Preparation of Pt/Al₂O₃ and PtPd/Al₂O₃ Catalysts by Supercritical Deposition and Their Performance for Oxidation of Nitric Oxide and Propene

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Abstract

Pt/Al₂O₃ and bimetallic PtPd/Al₂O₃ catalysts were prepared via supercritical deposition method using supercritical carbon dioxide. The effects of Pt loading of Pt/Al₂O₃ and Pd addition to Pt/Al₂O₃ on particle size, particle size distribution (PSD) and activity for NO and C₃H₆ oxidation and C₃H₆-selective catalytic reduction (C₃H₆-SCR) were investigated. Pt/Al₂O₃ catalysts were prepared with Pt loadings of 0.6, 1.2 and 2.1 wt% and a bimetallic PtPd/Al₂O₃ catalyst was prepared with total metal loading of 1.4 wt% and Pt:Pd molar ratio of 1.3:1. A small fraction of the particles agglomerated after calcination at 550 °C. Around 98% of the particles had an

average particle size of ~1 nm. The rest of the particles were larger and average size of these larger particles was ~10 nm for monometallic catalysts and ~6.5 nm for PtPd/Al₂O₃. All catalysts were found to be active for NO and C₃H₆ oxidation and C₃H₆-SCR reactions. NO oxidation performance of 1.2 wt% Pt/Al₂O₃ catalyst was the highest. C₃H₆ oxidation activity increased with increasing metal content. Light-off temperature for C₃H₆ oxidation shifted to higher temperature in the presence of NO, suggesting competitive oxidation of C₃H₆ and NO. Concentration profiles indicated that C₃H₆-SCR started when C₃H₆ conversion by oxidation reached 50%; C₃H₆ was consumed both by oxidation and C₃H₆-SCR at higher conversions.

Keywords: supercritical deposition, aftertreatment system, diesel oxidation catalyst, bimetallic catalyst, platinum, palladium

1. Introduction

Diesel oxidation catalyst (DOC) is usually the first reactor of the aftertreatment system (ATS) of a heavy-duty diesel vehicle, where toxic species such as NO, CO and unburnt hydrocarbons are oxidized to NO₂, CO₂, and H₂O. NO₂ resulting from oxidation of NO is used as an oxidant for passive regeneration of diesel particulate filter (DPF) placed after the DOC. In addition, the ratio of NO₂ to NO_x influences the rate of NO_x reduction in selective catalytic reduction (SCR) reactor, which is generally placed after the DPF [1]. Hydrocarbons and CO can exist in the exhaust gas as a result of incomplete fuel combustion in the engine, or as a result of diesel injection to the DOC to create an exotherm for regeneration of the DPF. Although C₃H₆ oxidation by O₂ is highly favored in lean exhaust conditions, NO_x reduction by C₃H₆ also takes place over the DOC, which is known as C₃H₆-SCR [2]. NO_x storage and reduction on the DOC offers practical benefits for automotive catalysts since it captures NO_x at low temperatures and reduces them at higher temperatures in the presence of hydrocarbons.

Platinum group metals (PGMs) are used as the active metal in DOCs. Among them, Pt is widely used in DOCs, and the addition of Pd was shown to increase the thermal stability and sintering resistance of the catalyst [1]. As PGMs are high cost components of ATSs, several efforts have concentrated on decreasing the amount of PGMs and increasing the stability and efficiency of PGMs by preparing DOCs with different PGM loadings, ratios, or particle sizes [3–10], and using different synthesis techniques [11–14].

The loading of the PGM plays a crucial role in the performance of a DOC. Xue *et al.* tested Pt/Al₂O₃ catalysts with Pt loadings of 0.1, 0.4, 2.0, and 5.0 wt% [3]. They found that the NO oxidation activity was not directly proportional to the loading. The highest NO oxidation performance was obtained at a loading of 2 wt%. Hauff *et al.* tested monolithic DOCs with different Pt loadings and showed that the light-off temperature for C₃H₆ oxidation decreased linearly with increasing Pt loading. Their results on NO oxidation indicated that there was a strong nanoparticle (NP) size effect [5,6]. In a study conducted by Boubnov *et al.*, NO oxidation was found to be most efficient when the NP size was larger than about 5 nm, while smaller particles remained less active [4]. Another study by Hansen *et al.* suggested that the overall activities for CO, NO and C₃H₆ oxidation were highest when the NP size was between 2 and 4 nm [7], pointing to the importance of NP size control during the synthesis of DOCs.

For bimetallic PtPd/Al₂O₃ catalysts, the results of the reports in the literature indicate that there is a certain Pt:Pd ratio range resulting in the optimum performance for the NO and hydrocarbon oxidation reactions while maintaining high durability upon ageing [8,9]. For example, Shakyia *et al.* compared PtPd/Al₂O₃ catalysts with Pt:Pd molar ratios of 1:5.7, 1:1.9, 1.6:1, and 5.7:1 for NO, CO and hydrocarbon oxidation reactions. They found that NO oxidation activity monotonically increased with increasing Pt:Pd ratio while increasing the Pt:Pd ratio to more than 1.6:1 did not increase hydrocarbon and CO oxidation performance significantly [8]. Daneshvar *et al.* compared washcoated monometallic Pt/Al₂O₃ and Pd/Al₂O₃ with bimetallic PtPd/Al₂O₃ catalysts with different loadings and showed that a Pt:Pd molar ratio of 1:1 is optimal ratio based on light-off temperatures for C₂H₄, C₇H₈, C₆H₁₄ and C₂H₆ oxidation [9]. Along this line, Kaneeda *et al.* improved the thermal stability and NO oxidation performance of 1.5 wt% Pt/Al₂O₃ with the addition of 0.32 wt% Pd, which corresponds to a Pt:Pd molar ratio of 0.77:0.3 [10].

Since particle size, metal loading and metal ratio were shown to be important factors affecting DOC performance, the attention in the field shifted to novel synthesis methods that can assert more control over the particle size and loading of PGMs. Cho and Regalbuto, and Wong *et al.* synthesized and catalytically tested PtPd/Al₂O₃ catalysts prepared by strong electrostatic adsorption (SEA), and compared the morphology and CO oxidation performance with PtPd/Al₂O₃ prepared by incipient wetness impregnation (IWI) [11,12]. PtPd/Al₂O₃ catalysts

prepared by SEA resulted in better dispersion and sharper particle size distribution (PSD) than those prepared by IWI. Overall, CO oxidation performances were better in SEA catalysts, and lower light-off temperature shifts were obtained after ageing. Casapu *et al.* prepared Pt/Al₂O₃ catalysts via IWI, flame spray pyrolysis (FSP), and supercritical deposition (SCD). Catalysts prepared by SCD resulted in a sharper and earlier light-off curve for CO oxidation than those obtained using catalysts prepared by IWI and FSP [13]. Later, Ogel *et al.* compared the effects of IWI, FSP, SCD and pulsed laser ablation (PLA) methods on catalyst morphology and CO and NO oxidation performances before and after hydrothermal ageing [14]. Among them, SCD and FSP resulted in the least particle growth after ageing at 800 °C. Both synthesis methods yielded the most active catalysts for NO and CO oxidation before and after ageing. Ogel *et al.* concluded that SCD and FSP methods required further investigation [14].

SCD is an emerging technique for the preparation of supported NPs with control over particle size and metal loading [15]. Supported NPs prepared by SCD usually have small average particle size and sharp PSD [13–20]. The SCD technique involves firstly the dissolution of the metal precursor in a supercritical fluid followed by the adsorption of dissolved metal precursor onto the support material, and then conversion of the metal precursor to its metallic form by means of thermal or chemical conversion [15,21,22]. Synthesis of supported bimetallic NPs via SCD can be sequential or simultaneous. In simultaneous SCD, both precursors are dissolved in a supercritical fluid simultaneously and the subsequent steps are carried out as in single component SCD. In sequential SCD, the single component SCD procedure is applied twice [17,18]. This technique has been used to prepare a wide range of supported monometallic NPs such as Pt, Pd, Ru, Au, Cu, Ni, and Ag; and bimetallic NPs such as PtPd, PtCu, PtRu, PtAu, and AgAu with numerous supports such as carbon aerogels [16,17,19,23], graphene aerogels [24], carbon nanotubes [25], SiO₂ [26–34], carbon black [18,35], Al₂O₃ [13,14,36–38], and TiO₂ [35,37]. Supercritical carbon dioxide (scCO₂) is commonly used in SCD since it is inexpensive, abundant, non-toxic, non-flammable, environmentally benign, has an easily accessible critical temperature and pressure ($T_c = 31.1\text{ }^{\circ}\text{C}$, $P_c = 7.38\text{ MPa}$), and leaves no residue on the treated medium.

In this study, Pt/Al₂O₃ catalysts with Pt loadings of 0.6, 1.2, and 2.1 wt% and PtPd/Al₂O₃ catalyst with a Pt:Pd molar ratio of 1.3:1 and a total metal loading of 1.4 wt%, were prepared by

SCD. These catalysts were characterized by high angle annular dark field scanning transmission electron microscopy (HAADF STEM) imaging and energy dispersive X-ray spectroscopy (EDXS) and tested for NO oxidation, C₃H₆ oxidation and C₃H₆-SCR reactions in a tubular fixed bed reactor via transient kinetic measurements in synthetic engine exhaust environment. To our knowledge, the effects of Pt loading of Pt/Al₂O₃ and Pd addition to Pt/Al₂O₃ prepared by SCD on particle morphology and activity towards C₃H₆ and NO oxidations along with C₃H₆-SCR were reported here for the first time.

2. Experimental

2.1. Materials

γ -Al₂O₃ (99.99%) and palladium(II) acetylacetonate (Pd(acac)₂) were purchased from Sigma-Aldrich. Dimethyl(1,5-cyclooctadiene)platinum(II) (Pt(cod)me₂) was purchased from STREM Chemicals, Inc.. Properties of the used metal precursors are given in Table 1. All chemicals were used as received. Carbon dioxide, nitrogen, and oxygen (99.998%) were purchased from Air Liquide. Water was deionized before usage (18 m Ω). C₃H₆ (49%, balance He) and NO (2%, balance N₂) gases were purchased from Elite Gaz.

2.2. Preparation of Pt/Al₂O₃ and PtPd/Al₂O₃

SCD was conducted in a custom-made 57 ml high-pressure stainless-steel vessel. The experimental setup is given in Figure 1. Pt/Al₂O₃ was prepared by filling the vessel with 1 g γ -Al₂O₃ and a certain amount of Pt(cod)me₂ to yield the desired metal loading. The vessel was then heated to 35 °C, pressurized with CO₂ to 15.5 MPa and kept at these conditions for 21 h. After dissolution and adsorption of Pt(cod)me₂, the vessel was depressurized at a rate of 0.7 MPa/min at 35 °C. The Pt(cod)me₂/Al₂O₃ composite was then placed in a tubular furnace for thermal conversion of Pt(cod)me₂ to Pt NPs under flowing N₂ at 100 ml/min at 200°C and atmospheric pressure for 4 h. Afterwards, Pt/Al₂O₃ was calcined at 550°C for 2 h with 10% O₂ and N₂ as the balance gas. The total gas flow rate during calcination was 1.0 L/min. The PtPd/Al₂O₃ catalyst was prepared in a similar manner. A certain amount of Pd(acac)₂ was added to the vessel along with Pt(cod)me₂ and 1 g γ -Al₂O₃ to yield the desired metal loading and a Pt:Pd molar ratio of 1.3:1 after conversion of the metal precursors to their metallic forms. All other steps of the PtPd/Al₂O₃ preparation were the same as for the Pt/Al₂O₃ preparation.

2.3. Characterization

Pore volume, average pore size and Brauner, Emmet and Teller (BET) surface area of γ - Al_2O_3 were determined by N_2 adsorption using a Micromeritics ASAP 2020 instrument. Pt and Pd content of the samples were determined using a Bruker Tiger S8 X-Ray Fluorescence (XRF) Spectrometer. X-ray Diffraction (XRD) measurements were done using a Bruker D8 Advance Diffractometer equipped with a $\text{Cu K}\alpha$ source in the 2θ range of $10^\circ - 90^\circ$ with an increment of 0.019° and time step of 4 s. Morphologies of the samples were characterized by STEM.

Specimens were prepared by grinding the samples in a mortar and pestle set, then adding ethanol into the mortar, and stirring carefully with the pestle until a uniform suspension was obtained. A few droplets of this suspension were placed on a Quantifoil 200 mesh copper TEM grid coated with holey carbon film. The specimens were allowed to dry in air and were then kept in a vacuum desiccator overnight to remove any residual moisture. HAADF STEM images were acquired using a Titan Themis probe-corrected STEM operated at an accelerating voltage of 300 kV. PSDs were obtained by measuring at least 100 particles for small particles and at least 80 particles for large particles, and plotting histograms binned in 0.2 nm and 2 nm increments, respectively for small and large particles. STEM X-ray maps were also obtained in the Titan Themis STEM, which is equipped with a Super-X silicon drift detector system that allows for rapid acquisition of EDXS data.

2.4. Activity Measurements

A tubular fixed bed reactor was used for activity measurements. The experimental setup is shown in Figure 2. 350 mg of catalyst was used in all experiments. The powder catalyst was first pressed, then crushed and sieved to 35-60 US mesh (500 – 250 μm diameter). F46 SiC particles (425 – 300 μm diameter) were used to dilute the catalyst 35x by mass to minimize the formation of hot spots especially during the highly exothermic C_3H_6 oxidation reaction. A 0.33 in ID stainless-steel tube was used as the reactor. A J-type thermocouple (Omega Inc.) was placed at the center of the bed. Quartz wool was placed at the end of the catalyst bed to keep the catalyst fixed. The bottom of the catalyst bed was filled with quartz beads to support the catalyst bed. The reactor was placed vertically in an electrical furnace (Split Tube Furnace XST-2-0-12-1V2-E28, Thermcraft). Water was delivered by an evaporator-liquid mass flow controller (MFC) system (CEM System W-202A-220-K, Bronkhorst). All other gas flows were controlled via

calibrated thermal MFCs (5850E, Brooks Instruments). The concentration of the gases leaving the reactor were measured by an FTIR continuous gas analyzer (MultiGasTM 2030, MKS Instruments). All lines to and from the reactor furnace were heated to 160°C. After each run, the catalysts were treated with 10% O₂ and N₂ as the balance gas at 450°C for 20 min to clean the surface of the catalyst of any residues. In all experiments, the space velocity was 0.63 L/min/mg_{Metal} and a feed gas stream consisting of 10% O₂, 5% H₂O, 7% CO₂ and N₂ as the balance gas was used to mimic exhaust gas composition. C₃H₆ and NO feed concentrations were 350 ppm and 500 ppm, respectively. Activity measurements were done with a temperature ramp of 10 °C/min. The temperature ramp was started after the effluent concentrations of all gases from the reactor were steady.

3. Results and Discussion

3.1. Physical Properties

Nitrogen physisorption analysis of bare γ -Al₂O₃ showed that the γ -Al₂O₃ support had a pore volume of 0.54 cm³/g, an average pore size of 8.9 nm and a BET surface area of 243 m²/g. The metal contents of the Pt/Al₂O₃ and PtPd/Al₂O₃ catalysts prepared by the SCD technique were determined by XRF. Table 2 summarizes the metal loadings in terms of weight percent, the Pt:Pd ratio of bimetallic PtPd/Al₂O₃ catalyst and the average particle size of the samples. Monometallic catalysts were named according to their total metal loadings: 0.6-Pt/Al₂O₃, 1.2-Pt/Al₂O₃, and 2.1-Pt/Al₂O₃, respectively for 0.6, 1.2 and 2.1 wt% Pt/Al₂O₃ catalysts.

The Pt loading of 1.2-Pt/Al₂O₃ in terms of wt% was similar to that of PtPd/Al₂O₃. The total metal loadings of 2.1-Pt/Al₂O₃ and PtPd/Al₂O₃ in terms of mol% were similar. The loadings were selected to investigate the effect of the Pd addition to the Pt/Al₂O₃ catalyst (by comparing 1.2-Pt/Al₂O₃ and PtPd/Al₂O₃) and to compare monometallic Pt/Al₂O₃ and bimetallic PtPd/Al₂O₃ performances while keeping the total metal loading in terms of mol% constant (by comparing 2.1-Pt/Al₂O₃ and PtPd/Al₂O₃). The morphologies of the prepared samples were characterized by HAADF STEM imaging and EDXS STEM mapping; examples of these data are shown in Figures 3 and 4 together with the corresponding PSD histograms. The average particle sizes before calcination were around 1.2 ± 0.3 nm for all of the Pt/Al₂O₃ samples; and 1.5 ± 0.4 nm for PtPd/Al₂O₃, with sharp PSDs in each case. The average particle sizes obtained are slightly lower than those for Pt/Al₂O₃ prepared by SCD previously in the literature [13]; this is probably due to

thermal reduction of the metal precursor, rather than chemical reduction with H₂ [39]. After calcination at 550 °C for 2 h, bimodal PSDs were obtained for all samples. HAADF STEM images of the samples after calcination are presented at two different magnifications to clearly show the bimodal PSD. Possible reasons for obtaining bimodal PSDs could include surface heterogeneities on the support [40] or transient states during Pt NP sintering [41]. ~98% of the particles were found to be smaller particles, whose average particle size remained at 1.1 ± 0.3 nm. ~2% of the particles were significantly larger in each of the samples. The average particle size of the larger particles for the Pt/Al₂O₃ catalysts were 8.8 ± 4.6 , 10.7 ± 2.9 and 10.5 ± 3.1 nm, respectively for 0.6-Pt/Al₂O₃, 1.2-Pt/Al₂O₃ and 2.1-Pt/Al₂O₃, while the average particle size of the larger particles in PtPd/Al₂O₃ was 6.5 ± 1.7 nm. The smaller average particle size for larger particles for 0.6-Pt/Al₂O₃ than for 1.2-Pt/Al₂O₃ and 2.1-Pt/Al₂O₃ can be attributed to the scarcity of particles due to lower loading, which may make it harder for the metal NPs to agglomerate and coalesce. The smaller average particle size for the large particles in PtPd/Al₂O₃ may be due to Pd, which prevents sintering of PtPd NPs [1,10]. To illustrate the possible effect of the two NP populations, we consider the specific surface areas of a representative collection of 100 spherical NPs on the surface of the 2.1-Pt/Al₂O₃ sample; thus there are 98 small (1 nm) and 2 large (10.5 nm) NPs. The total weight of these 100 NPs was calculated as $2.72 \cdot 10^{-17}$ g_{Pt}. The specific surface area provided by the 98 small NPs was calculated as 11.32 m²/g_{Pt} while for the 2 large NPs the value obtained was 25.57 m²/g_{Pt}. Since these two numbers differ by a factor of only ≈ 2.3 , it was concluded that small and large NPs may be contributing to a similar extent towards the oxidation performance of the catalyst. Related calculations are given in the Supplementary Data.

HAADF STEM images and EDXS maps of small particles in PtPd/Al₂O₃ are given in Figure 4 before and after calcination. NPs were bimetallic before and after calcination, without any significant change in shape of the NPs as a result of calcination. Alloy formation could not be concluded from the STEM images.

The powder XRD data collected from calcined fresh samples are given in Figure 5. The XRD patterns showed the presence of γ -Al₂O₃ in all samples [14]. Since the NP sizes are small, and the XRD peaks for Pt and Pd mostly overlap with those of γ -Al₂O₃, it was not possible to distinguish any peaks related to the presence of Pt and Pd NPs.

3.2. Catalytic Activity

3.2.1. NO Oxidation

NO concentration profiles at the exit of the reactor for Pt/Al₂O₃ and PtPd/Al₂O₃ with respect to temperature are shown in Figure 6. For each of the catalysts, the maximum NO conversion to NO₂ was obtained at around 350 °C. With increasing temperature above 350 °C, conversion started to decrease due to thermodynamic equilibrium.

A significant amount of NO_x storage and release was observed on 0.6-Pt/Al₂O₃. Although some alkaline earth metals such as Ba are usually added to Pt/Al₂O₃ to improve its NO_x storage capacity [42], Szanyi *et al.* showed that Al₂O₃ itself was also capable of storing NO_x as surface nitrates when exposed to NO₂ [43]. The mechanism of NO_x storage over Pt/Al₂O₃ when exposed to NO can be firstly the oxidation of NO to NO₂ on Pt, followed by the transfer of NO₂ to the support surface and storage as nitrate species, as suggested by Szanyi *et al.* [43]. NO_x-TPD experiments would be necessary for an in-depth analysis of NO_x storage and release on the prepared catalysts.

Because of the NO_x storage, NO oxidation activity of 0.6-Pt/Al₂O₃ could not be compared with the activity of 1.2- and 2.1-Pt/Al₂O₃. The activity of 1.2-Pt/Al₂O₃ was higher than that of 2.1-Pt/Al₂O₃. These results can be attributed to the effects of loading, particle size and Pt oxidation state on NO oxidation activity as also shown in the literature. Xue *et al.* reported an optimum loading for NO oxidation over Pt/Al₂O₃ [3]. Among Pt/Al₂O₃ with 0.1, 0.4, 2 and 5 wt% Pt loadings, they showed that the best performing catalyst was 2 wt% Pt/Al₂O₃. The average particle size of 2 wt% Pt/Al₂O₃ was 6 nm, whereas the average particle sizes of the other catalysts were less than 2 nm; which indicated that NO oxidation is favored by larger NPs. Ogel *et al.* [14] showed that Pt NP size and oxidation state play an important role in NO oxidation performance of Pt/Al₂O₃. They compared the NO oxidation performance of Pt/Al₂O₃ prepared by SCD and hydrothermally aged at different temperatures. When the ageing temperature was increased from 600 °C to 700 °C, NO oxidation performance increased significantly, which was accompanied by an increase in the average particle size and a decrease in the oxidation state of Pt. This also indicated that NO oxidation is favored by larger NPs. Boubnov *et al.* [4] showed that among Pt/Al₂O₃ with average particle sizes ranging between 1 and 10 nm, catalysts with 5 and 10 nm NPs performed the best for NO oxidation, and they related this to the abundance of reduced Pt planar crystal sites on larger NPs. Along these lines, the larger NPs were believed to

be mainly responsible for NO oxidation in this study. Although the average particle sizes of large NPs were very similar, at around 10 nm for 1.2-Pt/Al₂O₃ and 2.1-Pt/Al₂O₃, slightly different PSD profiles (Figures 3c, 3f, 3i) or different Pt oxidation states on the surface of the NPs may be responsible for difference in activities.

The NO oxidation performance of PtPd/Al₂O₃ was slightly better than that of 2.1-Pt/Al₂O₃, which had an equivalent amount of metal loading in terms of mol%. Since Pd/Al₂O₃ is known to be only slightly active for NO oxidation, the improvement in the NO oxidation performance by the addition of Pd can be explained by the synergistic effects between Pt and Pd when compared to 2.1-Pt/Al₂O₃ [10].

3.2.2. C₃H₆ Oxidation

The concentration profiles of C₃H₆ at the exit of the reactor with respect to temperature are shown in Figure 7. C₃H₆ light-off temperatures, which were calculated as the temperature required for 50% conversion of C₃H₆, are given in Table 3. Light-off temperatures shifted to lower values with increasing loading. This can be attributed to an increase in the number of active sites with increasing metal content. Conversion profiles of 2.1-Pt/Al₂O₃ and PtPd/Al₂O₃ catalysts were very similar, with PtPd/Al₂O₃ performing slightly better at high temperatures and 2.1-Pt/Al₂O₃ exhibiting higher conversion at temperatures less than 120 °C. Generally, improvement of hydrocarbon oxidation by bimetallic PtPd/Al₂O₃ was attributed to the prevention of Pt sintering by the addition of Pd, such that the NP size does not grow so large that the hydrocarbon oxidation performance decreases [44]. Since the average size of the small particles in 2.1-Pt/Al₂O₃ and PtPd/Al₂O₃ were already the same after calcination, obtaining similar activities for 2.1-Pt/Al₂O₃ and PtPd/Al₂O₃ was expected.

3.2.3. C₃H₆ – NO Co-oxidation and C₃H₆-SCR

The effects of simultaneous feeding of NO and C₃H₆ to the reactor were also investigated. Concentration profiles of NO and C₃H₆ at the exit of the reactor as a function of temperature are shown in Figure 8. All C₃H₆ oxidation light-off temperatures were shifted to higher values when NO was present in the feed as shown in Table 3, indicating competitive oxidation of NO and C₃H₆ on the catalysts [45]. This shift was more pronounced in monometallic catalysts 0.6-Pt/Al₂O₃ and 2.1-Pt/Al₂O₃. Although they showed very similar

performances for sole C₃H₆ oxidation (Figure 7), the light-off temperature was 26°C lower for PtPd/Al₂O₃, compared to 2.1-Pt/Al₂O₃, when NO was present in the feed. This may point to different competitive oxidation behaviors of NO and C₃H₆ over Pt and PtPd NPs. In all C₃H₆ concentration profiles, two different slopes were observed in the presence of NO. When conversion of C₃H₆ was roughly 50%, there was a change in the slope of the concentration versus temperature line indicating an additional reaction responsible for consumption of C₃H₆. This slope change coincides with the start of N₂O formation, which is a product of C₃H₆-SCR, whose overall reactions are given in Reactions (1-3), as proposed by Khosravi *et al.* [46].

In all catalysts, except for 0.6-Pt/Al₂O₃, the temperature at which NO oxidation started corresponded to the 100% conversion temperature for C₃H₆ oxidation. This is probably because of the combination of two phenomena. The first is the competitive oxidation of NO and C₃H₆ on the catalyst surface [45], as indicated by the light-off temperature shifts in C₃H₆ oxidation. The second reason may be the utilization of NO₂ for C₃H₆ oxidation by Reaction 3 [46]. NO₂ used for C₃H₆ oxidation may result from oxidation of NO or the release of stored NO_x as NO₂, as explained in Section 3.2.1. Interestingly, downstream NO₂ was observed before the C₃H₆ oxidation reached 100% conversion temperature with 0.6-Pt/Al₂O₃. However, this NO₂ clearly did not originate from NO oxidation, because the downstream NO concentration stayed constant until 170 °C while the NO_x concentration increased. This increase in NO₂ concentration was probably caused by the conversion and release of stored NO_x from the surface [47]. This storage/release phenomenon was observed the most with 0.6-Pt/Al₂O₃ catalyst with sole NO oxidation experiments as well (Figure 6).

As online FTIR was used to measure the downstream concentrations, N₂ concentration could not be measured, but the reduction of NO_x to N₂ by C₃H₆ was indicated by the decrease of the NO_x concentration below the feed NO concentration. Except for 2.1-Pt/Al₂O₃, NO_x concentrations reached the feed NO concentration at higher temperatures, along with an increase

in the NO concentration and a decrease in the NO₂ concentration, as the thermodynamic limit of NO oxidation was reached. However, for 2.1-Pt/Al₂O₃ NO_x reduction continued along with NO oxidation even at higher temperatures.

4. Conclusions

Pt/Al₂O₃ with loadings of 0.6, 1.2, and 2.1 wt% Pt and bimetallic PtPd/Al₂O₃ with Pt:Pd molar ratio of 1.3:1 and total metal loading of 1.4 wt% were successfully prepared by SCD. The effects of Pt loading on Pt/Al₂O₃ and Pd addition to Pt/Al₂O₃ were investigated in terms of morphology and activity towards NO and C₃H₆ oxidation and C₃H₆-SCR reactions. Preparation of Pt/Al₂O₃ and PtPd/Al₂O₃ resulted in an average particle size of roughly 1.2 nm for Pt/Al₂O₃ and 1.5 nm for PtPd/Al₂O₃ with sharp PSDs. After calcination at 550 °C, a small fraction of NPs agglomerated. Around 98% of the particles were considered as “small” and their average particle sizes were 1.1 ± 0.3 , 1.1 ± 0.3 , 1.0 ± 0.3 , and 1.2 ± 0.3 nm for 0.6, 1.2, 2.1 wt% Pt/Al₂O₃ and PtPd/Al₂O₃, respectively. The average particle sizes of the “large” particles were 8.8 ± 4.6 , 10.7 ± 2.9 , 10.5 ± 3.1 , 6.5 ± 1.7 nm for 0.6, 1.2, 2.1 wt% Pt/Al₂O₃ and PtPd/Al₂O₃, respectively. All catalysts were found to be highly active for NO and C₃H₆ oxidation as well as C₃H₆-SCR reactions. The highest activity for NO oxidation was obtained for Pt/Al₂O₃ with 1.2 wt% Pt loading. The activity for C₃H₆ oxidation increased with increasing metal content. Pt/Al₂O₃ and PtPd/Al₂O₃ that have the same total metal loadings showed very similar C₃H₆ oxidation performances. C₃H₆ oxidation light-off temperatures all shifted to higher values when NO was present in the feed, indicating a competitive oxidation of NO and C₃H₆. After roughly 50% of C₃H₆ was consumed by C₃H₆ oxidation, C₃H₆-SCR started and C₃H₆ was consumed by both oxidation and NO_x reduction. In this study, SCD was shown to be an effective method for the preparation of Pt/Al₂O₃ and bimetallic PtPd/Al₂O₃ catalysts for NO and C₃H₆ oxidations with small average particle sizes and sharp PSDs. To our knowledge, effect of Pt loading of Pt/Al₂O₃ and Pd addition to Pt/Al₂O₃ prepared by SCD on particle morphology and C₃H₆ and NO oxidations along with C₃H₆-SCR reaction performances were reported here for the first time. Further investigations for improvement of performance and stability for oxidation catalysts prepared by SCD are needed, especially upon hydrothermal ageing and NO_x storage/release phenomenon.

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a)

b)

c)

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Table 1. Properties of metal precursors used for the preparation of Pt/Al₂O₃ and PtPd/Al₂O₃

Precursor	Molecular Weight	Metal Content	Purity	Melting Point
Pt(cod)me ₂	333.33 g/mol	59 mol%	97 %	105 °C
Pd(acac) ₂	304.64 g/mol	35 mol%	99 %	205 °C

Table 2. Metal content and average particle sizes for Pt/Al₂O₃ and PtPd/Al₂O₃

Sample	Metal loading (wt%)		Pt:Pd ratio (mol:mol)	Average Particle Size before Calcination (nm)	Average Particle Size after Calcination (nm)	
	Pt	Pd			Small NPs	Large NPs
0.6-Pt/Al ₂ O ₃	0.6	-	-	1.2 ± 0.2	1.1 ± 0.3	8.8 ± 4.6
1.2-Pt/Al ₂ O ₃	1.2	-	-	1.2 ± 0.3	1.1 ± 0.3	10.7 ± 2.9
2.1-Pt/Al ₂ O ₃	2.1	-	-	1.1 ± 0.3	1.0 ± 0.3	10.5 ± 3.1
PtPd/Al ₂ O ₃	1.0	0.4	1.3:1	1.5 ± 0.4	1.2 ± 0.3	6.5 ± 1.7

Table 3. C₃H₆ Light-off Temperatures during C₃H₆ Oxidation and C₃H₆-SCR

Sample	C₃H₆ Light-off Temperature during C₃H₆ Oxidation (°C)	C₃H₆ Light-off Temperature during C₃H₆- SCR (°C)
0.6-Pt/Al ₂ O ₃	161	229
1.2-Pt/Al ₂ O ₃	150	182
2.1-Pt/Al ₂ O ₃	136	212
PtPd/Al ₂ O ₃	132	184