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Synthesis of Pd–alumina and Pd–lanthana Suspension for Catalytic Applications by One-step Liquid Flame Spray

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Abstract Catalytic materials of alumina and lanthana supported nanosized palladium particles (7 wt%) in a water suspension were prepared by Liquid Flame Spray (LFS) method. The particle production rate was 90 g/h, using liquid precursors containing $Al(NO_3)_3 \cdot 9H_2O$, $La(NO_3)_3$ $6H_2O$ and $Pd(NH_3)_4NO_3$ in water solution. In the LFS method, a turbulent, high-temperature (T_{max} ~ 2,700 °C) H_2–O_2 flame is used. The liquid precursor is atomized into micron sized droplets by high velocity H_2 flow and introduced into the flame where the droplets will evaporate. The evaporated compounds decompose and the reaction product re-condenses into particulate material. Here, the nanosized particles are formed by gas-to-particle conversion and the micron sized particles via liquid-to-solid route. In this study, the produced particulate material was collected by thermophoresis along with condensing water into a suspension (nanoparticles in water) in a one-step process. Thus, the whole suspension was produced from the end products of the flame. According to TEM-EDS analysis, the particulate material contained micron sized porous aluminum oxide or lanthanum oxide carrier particles, coated by nanosized palladium particles (~2–10 nm). The surfactant (Rhodasurf-La 42) was injected into the suspension just after collection to reduce agglomeration. Catalytic performance of the produced Pd–lanthana containing suspension was tested in laboratory with synthetic gases, in order to use it as a possible raw material for three-way catalyst (TWC). The suspension was used as Pd raw material in TWC washcoat and dispersed onto a metallic honeycomb.

Keywords Nanoparticles · Suspension · Lanthana · Alumina · Palladium · TWC catalyst

1 Introduction

Tailored nanoparticles have an important role in present catalyst development. Composite nanoparticles have been generated by several aerosol techniques, including flame methods such as vapor fed flame reactors [1], Flame Spray Pyrolysis (FSP) [2] and Liquid Flame Spray (LFS) [3]. Flame made composite titania–silver [4] and titania–platinum [5] nanoparticles exhibit higher photoactivity than pure titania material. In addition, flame-made composite palladium– or platinum–alumina particles have been used for catalyst materials [6–8]. For these catalyst applications, high surface area and highly dispersed noble metals in oxide matrix are needed. The flame methods have been proved to have high capacity to produce such materials.

In the LFS [9], a liquid precursor spray is injected into a high-temperature flame (T_{max} ~ 3,000 °C) [10] to produce nanoparticles or coatings. LFS-made nanoparticle compositions studied earlier include silver, palladium, iron oxides

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[11], silver–palladium composites [12], titania, and titania–silver composites [3, 4]. In this study LFS was used for particulate suspension synthesis. We produced a water suspension of composite Pd–alumina and Pd–lanthana particles in a one-step synthesis process by LFS. Palladium is a commonly used precious metal in automotive three-way catalysts (TWC), often together with rhodium (Rh) and/or platinum (Pt). Other components of these so-called washcoats are usually gamma-alumina as a high surface area source, thermal stabilizers and promoters (such as lanthanum), and oxygen storage materials that are commonly ceria-zirconia particles [13]. The aim of the present study was to decrease the amount of highly priced palladium in the catalyst, but to still keep the specific surface area constant due to highly porous and well dispersed platinum group metal (PGM) containing secondary raw material. The morphology of the Pd–alumina and Pd–lanthana particles in the suspension were investigated by transmission electron microscopy (TEM) and chemical composition by EDS. Pd–lanthana suspension produced was directly used for TWC catalyst preparation. In addition, tests were carried out for the catalyst to measure catalytic activity for CO, THC, and NO_X conversions. Comparison to a reference catalyst was also carried out.

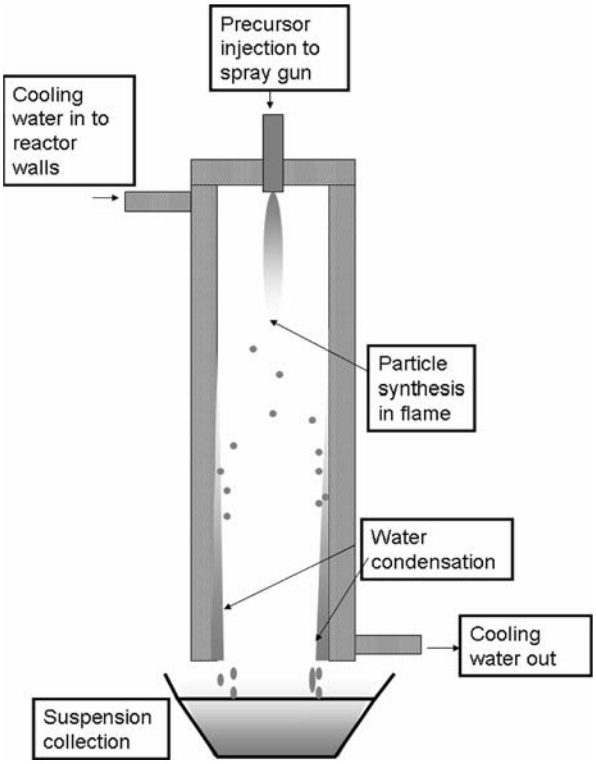

Fig. 1 Schematic diagram of the LFS-process for composite particle suspension generation

2 Experimental

The precursors were metal salts in water solution: $Pd(NH_3)_4NO_3$, $La(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$. Calculated as the end products, the precursor solution for the Pd–alumina system contained 20 g of alumina (Al_2O_3) and 1.4 g of palladium in 100 mL of water. For Pd–lanthana system the corresponding numbers were 20 g of lanthana (La_2O_3) and 1.4 g of palladium in 100 mL of water. In both cases the mass of palladium was 7% of the calculated oxide mass.

A schematic diagram of the LFS-process for composite particle suspension generation is shown in Fig. 1. In the LFS method, liquid precursor is fed into a high-temperature (~2,700 °C) H_2–O_2 flame, using H_2 as the atomizing gas. The precursor was fed into the spray gun atomizer with a manually controlled infusion pump. Particle production rate (g/min) could be controlled by adjusting the precursor concentration (g/L) and liquid feed rate (mL/min). In this study, the denoted mass flow rate is calculated for end product compounds (e.g. alumina or palladium), using atomic weights. The liquid feed rate was 8 mL/min, the hydrogen flow rate 40 L/min, and the oxygen flow rate 20 L/min. The particle production rate was 6 g/h for palladium and 84 g/h for Al_2O_3 and La_2O_3. The total particle production rate was 90 g/h. The collection time was ~15 min for Pd–alumina and ~50 min for Pd–lanthana. This corresponds to 21 g and 70 g of particle material of Al_2O_3/Pd and La_2O_3/Pd, respectively.

The water vapor formed in the H_2–O_2 flame was utilized in producing the composite particle suspension. As indicated in Fig. 1, the flame was directed downwards to a water cooled open-end cylinder (inner diameter 0.15 m, shell thickness 0.015 m and length 1.3 m). Because of the cooling, there is a flux of water and the formed composite particles towards the cylinder wall where the water condenses. The particle material and the water form a suspension flowing downwards on the cylinder surface. The suspension is collected into a vessel below the cylinder and surfactant is inserted to keep the particles separate. The authors are not aware of this technique to have been utilized before in a similar manner, to collect the water generated by the H_2–O_2-flame to be used as a carrier liquid in the product suspension.

For the particles in the suspension, we studied morphology and chemical composition using Transmission Electron Microscope (TEM), Energy Dispersive Spectroscopy (EDS) and X-ray Diffraction (XRD). The TEM (JEM 2010 from JEOL, Tokyo, Japan) equipped with an EDS, Model Noran Vantage from ThermoNoran (The Netherlands) was used. Samples for TEM and XRD were taken before inserting a surfactant into the suspension.

A laboratory scale catalyst was coated onto a metallic honeycomb for catalytic activity tests. Due to the small amount of Pd–alumina raw material, only Pd–lanthana suspension could be used for preparing a test sample. The catalyst sample was prepared by mixing the Pd–lanthana suspension with La-stabilized gamma-alumina and zirconia–ceria particles in a ball mill. This mixture was then used for coating a metallic foil as a bottom layer, dried overnight at 120 °C and calcined in air for 4 h at 550 °C. After calcination a separate similar top-layer washcoat without Pd–lanthana suspension raw material was coated onto the bottom layer washcoat, and then dried and calcined again. The last steps of the preparation were impregnation of this double-layered washcoat with rhodium nitrate solution, drying, and final calcination. The total amount of washcoat in the catalyst was 45 g/m^2, and platinum group metal (PGM) loading was 1.24 g/dm^3 (35 g/ft^3), Pd:Rh 5:1. Similar PGM loadings and ratios can be found in a typical modern TWC. The LFS raw material containing sample and reference sample were made alike except for the Pd starting material (LFS material vs. impregnation of Pd from $Pd(NH_3)_4NO_3$ into Ce–Ze-oxide raw material).

Catalytic activity tests were carried out in a ceramic tube reactor at atmospheric pressure using laboratory scale cylindrical catalysts with diameter 14 mm and length 75 mm, and cell density of 500 cells per square inch (cpsi). Space velocity was 50,000 h^{-1}. Individual inlet gases were mixed with mass flow meters and valves controlled by a computer. Test mixture contained 0.65% O_2, 1,500 ppm NO, 10% H_2O, 20% CO_2, 10,000 ppm CO, 375 ppm C_3H_6, 125 ppm C_3H_8, and N_2 balance with O_2 perturbation of ±0.22% with a frequency of 1 Hz. The gas composition was analyzed with an FTIR (Gasmet) analyzer or with single analyzers (IR for CO/CO_2, FID for HC, chemiluminescence for NO_X and paramagnetic for O_2). The catalytic activities of the samples were measured using light-off tests (150–400 °C, heating rate 10 °C/min) and end conversions at 400 °C. The light-off temperature was determined as the temperature where 50% conversion was reached. Ageing of the samples was performed in an oven in normal atmosphere for 3 h at 850 °C and at 1,050 °C. Specific surface areas (BET method) of the samples were determined from N_2 adsorption isotherms at –196 °C as fresh and as aged, using a volumetric analyzer Sorptomatic 1990.

3 Results

In a previous study for pure palladium, it was concluded that the palladium nanoparticles were formed by gas-to-particle conversion [11]. In that case, the precursor was first vaporized, subsequently nucleated, and then re-condensed as nanoparticles. However, total precursor vaporization does not necessarily take place for a high boiling point material. For nitrates the decomposition temperatures are quite low (for $La(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ below 200 °C). Instead, for Al_2O_3 and La_2O_3 the boiling points are extremely high (2,980 and 4,200 °C). Therefore, a large part of alumina or lanthanum oxide particles are assumed to be formed by liquid to solid process. Assumedly, only the solvent evaporates and aluminum or lanthanum is decomposed in the particle phase and forms dense or hollow particles [14, 15].

After the collection the Pd–alumina suspension, the collected liquid has a rather low pH ~2 and contains a high amount of the un-decomposed precursor. Therefore, it was impossible to calculate the collection efficiency. On the other hand, for the Pd–lanthana system, the pH was close to neutral. Here, 2,800 mL of water was sampled containing 64 g of particulate material. This indicates of a surprisingly high collection efficiency of ~90%. For both combinations of the powder, morphology characterization was carried out by TEM. The TEM photos from the particles in Pd–alumina suspension are shown in Fig. 2. The particulate material consisted of micron sized spherical particles and clearly smaller spherical particles with size below 10 nm (Fig. 2a). These nanosized particles were arranged to spherical larger particles (Fig. 2a, b, c) form. In Fig. 3a and b are TEM photos of Pd–lanthana suspension. Also here there are clearly two different size modes of particles at micron and nanometer scale. From both suspensions EDS analyses showed that these micron sized spherical particles consisted of mostly aluminum/lanthanum and oxygen (Fig. 2b/Fig. 3a, number 1). Instead, the smaller particles were clearly palladium enriched (Fig. 2b/Fig. 3a, number 2).

Pd–alumina containing sample was analyzed by XRD. There were clear peaks of γ-Al_2O_3 and palladium. The spectrum indicated that the sample could also contain some amorphous species (most probably aluminum hydroxide), see Fig. 4.

In previous study [11], the geometric number mean diameter was ~20 nm with the same palladium production rate as in the present study (6 g/h), and it was measured after the flame from gas phase using aerosol measurement technique (Scanning Mobility Particle Sizer, SMPS). The palladium particles covering the larger oxide particles in Figs. 2 and 3 are also nanosized, indicating that the particles have been formed through a similar process (gas-to-particle conversion) as in the case of pure palladium.

The primary droplets are known to be in the size range of 1–10 μm [9]. If one assumes a 1 μm sized initial precursor droplet with recorded aluminum concentration in liquid, the calculated size for the liquid to solid particles is

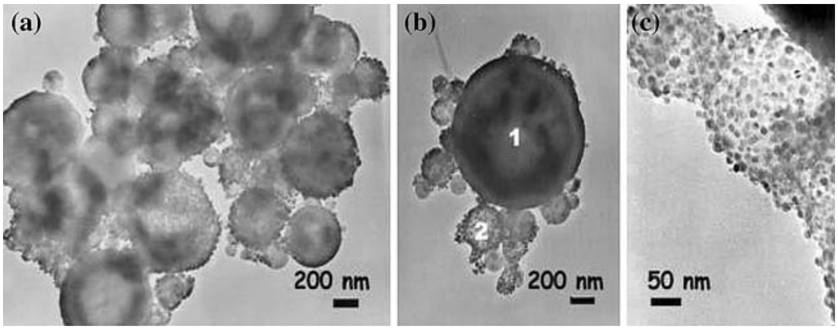

Fig. 2 TEM photos of (**a**) Pd–Alumina particulate material in suspension (**b**) 1 EDS, 2 EDS (**c**) closer look at the part containing palladium

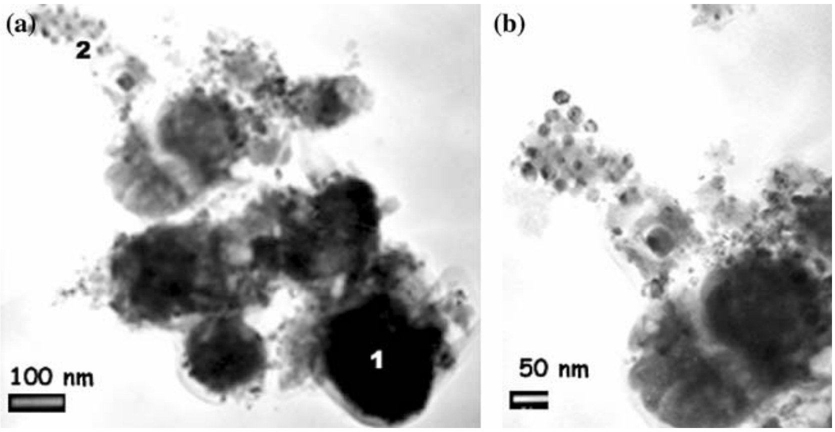

Fig. 3 TEM photos of (**a**) Pd–lanthana particulate material in suspension (**b**) closer look at the part containing palladium

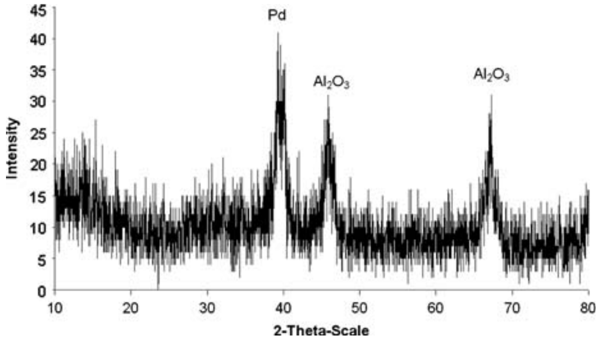

Fig. 4 XRD diffractogram of dried alumina–Pd powder

~0.7 µm. This is close to the observed size range for alumina particles (Fig. 2). When looking at the TEM-graphs more closely, the alumina particles seem to be relatively light, indicating of a hollow sphere structure. Such morphologies have been reported in many studies where nitrates have been used as precursors [14, 15]. The lanthanum containing particles have not so spherical form but are in the same size range and are also most probably formed by liquid to solid conversion, and not via gas phase (Fig. 3).

Catalytic activity test results (light-off temperatures and conversions at 400 °C) for Pd–lanthana containing LFS sample and reference sample are presented in Fig. 5. Light-off temperature T_{50} is defined as the temperature, where 50% of the inlet concentration is converted.

Figure 6a shows that the LFS based catalyst had a clearly better light-off behavior as fresh compared to the reference sample. A difference of ca. 20 °C could be observed for all three components (CO, THC and NO_X) as fresh. Similarly, the conversions at 400 °C were significantly higher for the LFS sample as fresh (Fig. 5e, f). It is quite obvious that the reason for higher activity of LFS sample is due to preparation method. Presumably the preparation method of Pd–La_2O_3 raw material, i.e., LFS method, has produced well oxidized Pd particles, analogously to what was found by Strobel et al. using methane–oxygen flame, although with different precursors [16]. Both flames have approximately the same adiabatic flame temperature if burnt at stoichiometry, viz. ca. 3,053 and 3,080°K for methane and hydrogen in oxygen, respectively [17]. In addition, according to TEM studies Pd was highly dispersed on La_2O_3 particles. In contrast, the preparation method used in preparing the reference sample has been observed to produce somewhat poorer Pd dispersion in as prepared state.

However, as the catalysts were aged at 850 °C, the reference sample was observed to have deteriorated clearly less than the LFS sample and hence, to have a somewhat better light-off than the LFS sample (Fig. 5b). After ageing

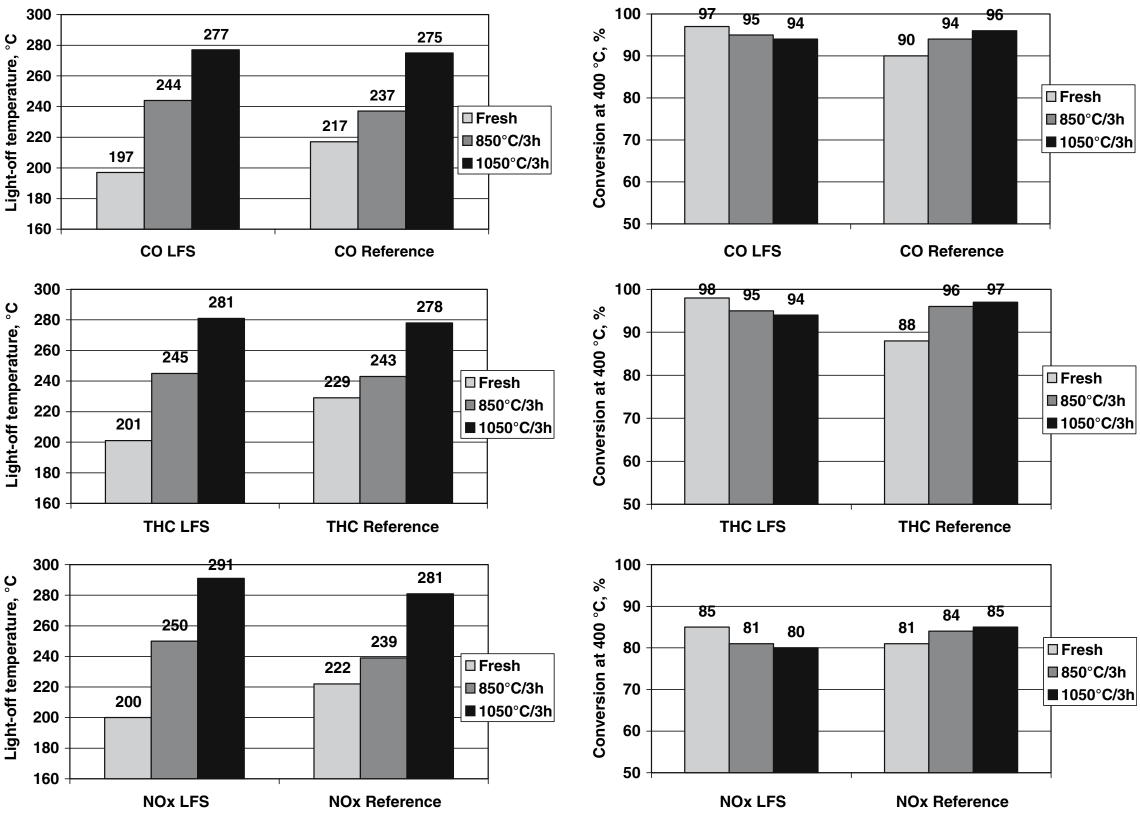

Fig. 5 TWC performance (T_{50} and conversion at 400 °C) for fresh and aged (3 h at 850 °C and 1,050 °C) Pd–lanthana and reference catalysts: the light-off temperatures for (**a**) CO (**b**) THC and (**c**) NO_X and conversions at 400 °C for (**d**) CO, (**e**) THC and (**f**) NO_X

at 1,050 °C the light-off values for both samples were basically equal, except for the NO_X (Fig. 5c). In addition, the LFS sample also suffered from decreasing conversions at 400 °C as a function of ageing temperature, whereas the reference sample had improved conversions at 400 °C after same conditionings (Fig. 5d, e, f).

Specific surface area for reference and LFS sample was quite similar as fresh, and in both samples it decreased with ageing, see Table 1. This indicates expected sintering of the washcoat constituent particles. The porosity of both samples was slightly decreased with ageing, and the average pore diameter increased due to collapse of the smaller pores. Comparable decrease in specific surface area was anticipated due to great similarity in washcoat composition except for the Pd–lanthana starting material itself. Hence, the origin of the higher deterioration of the LFS sample could be a different interaction between the Pd particle and the carrier component, i.e., lanthana or alumina. In fresh state, where higher activity for the LFS sample was observed, Pd-oxide in the LFS sample is finely dispersed together with lanthana, which acts both as stabilizer and promoter (Fig. 6A). During ageing Pd particles in the LFS sample are more easily sintered because of weaker interaction with the support than in the reference sample (Fig. 6B: option 1). It could be observed that the most significant degradation in light-off activity happened between ageing at 850 °C and 1,050 °C, especially in the case of reference sample. This is in agreement with the PdO nbsp; → Pd transition and corresponding increased mobility of the Pd phase, which leads to quick sintering of Pd [18, 19]. After ageing at 1,050 °C both samples had quite similar activities, regardless of preparation method of the sample. Comparable behavior has been observed in methane combustion tests with similar preparation methods [20].

Table 1 Measured specific surface area and pore volume/diameter values

Conditioning	Reference		LFS	
	Fresh	Aged	Fresh	Aged
Specific surface area BET (m^2/g washcoat)	87	33	81	40
Pore volume (cm^3/g washcoat)	0.22	0.10	0.21	0.13
Pore diameter (nm)	10	12	11	13

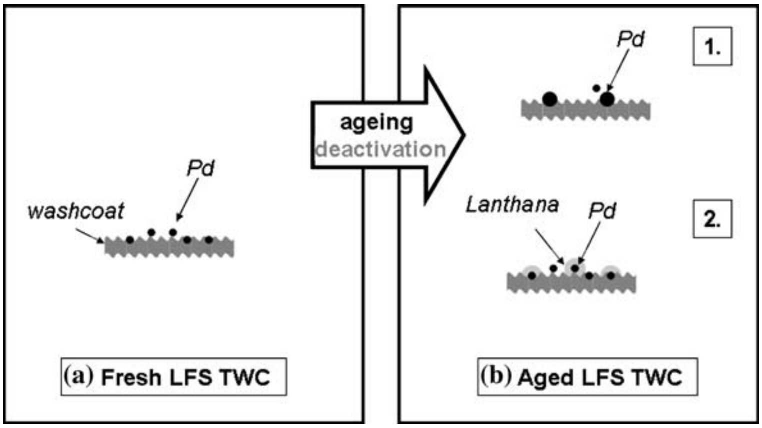

Fig. 6 Illustration of expected morphology for LFS-prepared TWC (**A**) At fresh stage and (**B**) The possibilities for the causes of deactivation after ageing: 1. Coalesced palladium particles and 2. lanthana decorated palladium particles

Another reason could be decoration of palladium nanoparticles by a thin layer of lanthana (Fig. 6B: option 2), similarly that has been observed for ceria [21]. However, this phenomenon is induced by a reductive treatment at high temperature, and can be recovered by an oxidative treatment at high temperature [22]. Ageing treatments performed in this study should have recuperated the Pd surface, hence, this deterioration mechanism is not considered very viable in the current study.

4 Conclusions

Catalyst particulate suspension has been successfully prepared in one-step by Liquid Flame Spray method. Particulate material from Pd–alumina precursor in suspension consisted of un-decomposed precursor and micron-sized γ-Al_2O_3-spheres coated by nanosized Pd particles.

Suspension prepared from lanthanum/palladium precursor consisted of lanthanum and oxygen containing irregular micron sized particles coated by palladium enriched particles. The collection efficiency was high (~90%) for this suspension. In addition to the particles, also a part of the flame-generated water was collected to act as the carrier fluid in the suspension. The Pd–lanthana suspension was used directly for TWC catalyst preparation as a palladium source. The LFS based catalyst had clearly better light-off behavior as fresh, compared to the reference sample. Similarly, also the conversions at 400°C were significantly higher for the LFS sample as fresh. Pd in the LFS sample is finely dispersed together with lanthana, which acts both as stabilizer and promoter. In addition, due to preparation method of the LFS material, more Pd is likely in oxidized state than in the reference sample. After ageing, especially at 850 °C, the LFS sample had poorer properties than the reference. This deactivation is most probably due to sintering of Pd-particles during ageing. However, overall the catalytic activity of the LFS sample could be considered to be at good level.

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