass flow controllers (Brooks 5850TR) and the total gas flow during the experiments was 1 l/min. Temperature of the catalyst was increased from room temperature up to 500 °C, with a linear heating rate of 10–15 °C/min. Concentrations of the feed and product gases were measured as a function of temperature every 5 s by a FTIR gas analyzer (Gasmet^{TM} CR2000).

2.4. Catalyst characterization

BET surface areas and catalytic activities of the phosphorus poisoned catalysts were measured and compared to the results of the fresh catalyst samples. All the catalysts were also studied by X-ray diffraction spectroscopy (XRD) and X-ray fluorescence spectroscopy (XRF). In addition, studies with scanning electron microscope equipped with energy dispersive spectrometer (SEM–EDS) were carried out for the reference catalysts. Physisorption measurements were carried out to characterize the catalysts before and after the ageing. Specific surface areas (m^2/g) were measured according to the standard BET method from N_2 adsorption isotherms at −196 °C by assuming the cylindrical shape of pores. Phosphorus content of the poisoned catalyst samples was determined by XRF, and SEM–EDS as well as XRF were used to detect contaminant levels in the reference catalysts. XRD was used to identify the phosphorus compounds in the aged catalyst samples. XRD patterns were obtained with Philips X'PERT X-ray analysis unit, which uses Cu Kα radiation and graphite monochromator. Scans were made in the 2θ range of 10°–65° with a step size of 0.02° and a time per step of 0.5 s. XRF measurements were carried out by using Philips MagiX apparatus with Super Q Analytical software. Equipment used for SEM studies was Jeol JSM-6400.

3. Results and discussion

3.1. Activity measurements

On the basis of the light-off temperatures, both phosphorus treatments had a strong deactivating impact on the activity of the catalyst samples. As illustrated in Fig. 1, the light-off temperatures of all the phosphorus treated samples were significantly higher than the ones of the fresh catalysts. The measurements

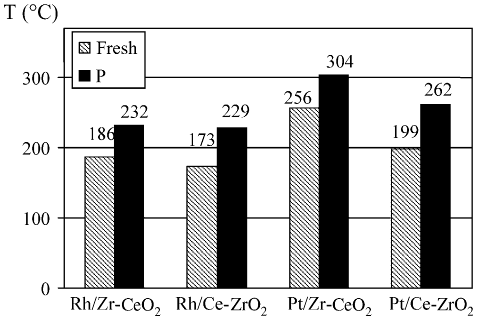

Fig. 1. The light-off temperatures of CO for the Rh/OSC samples and the light-off temperatures of C_3H_6 for the Pt/OSC samples as fresh and after the phosphorus treatments (P).

showed that the increase in the light-off temperatures of the cerium rich Rh/Zr–CeO_2 and Pt/Zr–CeO_2 samples after the phosphorus ageing was smaller compared with the results of zirconium rich Rh/Ce–ZrO_2 and Pt/Ce–ZrO_2 samples. Therefore, it can be concluded that cerium rich mixed oxides studied in this work can better sustain the deactivating impact of phosphorus than the zirconium rich mixed oxides in terms of catalytic activity. On the other hand, the catalytic activities of the fresh zirconium rich mixed oxide samples were better than the activities of cerium rich samples in the oxidation reactions, and even after the gaseous phase phosphorus treatment the catalytic activity of the Pt/Ce–ZrO_2 sample remained substantially higher than the activity of the Pt/Zr–CeO_2 sample after the same treatment. The CO light-off temperatures of the Rh/Ce–ZrO_2 and Rh/Zr–CeO_2 samples were approximately the same after the phosphorus impregnation but the relative decrease in the activities of the phosphorus treated Rh/Zr–CeO_2 and Pt/Zr–CeO_2 was almost equal.

It is important to point out that the deactivation of the reference catalysts is a result of a combination of several ageing phenomena instead of purely phosphorus poisoning. However, on the basis of the activity measurements carried out with the vehicle-aged TWC reference, poisoning contributes to approximately 20% of the total deactivation with phosphorus being the major contaminant [4].

3.2. Surface characterization

Phosphorus accumulation was detected in aged catalyst powders by XRD and XRF. The semi-quantitative phosphorus contents measured with XRF were 1 wt% for the Rh loaded powder samples, 2 wt% for Pt/Zr–CeO_2, and 3 wt% for Pt/Ce–ZrO_2. The difference between the amounts of phosphorus accumulated into the catalyst samples during the gas phase ageing can be explained by the dissimilar tendencies of different materials towards accumulating of impurities. In contrast, in the impregnation ageing procedure, the final phosphorus content in the sample is equal with the amount of phosphorus impregnated into the sample. Therefore, the gas phase ageing procedure can be used as a tool for studying the possible distinctions in the behavior of different catalyst components in chemical ageing conditions.

Poisoning was a relevant deactivation mechanism of the vehicle-aged reference catalysts. The XRF analyses (see Table 1) showed that the TWC reference catalyst was poisoned by phosphorus, calcium, and zinc but not by sulfur. The front zone of the vehicle-aged catalyst (first 2 cm from the inlet) was the most highly poisoned zone, and the elemental analyses carried out with XRF showed that the frontal part of the TWC reference cata-

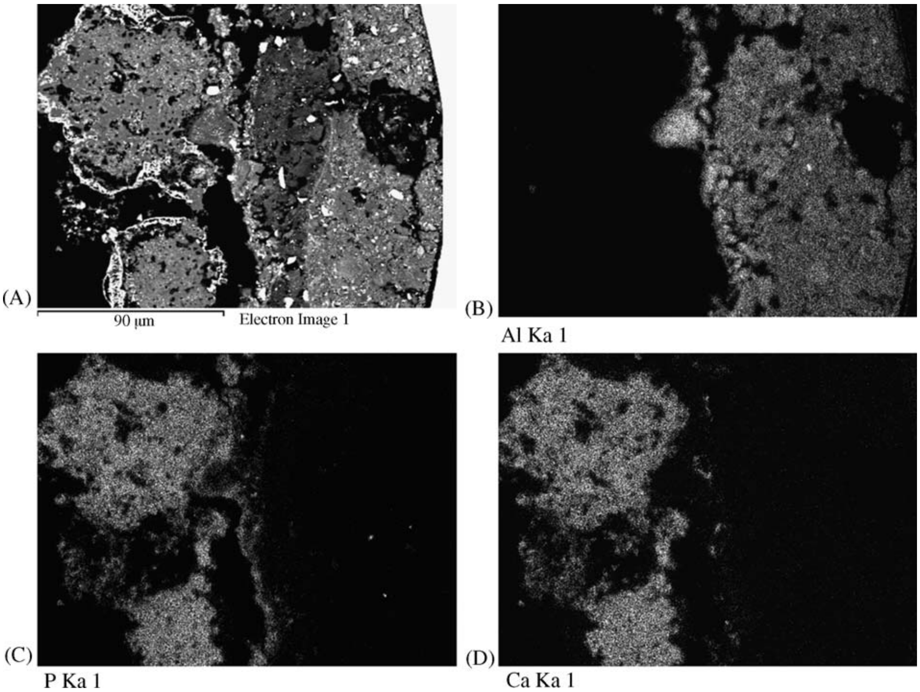

Fig. 2. Elemental analyses (X-ray maps) taken at the inlet of the vehicle-aged TWC catalyst. (A) Backscattered electron image showing the metal foil, washcoat, and contaminant overlayer. EDS elemental maps of: (B) Al, (C) P, and (D) Ca.

Table 1
Contaminant levels in the front zones of the vehicle-aged three-way and diesel catalysts

Catalyst	Contaminant levels (wt%)			
	P	S	Ca	Zn
Three-way catalyst[a]	3.5	<0.1	2.3	1.6
Diesel catalyst[b]	0.4	6.3	0.2	0.1

[a] Rh/Pd/Al_2O_3/La_2O_3/OSC catalyst.

[b] Pt/Al_2O_3/La_2O_3/OSC catalyst.

lyst contained 3.5 wt% phosphorus. Fig. 2 presents the elemental analysis data from the inlet region of the TWC, including a backscattered electron image and selected elemental distribution maps (X-ray maps) obtained by EDS. As can be seen in Fig. 2, the surface of the top overlayer of the vehicle-aged catalyst was the poisoned layer. According to the chemical analyses, the contaminated overlayer in the inlet region contained phosphates, mainly $Ca_3(PO_4)_2$. Furthermore, the penetration of phosphorus and calcium into the upper areas of the washcoat was observed. According to XRF analyses (Table 1), phosphorus content of the diesel reference catalyst was 0.4 wt%. The catalyst was mainly poisoned by sulfur, and small concentrations of calcium and zinc were also detected. SEM–EDS studies (Fig. 3) did not show any contaminated overlayer in the diesel catalyst but instead, phosphorus had accumulated in the uppermost layer of the catalyst. Due to the overlapping peaks of phosphorus and zirconium, quantitative EDS analyses were used to indicate that phosphorus was located only on the upper areas, whereas zirconium was detected throughout the catalyst. By contrast to phosphorus, sulfur had penetrated evenly to the entire depth of the washcoat.

XRD was used for the identification of phosphorus compounds on the catalytic surfaces. Phosphorus compounds formed with OSC components could be detected after both chemical ageing procedures. Fig. 4a presents the comparison of XRD diffractograms of the phosphorus impregnated Rh/OSC samples and the TWC reference catalyst. As indicated, $Ce(PO_4)$ was present in the Rh/Zr–CeO_2 (Fig. 4a, trace A), Rh/Ce–ZrO_2 (Fig. 4a, trace B) and TWC reference (Fig. 4a, trace C) samples. The formation of $CeAlO_3$ was also observed in the TWC reference due to the reactions of Al_2O_3 with the pure CeO_2 in the catalyst's washcoat [4,5]. Fig. 4b shows XRD diffractograms of the gaseous phase phosphorus poisoned Pt/OSC samples and the diesel reference catalyst. According to the XRD studies, phosphorus had formed $Ce(PO_4)$ with the Rh/Zr–CeO_2 sample (Fig. 4b, trace D). In the case of gaseous phase treated Pt/Ce–ZrO_2 sample (Fig. 4b, trace E), phosphorus was attached as zirconium phosphate but the exact formula of the compound could not be verified. In the diesel reference catalyst (Fig. 4b, trace F) used in this study, the only contaminant detected in the XRD studies was an orthorhombic SO_3. Reason for this may be the accumulation of carbon on surface of the catalyst. However, according to the literature [9], the role of phosphorus in the deactivation of diesel catalysts has been shown by detecting phosphates in the aged catalytic converters.

The poisoning effect of phosphorus was also observed as alterations in specific surface areas of the catalyst samples. BET surface areas of all the poisoned catalyst powders were diminished compared to the fresh catalyst powders (see Fig. 5). The ageing treatments affected most the surface areas of the cerium rich mixed oxide (Zr–CeO_2) samples. The BET area of the poisoned Pt/Zr–CeO_2 was one-fifth of the surface area of

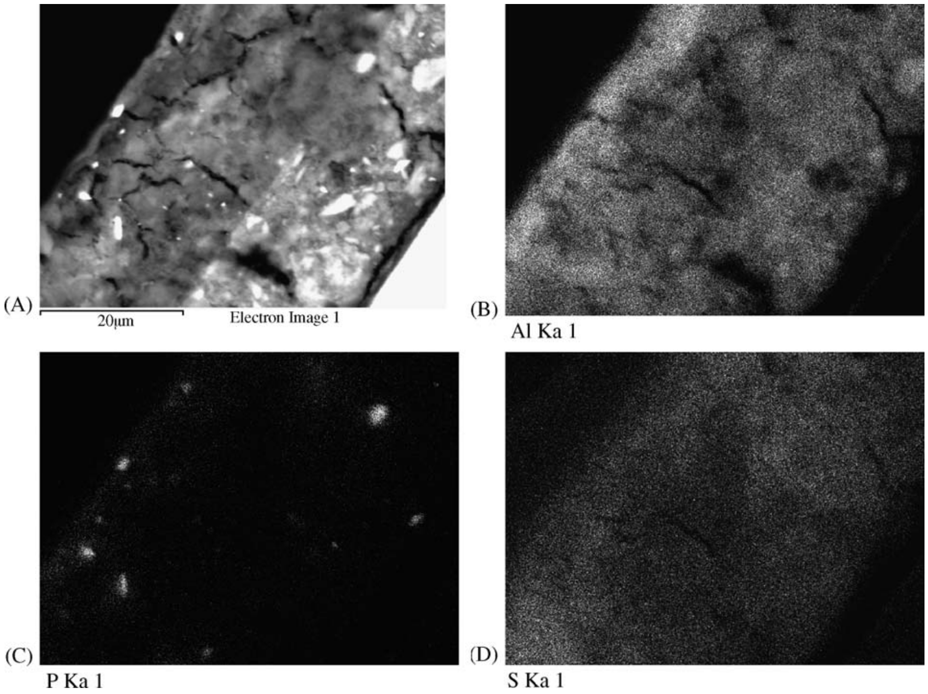

Fig. 3. Elemental analyses (X-ray maps) taken at the inlet of the vehicle-aged diesel catalyst. (A) Backscattered electron image showing the metal foil and contaminated washcoat. EDS elemental maps of: (B) Al, (C) P, and (D) S.

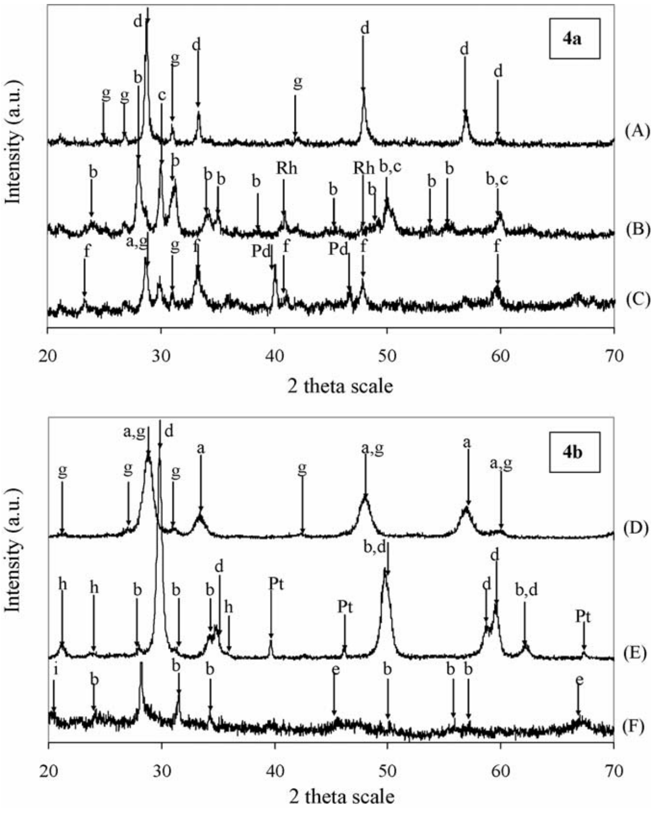

Fig. 4. XRD diffractograms for: (A) Rh/Zr–CeO_2 + P; (B) Rh/Ce–ZrO_2 + P; (C) vehicle-aged three-way catalyst; (D) Pt/Zr–CeO_2 + P; (E) Pt/Ce–ZrO_2 + P; (F) vehicle-aged diesel catalyst. (a) CeO_2 (monoclinic); (b) ZrO_2 (monoclinic); (c) ZrO_2 (tetragonal); (d) Zr–CeO_2 (cubic); (e) Al_2O_3; (f) $CeAlO_3$; (g) Ce(PO_4); (h) unidentified Zr phosphate; (i) SO_3 (orthorhombic).

the fresh sample, and the surface area of phosphorus treated Rh/Zr–CeO_2 had collapsed even more dramatically being only less than one-tenth of the surface area of the fresh sample. The observed decrease in the BET surface areas after the phosphorus treatments is consistent with the results from the activity measurements. In addition to the above mentioned phosphorus compounds formed with washcoat components (i.e. cerium phosphates and zirconium phosphates in this study) it is also possible that the accumulated contaminants act rather as impurities than as poisons in the catalyst. As a result, surface area as well as catalytic activity may be reduced due to phosphorus blocking the pores and, therefore, gas molecules are prevented from reaching catalytically active sites in the catalyst. This was indicated in this study by an increase in the average pore widths and a decrease in the pore volumes observed after the phosphorus treatments. For instance, the pore width and pore volume (BJH) of the fresh Pt/Zr–CeO_2 were 4 nm and 0.18 cm^3/g, respectively. After the gaseous phase phosphorus poisoning, the values were 11 nm and 0.10 cm^3/g.

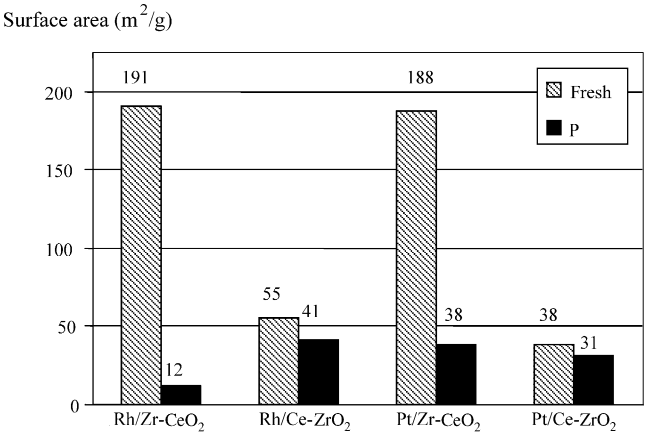

Fig. 5. BET surface areas for the Rh/OSC and Pt/OSC samples as fresh and after the phosphorus treatments (P).

As a conclusion, phosphorus added in the ageing treatments decreased the characteristic surface areas of all the powder catalyst samples and reduced the catalytic activity by forming compounds with the catalyst components or by blocking the pores on the catalytic surfaces. Furthermore, the results from the surface characterizations of the powder samples (phosphorus contamination and phosphorus compounds formed during the ageing procedures) are congruent with the results observed with the reference catalysts used in this work as well as with other studies [4–9] carried out with aged catalysts.

4. Conclusions

According to these results, poisoning by both methods described above, the incipient wetness impregnation with the aqueous salt solution of $(NH_4)_2HPO_4$ and the adding of the aqueous salt solution of $(NH_4)_2HPO_4$ into a gaseous phase produces the same poison compounds as can be found in vehicle-aged catalysts. By both methods, phosphorus can be added to samples repeatably, time-savingly, affordably, and safely. These methods are therefore considered to be potential ageing procedures when studying accelerated chemical poisoning of powdery automotive exhaust catalyst components in laboratory-scale.

In further studies, the gaseous phase ageing can be carried out by using different poison sources in order to simulate accumulation of other lubrication oil-derived impurities, such as zinc, calcium or magnesium, to an exhaust gas catalyst. In addition, the gas composition and flow rate as well as the ageing time and temperature can be varied depending on the real driving conditions that are desired to be simulated by the accelerated chemical ageing procedure. Due to its versatility, the gaseous phase laboratory-scale chemical ageing procedure developed in this work can be utilized in different types of exhaust gas catalyst ageing studies including both three-way catalyst and diesel catalyst applications.

Acknowledgements

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