

The effect of phosphorus exposure on diesel oxidation catalysts - Part II: Characterization of structural changes by transmission electron microscopy

Mari Honkanen^{(a),*}, Marja Kärkkäinen^(b), Olli Heikkinen^(c), Kauko Kallinen^(d), Tanja Kolli^(b), Mika Huuhtanen^(b), Jouko Lahtinen^(c), Riitta L. Keiski^(b), Toivo Lepistö^(a) and Minnamari Vippola^(a)

^(a)Tampere University of Technology, Department of Materials Science, P.O. Box 589, 33101 Tampere, Finland

^(b)Faculty of Technology, Mass and Heat Transfer Process Engineering, P.O. Box 4300, 90014 University of Oulu, Finland

^(c)Aalto University, Department of Applied Physics, P.O. Box 14100, 00076 Aalto, Finland

^(d)Dinex Ecocat Oy, Typpitie 1, 90620 Oulu, Finland

* Corresponding author, e-mail: mari.honkanen@tut.fi, telephone +358408490133

Abstract

Phosphorus poisoning and its effect on the diesel oxidation catalysts morphology was studied by transmission electron microscopy (TEM). The studied catalyst samples were PtPd or Pt supported on the alumina-based washcoat including additives. The laboratory-scale phosphorus exposures were carried out with two different phosphorus concentrations. The cross-sectional TEM samples were prepared from the fresh and phosphorus-treated catalysts. After phosphorus exposures, significant structural changes were observed compared to the fresh catalysts. The shape of the noble metal particles had changed from irregular to more spherical-shaped particles. In addition, phosphorus was detected throughout the catalyst TEM samples but the amount varied depending on the local composition of the support. Phosphorus accumulated mainly in the alumina-containing areas of the support and indications of dense and amorphous aluminium phosphates were found. Based on the results gained, cross-sectional TEM characterization is essential to observe these kinds of morphological changes in the catalysts caused e.g. by phosphorus exposures. In addition, cross-sectional TEM samples are needed to study the effect of local variation in the support composition on the phosphorus accumulation.

Keywords:

Diesel oxidation catalyst, phosphorus poisoning, structural characterization, transmission electron microscopy

1. INTRODUCTION

Nowadays, to meet still tightening emission legislation, an exhaust gas purification system in diesel engines consists of e.g. a particulate filter, a nitrogen oxides (NO_x) reducing system, and a diesel oxidation catalyst (DOC) [1]. DOCs oxidize carbon monoxide (CO), hydrocarbons (HCs), and the soluble organic fraction (SOF) of the diesel exhaust to less harmful compounds. Even as catalytic converters were introduced in the 1970s and remarkable effort has been put in development, the deactivation of the catalysts is still a major problem and it is not fully understood. The causes of deactivation are: mechanical, thermal, and chemical. In many cases, they exist as combinations. Mechanical deactivation is caused by e.g. loss of catalytic material by abrasion. Fouling, i.e. physical deposition of species from fluid onto the catalyst surface causing blocking of active sites and pores, is also mechanical deactivation of the catalyst. Thermal aging, like sintering and phase transformations, causes the loss in active surface. Chemical poisoning means strong chemisorption of impurities on the catalytic sites resulting in blocking active sites for catalytic reactions [2-4].

Because of moderate temperatures in the diesel engines compared to for example spark ignition engines, thermal deactivation is not a very crucial problem for the DOCs. However, phosphorus, sulfur, calcium, zinc, and magnesium impurities originating from lubricants and/or diesel fuel cause chemical deactivation [2]. In the chemical deactivation, poisoning elements adsorb on the active sites of the noble metal particles thus preventing the oxidation reactions of CO and HCs [3,5]. In addition, poisoning elements may disturb the surface diffusion of adsorbed reactants [3].

Phosphorus is one of the most harmful poisoning elements for the oxidation catalysts, as reported e.g. in [6,7]. It is suggested that phosphorus continues its accumulation into the catalysts even after adsorption on the active sites [5]. Adsorbed phosphorus causes fouling of the catalyst surface and noble metal particles and clogging of the catalyst pores. In addition, phosphorus may modify the composition of the support. Phosphorus compounds may sinter and form glassy layer and in addition, dense and amorphous aluminum phosphate can form with the alumina support. Formed aluminum phosphate can have an effect on chemical environment near the noble metal particles [5,8,9]. According to Matam et al. [9,10], phosphorus-induced chemical aging of the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst leads to formation of AlPO_4 like species and phosphorus also adsorbs on the surface of the Pd particles.

The aim of this study was to characterize the structural changes of two DOCs caused by phosphorus. The catalyst support is similar in both DOCs but another catalyst contains PtPd

particles and another Pt particles only. The aim was also to study possible effect of various noble metal particles on phosphorus poisoning phenomena. The fresh and phosphorus-treated catalysts were studied with transmission electron microscopy (TEM). The phosphorus exposure was carried out with two different phosphorus concentrations. Cross-sectional TEM samples from the catalyst surface region were prepared to study the detailed morphology of the fresh DOCs and more specifically the morphological and chemical changes of the noble metal particles and the support due to phosphorus poisoning. This is one of the first published cross-sectional TEM studies of the DOC catalysts and their poisoning.

2. EXPERIMENTAL

2.1. Studied catalysts

The studied catalyst materials were two metallic DOCs containing PtPd (4:1) particles or Pt particles only supported on alumina-based washcoat including additives. The catalysts were studied as fresh form and after laboratory-scale phosphorus treatments. The P-treatment was performed for 5 h at 400°C in ambient pressure under the following gas stream: 10 vol% $(\text{NH}_4)_2\text{HPO}_4$ (aqueous), 10 vol% air, balanced with N_2 , total gas flow 1 L. Two aqueous phosphorus feeding concentrations (0.065 mol/L and 0.13 mol/L assigned as LPW and HPW, respectively) were used. Aqueous P-solution was added through a peristaltic pump into the gas flow and vaporized at 400°C before the monolith placed in the tube furnace.

2.2. Structural characterization

The catalysts were studied as fresh and after phosphorus exposures with a transmission electron microscope (TEM, Jeol JEM-2010) equipped with an energy dispersive X-ray spectrometer (EDS, Noran Vantage with Si(Li) detector, Thermo Scientific). Cross-sectional samples for TEM studies were prepared as follows: two small pieces of catalyst monolith were attached together so that the catalyst layers were situated face-to-face. The pieces were placed on a titanium grid by carbon glue and the grid was pre-thinned by hand to the thickness of ~100 μm and then thinning was continued with a dimple grinder (Model 656, Gatan Inc.) to the thickness of ~20 μm . The final thinning for electron transparency was made with a precision ion polishing system (PIPS, Model 691, Gatan Inc.). The image of the thinned TEM sample is presented in Fig. 1. Characterization of the catalysts was

concentrated especially on the surface region (maximum ~1 mm from the surface) as according to many studies, e.g. [6,7,11], it has been observed that the phosphorus amount is highest in the surface region of the catalyst.

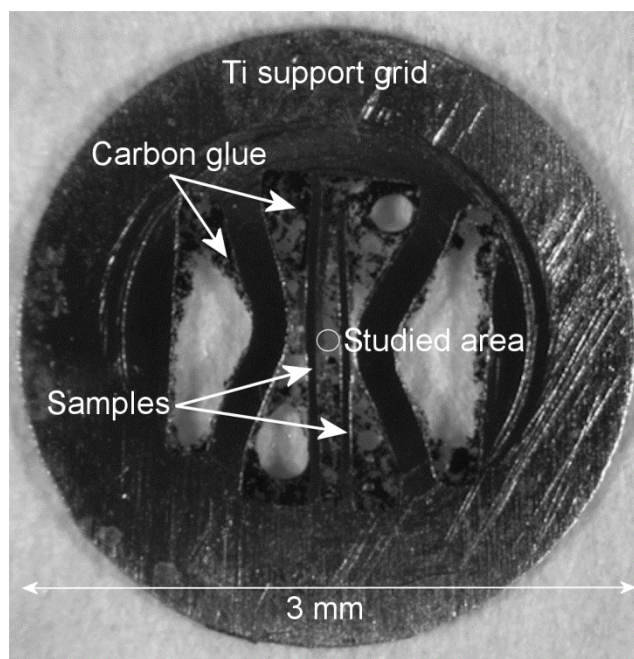


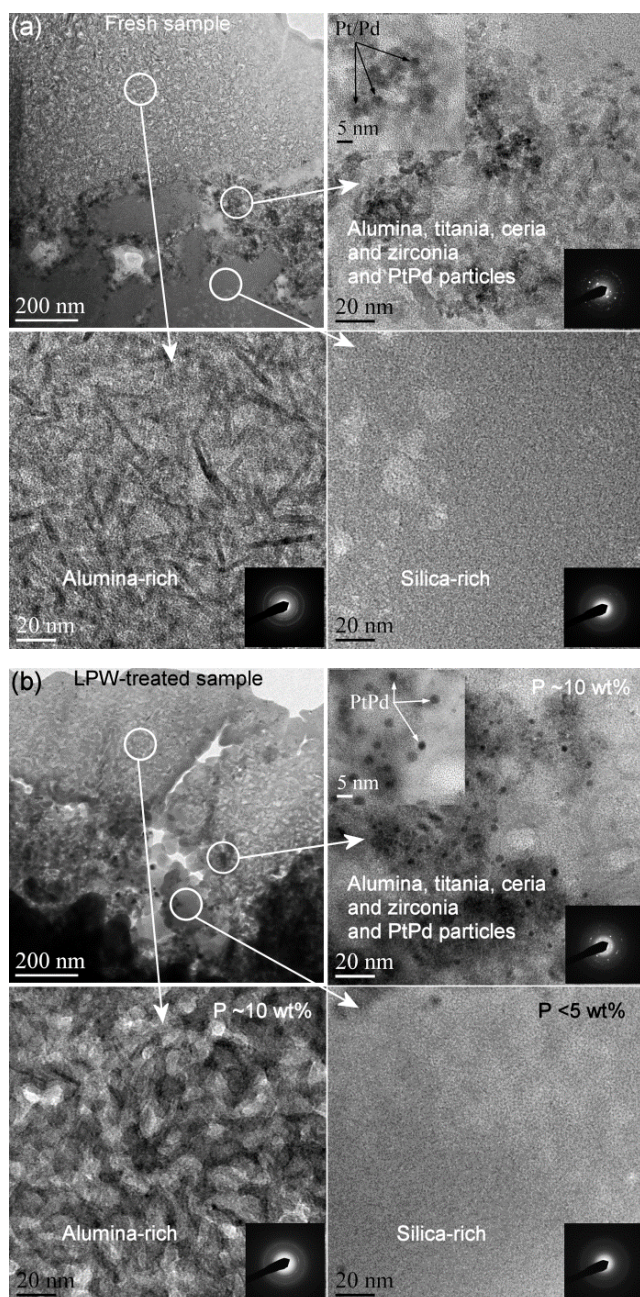
Fig. 1 The image of the prepared cross-sectional TEM sample, the titanium support grid with the samples

3. RESULTS AND DISCUSSION

The cross-sections of the catalyst surface regions were characterized with TEM as fresh and after two different phosphorus treatments, i.e. LPW and HPW. Many areas in the same cross-sectional TEM sample were studied and results were similar everywhere in the studied region. Example TEM images of the PtPd catalyst and Pt catalyst are presented in Figs. 2 and 3, respectively. The fresh PtPd catalyst contains very small (<5 nm) PtPd particles supported on the fine-grained alumina, titania, ceria, and zirconia containing washcoat (Fig. 2 (a)). In addition, nanocrystalline alumina-rich and amorphous silica-rich areas without noble metal particles were detected (Fig. 2 (a)). According to X-ray photoelectron spectroscopy (XPS), platinum exists as PtO or Pt(OH)₂ forms in the fresh and phosphorus-treated PtPd catalysts and palladium is in oxidized form in the fresh and phosphorus-treated PtPd catalysts [11,12]. In addition, phosphorus was observed to be as phosphate form in the phosphorus-treated PtPd catalysts [11].

The LPW-treatment affected the surface structure of the PtPd catalyst (Fig. 2 (b)); generally the structure of the LPW-treated PtPd catalyst was denser than the structure of the fresh PtPd catalyst. After the LPW-treatment, the size of the PtPd particles slightly increased, however, their average diameter was still below 5 nm. Phosphorus was detected throughout the LPW-treated PtPd catalyst TEM sample but the amount varied significantly depending on the local composition of the support. In the areas containing alumina, titania, ceria, zirconia, and in the alumina-rich areas the amount of phosphorus was ~10 wt% and in the silica-rich areas it was less than 5 wt%. In the selected area electron diffraction (SAED) pattern (inset in Fig. 2 (b)), taken from alumina-rich areas, crystalline and amorphous rings were observed indicating that both nanocrystalline and amorphous forms were present. Based on the TEM studies, phosphorus accumulated mainly to the alumina-containing areas. Thus, phosphorus can be concluded to form aluminum phosphate with the support compounds [11]. After the LPW-treatment, the specific surface area of the PtPd catalyst was slightly decreased (by ~10 %) and its light-off temperature (T_{90}) for propene oxidation was higher (~50°C) compared to the fresh catalyst (Table 1). It can be concluded that the LPW-treatment caused morphological and chemical changes in the PtPd catalyst resulting in slight deactivation of the catalyst.

The HPW-treatment caused significant structural changes in the surface region of the PtPd catalyst (Fig. 2 (c)). The average size of the PtPd particles increased from well below 5 nm to about 5 nm. The phosphorus accumulated similarly to the LPW-treated catalyst; in the areas containing alumina, titania, ceria, and zirconia the amount of phosphorus was ~10 wt%, in the alumina-rich areas it was ~20 wt%, and in the silica-rich areas it was below 5 wt%. In the SAED pattern (inset in Fig. 2 (c)), taken from alumina-rich areas, only amorphous rings were observed, thus the alumina-rich areas had changed from a nanocrystalline structure of the fresh catalyst (Fig. 2 (a)) to an amorphous form in the HPW-treated catalyst (Fig. 2 (c)). Thus, phosphorus accumulated mostly to the alumina-containing areas and it can be assumed that dense and amorphous aluminum phosphate has formed [11]. After the HPW-treatment, the specific surface area of the PtPd catalyst was decreased by ~30 % compared to the fresh PtPd catalyst (Table 1). With HPW-treated PtPd catalyst, the light-off temperature (T_{90}) for propene oxidation was not achieved in the examined temperature range and its light-off temperature for carbon monoxide oxidation was remarkable higher (~95°C) compared to the fresh PtPd catalyst (Table 1). Thus, the HPW-treatment caused significant structural changes in the PtPd catalyst that resulted in remarkable deactivation of the catalyst.



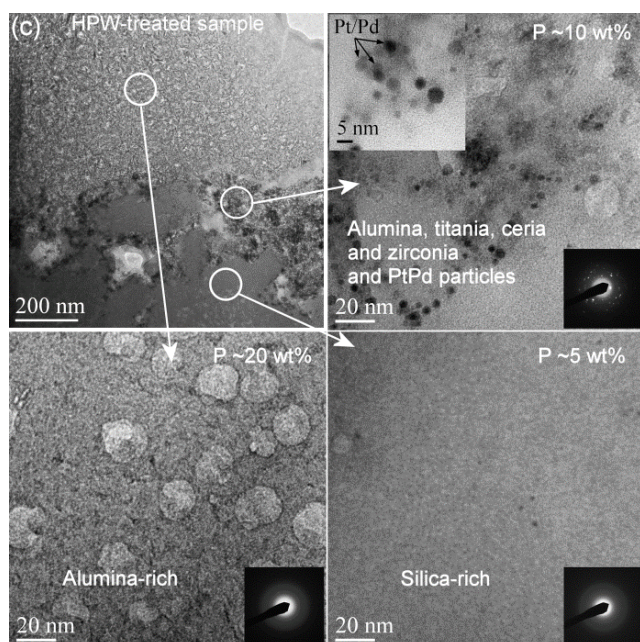
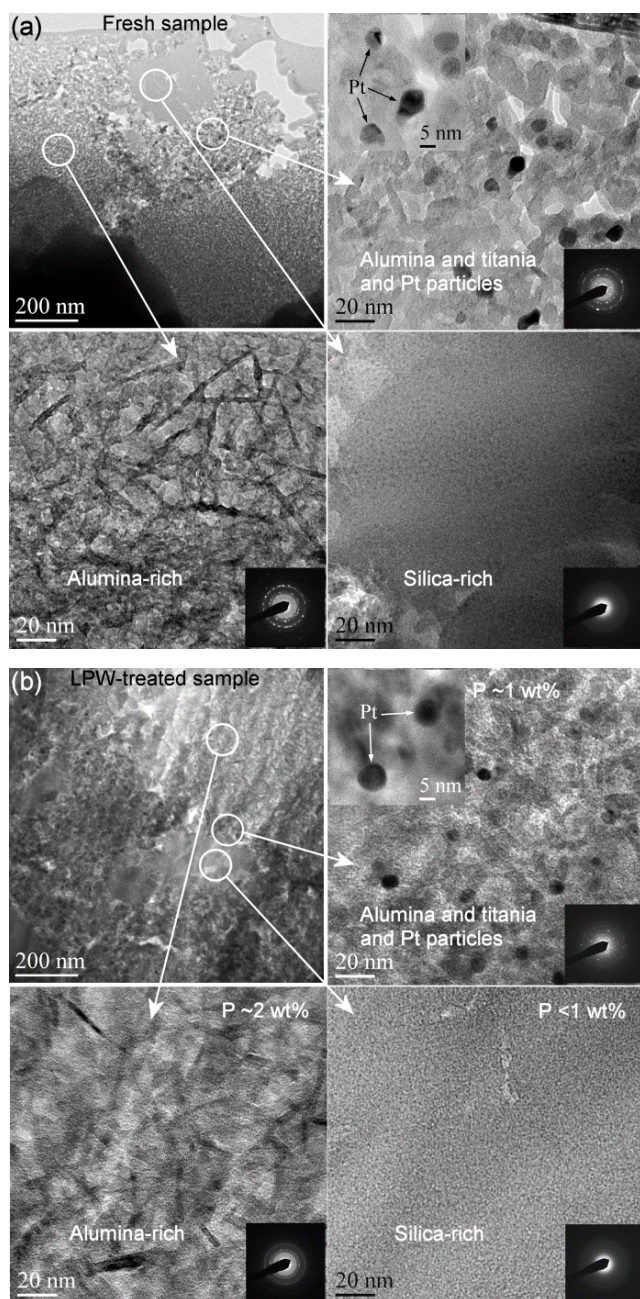


Fig. 2 Cross-sectional TEM images of the PtPd catalyst, (a) fresh, (b) LPW-treated (0.065 mol/L $(\text{NH}_4)_2\text{HPO}_4$), and (c) HPW-treated (0.13 mol/L $(\text{NH}_4)_2\text{HPO}_4$)

The fresh Pt catalyst has small (5- 10 nm) Pt particles supported on the fine-grained alumina and titania containing areas (Fig. 3 (a)). Also alumina-rich and amorphous silica-rich areas without noble metal particles can be detected (Fig. 3 (a)). According to TEM studies, the Pt particles appear as spherical- or irregular-shaped (an inset in Fig. 3 (a)). According to the XPS results, Pt is in a metallic form both in the fresh and in the phosphorus-treated Pt-catalysts [11]. In addition, phosphorus was observed to be as phosphate form in the phosphorus-treated Pt catalysts [11].

After the LPW-treatment, the surface structure of the Pt catalyst was slightly denser (Fig. 3 (b)) than the structure of the fresh Pt catalyst (Fig. 3 (a)). The shape of the Pt particles changed from mixture of spherical and irregular ones to mainly spherical particles. This agrees with the findings of Matam et al. [10] that phosphorus interacts with Pt particles and smoothens their edges resulting in the change from cuboctahedral-shaped particles to spherical-shaped particles. They have also noticed slight increase in the average Pt particle size due to phosphorus [10]. A small amount of phosphorus was detected uniformly in the LPW-treated Pt-catalyst TEM sample. According to our studies reported in Kärkkäinen et al. [11], the specific surface area of the LPW-treated Pt catalyst had decreased by ~30 % compared to the fresh Pt catalyst. In addition, the light-off temperature (T_{90}) for propene and carbon monoxide oxidation was higher (~20°C and ~10°C, respectively) than that of the fresh Pt catalyst (Table 1). It can be concluded that the LPW-treatment caused morphological and chemical changes in the Pt catalyst and resulted in slight deactivation of the catalyst.

After the HPW-treatment, the surface structure of the Pt catalyst had significantly changed (Fig. 3 (c)) compared to the fresh catalyst (Fig. 3 (a)). The morphology of the HPW-treated Pt catalyst was dense and phosphorus was detected everywhere in the catalyst TEM sample but its amount varied depending on the local composition of the support. In the areas containing alumina, titania and Pt particles and in the alumina-rich area, the amount of phosphorus was ~20 wt% and in the silica-rich areas it was ~5 wt%. In the SAED pattern (inset in Fig. 3 (c)), taken from alumina-rich areas, mainly amorphous rings were observed, thus the alumina-rich areas changed from a nanocrystalline structure of the fresh catalyst (Fig. 3 (a)) to mainly an amorphous form in the HPW-treated catalyst. So, again it seems that dense and amorphous aluminum phosphate has formed [11]. The shape of the Pt particles was as after the LPW-treatment. After HPW-treatment, the specific surface area of the Pt catalyst was significantly decreased (by ~40 %) compared to the fresh Pt catalyst (Table 1). With HPW-treated Pt catalyst, the light-off temperature (T_{90}) for propene and carbon monoxide oxidation was higher (~110°C and ~35°C, respectively) compared to the fresh Pt catalyst (Table 1). The HPW-treatment caused significant structural changes in the Pt catalyst and resulted in significantly decreased catalytic activity.



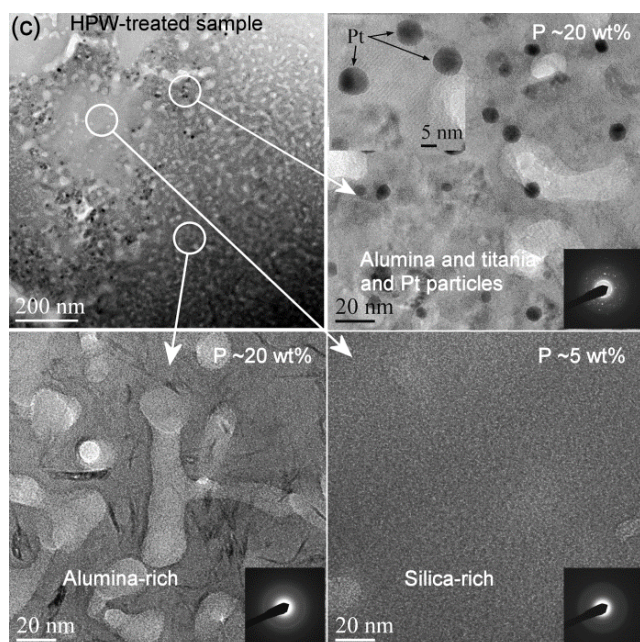


Fig. 3 Cross-sectional TEM images of the Pt catalyst, (a) fresh, (b) LPW-treated (0.065 mol/L $(\text{NH}_4)_2\text{HPO}_4$), and (c) HPW-treated (0.13 mol/L $(\text{NH}_4)_2\text{HPO}_4$)

Table 1 Specific surface area and light-off temperature (T_{90}) of the studied catalysts, based on [11]

Catalyst		Specific surface area [m ² /g]	Light-off temperature (T_{90}) [°C] (measured from RT to 300°C)	
			C ₃ H ₆ oxidation	CO oxidation
PtPd catalyst	Fresh	222	212	193
	LPW-treated	194	267	196
	HPW-treated	165	not achieved (max. conv. 78 %)	288
Pt catalyst	Fresh	225	186	160
	LPW-treated	163	203	171
	HPW-treated	137	295	196

It can be concluded that phosphorus caused significant morphological and chemical changes in the structure of the studied catalysts even with lower concentration used in this study. Phosphorus-poisoning behavior of both catalysts was similar even if they have different noble metal particles, PtPd particles or Pt particles only. Due to phosphorus treatments, the average size of the noble metal particles slightly increased and the shape of the particles changed from irregular to mainly spherical particles. Both of these can be assumed to decrease active surface area of the noble metal particles. Phosphorus accumulated mainly in the alumina-containing areas of the support and dense and mainly amorphous aluminum phosphate formation could be detected. Structural changes in the studied catalysts, caused by phosphorus, decreased their catalytic activity [11]. In this work, it was noticed that the cross-sectional TEM studies are good alternative and give valuable information for the detailed verification of the phosphorus poisoning in the catalysts. The cross-sectional TEM

studies are essential for example to detect changes in the size and shape of the noble metal particles and variation in the amount of phosphorus depending on the local composition of the support. For example, modern high-resolution field-emission scanning electron microscopes (FESEMs) are insufficient to study the local composition of the catalyst support and its effect on the accumulated phosphorus amount or to study the size and shape of the noble metal particles. In addition, the cross-sectional TEM studies are valuable method for detailed local area observations as, typically, phosphorus poisoning have reported to exist mainly in the surface area of the catalyst and cross-sectional TEM technique enables the selection of the sample area in more controllable manner. In the future, for example electron energy loss spectroscopy (EELS) studies are needed to get detailed knowledge of the existence of aluminum phosphate and possible interaction between phosphorus and noble metal particles. Also the sample preparation with focused ion beam technique could be used to study phosphorus poisoning as a function of depth from the catalyst surface.

4. CONCLUSIONS

The aim of this study was to characterize detailed structural changes in two DOCs caused by phosphorus treatments. The phosphorus exposure was carried out with two different phosphorus concentrations (0.065 mol/l and 0.13 mol/l). Cross-sectional samples were prepared from the fresh and phosphorus-treated catalysts and the samples were characterized with TEM. Already low-concentration phosphorus exposure (LPW) was observed to have significant effects on the catalyst structure, both on the noble metal particles and on the support. The size of the noble metal particles increased slightly during the exposure. In addition, the shape of the noble metal particles changed from irregular to more spherical-shaped particles due to the phosphorus exposure. This kind of morphological changes in the noble metal particles decrease their active surface area. Phosphorus accumulated mainly to the alumina-containing areas and it seemed to form dense and amorphous aluminum phosphate. These morphological and chemical changes decreased the oxidation performance of the catalysts especially after high-concentration phosphorus exposure [11]. In this study, it was shown that cross-sectional TEM characterization of the catalysts is essential to get detailed knowledge of phosphorus poisoning.

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