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Pt/CeO_2-Al_2O_3 Nanosheet Three-way Catalysts with Enhanced Stability upon Redox Hydrothermal Aging

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Abstract

The synthesis of Rh-free, especially Pt-only, three-way catalysts with improved low-temperature activity and stability during redox hydrothermal aging is highly desirable in the automotive industry. Herein, we illustrate that tuning the surface coverage of penta-site rich γ-Al_2O_3 nanosheet (AlNS) supports by CeO_2 "nano-islands" can lead to the synthesis of 1 wt.% Pt/CeO_2(60 wt.%)-AlNS catalysts that have lower light-off temperatures for CO, hydrocarbons, and NO compared to conventional Pt/CeO_2 and Pt/Al_2O_3 catalysts by 100-200 ºC. Moreover, 1 wt.% Pt/CeO_2 (60 wt.%)-AlNS showed a comparable activity and durability with the state-of-the-art Rh-based three-way catalyst (0.5 wt.% Rh/TiO_2(12 wt.%)-Al_2O_3). Combining detailed characterization including X-ray diffraction, scanning transmission electron microscopy, H_2 temperature-programmed reduction, and CO diffuse reflectance infrared Fourier transform spectroscopy, we suggest that incorporation of CeO_2 on the surface of AlNS can retard the growth of CeO_2 crystalline size and Pt can be maintained as nanoclusters even after harsh redox hydrothermal aging. The improved low-temperature activity and redox hydrothermal aging stability can be attributed to the balanced Pt sintering and Pt redispersion that allows Pt to be maintained as Pt nanoclusters on CeO_2, which are the most active species for three-way catalyst applications.

Keywords: Pt; CeO_2, Al_2O_3 nanosheets; hydrothermal stability; three-way catalysts.

1. Introduction

Three-way catalysts (TWCs), as the key component for the stoichiometric spark ignition engine emissions control, have been quite successful in the past four decades.[1-4] TWCs have been widely applied in gasoline vehicles, such as passenger cars and light-duty trucks.[5] TWCs can simultaneously oxidize carbon monoxide (CO), hydrocarbons (HCs) and reduce nitrogen oxides (NOx) to less-hazardous products including carbon dioxide (CO_2), water (H_2O), and nitrogen (N_2).[6] Modern TWCs are highly efficient when the exhaust temperature is greater than 350 ºC, which is typically lower than the emission temperature at regular driving conditions. To decrease the CO_2 emission, however, the engine efficiency will need further improvement, and therefore the vehicle emissions temperature will be decreased.[7] Moreover, current TWCs are relatively inactive during cold-start (first 1-3 min of vehicle operation), with approximately 80% of the vehicle emissions released into the atmosphere during this period.[8] Both improved engine efficiency and the "cold-start" challenge require significant improvement in the low-temperature activity of TWCs. Moreover, the TWCs can be exposed to temperature >800 ºC under redox atmosphere (10-13% H_2O, 3% CO + 1% H_2 or >3% O_2) and need to maintain their activity after 150,000 miles of driving.[5] Therefore, apart from enhanced low-temperature activity, excellent redox hydrothermal stability/durability is also required.

Rh is the key component in modern TWC systems, due to its high NO dissociation activity and N_2 selectivity even in the presence of O_2 compared to other platinum group metals.[9-11] For example, one of the state-of-the-art Rh-based TWCs (0.5 wt.% Rh/Ti-Al_2O_3) reported by Getsoian et al. can convert c.a. 90% of NO below 200 ºC.[5] However, the price of Rh is prohibitive and volatile because of its limited global reserves and the growing use of Rh in the automobile industry for meeting the increasingly stringent emission regulations. Therefore, developing Rh-free TWCs without compromising the low-temperature activity and durability is highly desirable.[12-14] Among the Rh-free TWCs, Pt-based catalysts have attracted wide interest attributed to their lower price and higher resistance to lead and SO_2 poisoning compared to Pd-based catalysts.[15,16] Combining Pt with CeO_2 can significantly boost the TWC low-temperature activity,[20,21] because of the ability of CeO_2 to store oxygen under lean conditions and release O_2 under rich conditions by its Ce^{3+}/Ce^{4+} redox pair. Thus, CeO_2 can buffer the vehicle emissions fluctuating around the stoichiometric point.[17-19] However, both Pt and CeO_2 can undergo severe sintering and surface area loss when exposed to high temperatures for a long period of time, especially in the presence of steam.[3,22]

Therefore, high temperature exposure in the presence of steam can lead to significant TWC activity loss. Several strategies have been applied to improve the thermal stability of CeO_2, such as Zr incorporation[18] or deposition of CeO_2 on a thermally stable support,[23,24] such as γ-Al_2O_3. Incorporating Pt/CeO_2 over hydrothermally stable γ-Al_2O_3 has shown the potential to retard the deactivation of Pt/CeO_2 based catalysts.[23,25,26] For example, Jeong et al. showed that 1 wt.% Pt/CeO_2-rAl_2O_3 can obtain superior durability even after hydrothermally aged at 900 ^oC, even though a reductive pretreatment is required before evaluation.[23] The improved hydrothermal stability of Pt/CeO_2 was attributed to the coordinatively unsaturated penta-sites of γ-Al_2O_3 that can anchor metal and metal oxides.[23,27-29]

The state of Pt species also plays a key role in the catalytic activity of Pt/CeO_2. Atomically dispersed Pt_1/CeO_2 has shown excellent activity towards CO oxidation,[30,31] however, catalytic oxidation of HCs requires metal ensemble sites.[32,33] Furthermore, Pt ensembles/nanoclusters are more active in TWC applications than atomically dispersed Pt and large Pt particles.[23] Therefore, maintaining small Pt nanoclusters during the harsh aging conditions for TWC applications is highly desirable. It has been reported that the interaction between Pt and CeO_2 can mitigate Pt and CeO_2 sintering by forming Pt-O-Ce bonds under an oxidative environment.[34] However, the catalysts can be exposed to highly reductive environments during TWC applications and it is expected that the stabilization effect of Pt-O-Ce can be weakened under such conditions.[35] Therefore, new strategies are required to obtain Pt/CeO_2 based TWCs with an enhanced low-temperature activity and excellent durability under redox environments.

Herein, we describe a facile strategy to develop Pt/CeO_2-based catalysts that can obtain comparable low-temperature activity and durability as the state-of-the-art Rh-based catalysts. In particular, CeO_2 nanocrystals were anchored on penta-site rich γ-Al_2O_3 nanosheets and 1wt.% Pt was deposited on CeO_2. Both Pt and CeO_2 sintering can be mitigated during the harsh redox aging conditions by optimizing the CeO_2 loading/coverage over γ-Al_2O_3 nanosheets. Moreover, the optimal catalyst, 1 wt.% Pt/60%CeO_2-γ-Al_2O_3 nanosheets, showed excellent low-temperature activity with minimal deactivation after redox hydrothermal stability. We propose that the improved redox hydrothermal stability of 1 wt.% Pt/60%CeO_2-γ-Al_2O_3 was obtained by tuning the detachment and re-dispersion of Pt from and to CeO_2 nanocrystals, respectively, that facilitates maintaining Pt as nanoclusters over CeO_2.

2. Experimental

2.1. Catalyst synthesis

Al_2O_3 nanosheets were synthesized based on the synthesis procedure reported previously.[36-38] Specifically, xx amount of aluminum nitrate ($Al(NO)_3$•$9H_2O$) (99+%, Acros Organics) and xxx g of urea (CH_4N_2O) (Certified ACS, Fisher Chemical) were dissolved in xx mL D.I water. The obtained solution was then transferred to a 100 mL PTFE liner and sealed in an autoclave. The autoclave was stored in an oven set to 110 ºC for 48 h. After the completion of the hydrothermal synthesis, the resulting material was separated by vacuum filtration and washed with D.I. water until the pH was close to neutral. The obtained sample was dried at 110 ºC overnight and calcined at 600 ºC for 5 h (2 ºC/min). CeO_2 nanocrystals were deposited onto Al_2O_3 nanosheets by wet impregnation. A varying amount of 1 M $Ce(NO_3)_3$•$6H_2O$ (99% purity, Sigma-Aldrich) solution diluted with 5 mL D.I. water was added to the 400 mg Al_2O_3 nanosheets, and the liquid was evaporated at 40 ºC while stirring. The resulting powder was then calcined at 550 ºC for 5h (2 ºC/min). Pt was then loaded onto the supports by wet impregnation to obtain 1 wt.% using tetraammineplatinum(II) nitrate ($Pt(NH_3)_4(NO_3)_2$) (99% purity, Strem) as the precursor. All the chemicals were used as received. D. I. water was purified to 18.2 MΩ•cm.

2.2. Characterization

The Brunauer-Emmett-Teller (BET) surface areas and Barrett-Joyner-Halenda (BJH) pore volumes of as-synthesized and redox hydrothermally aged catalysts were measured by a Micromeritics surface area and porosity analyzer (Tri-Star II). All samples were first degassed using a Micromeritics VacPrep 061 for 3 h at 150 ºC. The N_2 adsorption/desorption isotherms were collected at -196 ºC and the BJH pore volumes were calculated from the desorption branch.

The crystallite structures of the studied catalysts were evaluated by x-ray diffraction (XRD) using a Rigaku Ultima IV with a Cu Kα X-ray source. The XRD patterns were collected from 2θ = 5 to 90º with a step size of 1.0167º and scan speed of 2º/min.

A JEOL NeoARM 200CF transmission electron microscope equipped with spherical aberration correction and an Oxford Aztec Energy Dispersive System (EDS) for elemental analysis was used for sample imaging. The microscope is equipped with two large area JEOL EDS detectors for higher throughput in acquisition of x-ray fluorescence signals. Images were recorded

in high-resolution TEM (HRTEM), annular dark field (ADF), and annular bright field (ABF) modes.

Raman spectra were collected with an excitation wavelength of 514 nm using a Renishaw inVia Raman Microscope. All spectra were collected with 3 accumulations.

CO diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was conducted in a FTIR spectrometer (Nicolet Is50, Thermo Fisher) with a high temperature reaction chamber (Harrick Praying Mantis). In each measurement, about 20 mg of sample was loaded in the sample holder and pretreated under 10% H_2O, 13% CO_2/Ar (600 ^oC/20 min). The sample was then cooled down to 200 ^oC and purged with pure Ar for 30 min to remove moisture. The sample was then cooled down to room temperature, followed by background spectrum collection. CO DRIFTS spectra were then collected by exposing the sample to 100 sccm 1% CO/Ar for 30 min, followed by purging with Ar for 30 min to remove gas-phase CO. DRIFTS spectra were recorded with a resolution of 4 cm^{-1} and 32 scans.

The redox properties of catalyst supports were investigated by H_2 temperature-programmed reduction (H_2-TPR) using a Micromeritics AutoChem II 2920 instrument. In each test, about 50 mg of catalyst was pretreated at 400 ^oC for 30 min under 20% O_2/Ar. The catalyst was then cooled to room temperature under Ar, followed by 10% H_2/Ar (50 sccm). After the thermal conductivity detector (TCD) signal was stabilized, the catalyst was heated to 1010 ^oC with a ramp of 10 ^oC/min. The H_2 consumption profile was recorded by a TCD.

The dispersion of Pt in the fresh catalysts was determined by CO pulse chemisorption using a Micromeritics AutoChem II 2920. Approximately 50 mg of catalyst was pretreated at 500 ^oC for 1 h under 10% H_2/Ar, followed by purging with He for 30 min before cooling to -68 ^oC using a dry ice and ethanol bath. After the temperature of the catalyst was stabilized at -68 ^oC, a series of 10% CO/He pulses was injected into the reactor to titrate the surface Pt atoms. The Pt particle size/dispersion was calculated based on the stoichiometric ratio of Pt/CO = 1. The CO pulse chemisorption was conducted at -68 ^oC to avoid any CO spillover to CeO_2.[39]

2.3. Catalytic performance evaluations

The performance of the TWCs was evaluated based on the stoichiometric gasoline direct injection (S-GDI) gas compositions from the low-temperature oxidation catalyst test protocol developed by U.S. DRIVE using a custom-built micro-reactor as reported previously.[32,40,41] In

particular, 100 mg of 250-500 μm catalyst was loaded in a U-shaped quartz reactor (I.D. = 8 mm), and it was stabilized by two plugs of quartz wool. Fresh, degreened, and redox hydrothermally aged catalysts were evaluated for their catalytic performance. Fresh catalysts were initially pretreated at 600 ºC/20 min under 10% H_2O, 13% CO_2, balance Ar (gas hourly space velocity (GHSV) = 200 $Lg_{cat}^{-1}h^{-1}$). The catalysts were then cooled to 500 ºC and a simulated reaction mixture that contains 10% H_2O, 13% CO_2, stoichiometric amount of O_2, 0.5% CO, 0.1% NO, 0.167% H_2, and 3000 ppm total hydrocarbons (THCs) (350 ppm C_2H_4, 333 ppm C_3H_6; 100 ppm C_3H_8, 125 ppm i-C_8H_{18}, HCs are on C_1-basis) was introduced to the reactor. After the gas concentrations were stabilized, the catalysts were cooled to 80 ºC (5 ºC/min) and held at 80 ºC for 30 min, followed by heating to 500 ºC (5 ºC/min). The reactant concentrations as a function of inlet temperature were recorded by a mass spectrometer and a MKS MultiGas 2030 FTIR gas analyzer. For evaluating the degreened state of the studied catalysts, the catalysts were first degreened at 700 ºC for 4 h in 10% H_2O, 13% CO_2, balance Ar, followed by a pretreatment at 600 ºC for 20 min and catalytic evaluation as described before. Finally, redox hydrothermal aging was conducted at 800 ºC for 10 h by switching between a rich (10% H_2O, 10% CO_2, 3% CO, 1% H_2) and a lean (10% H_2O, 10% CO_2, 3% O_2) feed every 10 sec. It is noted that the catalysts were heated up and cooled under the lean/rich switching feed. After completing redox hydrothermal aging, the catalysts were pretreated at 600 ºC for 20 min in 10% H_2O, 13% CO_2, balance Ar before evaluation. The light-off data reported in this work is from the heat up portion of the cycle. The conversions of reactant gas were calculated using Eq. (1) as follows:

$$X_R = \frac{(C_{R,in} - C_{R,out})}{C_{R,in}} \times 100\% \quad (1)$$

where X_R stands for the conversion of a specific reactant, $C_{R,in}$ and $C_{R,out}$ represent the concentrations of specific reactants at the inlet and outlet of the reactor, respectively.

3. Results and discussions

3.1. Effect of the catalyst composition

Catalyst performance was evaluated based on the protocol established by the U.S. DRIVE.[40] Fresh, degreened, and redox hydrothermally aged Pt/xCe-AlNS (x = 10-80%) catalysts were evaluated by light-off tests with a simulated gasoline vehicle emission mixture. Pt/CeO_2, Pt/Al_2O_3, and state-of-the-art Rh-based catalyst (Rh/TiAl) were also evaluated for comparison

purposes. The performance of the fresh studied catalysts is shown in Fig. S1. Pt/CeO_2 shows a significantly improved performance compared to Pt/Al_2O_3 catalysts. Specifically, the temperature that 90% CO, THC, and NO conversions are achieved (T_{90}) over Pt/CeO_2 is 193, 233, and 248 °C, respectively, which is 115, 72, and 87 °C lower than that of Pt/Al_2O_3. This observation suggests that the Pt species over CeO_2 are much active than those over Al_2O_3 for TWC applications. Interestingly, the $Pt/xCeO_2$-AlNS (x = 10-80%) catalysts have a similar activity as Pt/CeO_2 with Pt/(50, 60%)CeO_2-AlNS having a slightly improved activity. The similarity in activity between Pt/CeO_2 and $Pt/xCeO_2$-AlNS catalysts indicates that the Pt species over $Pt/xCeO_2$-AlNS (x = 10-80%) are mostly deposited over CeO_2 instead of Al_2O_3. The $T_{50,90}$'s for CO, THCs, and NO over those catalysts are summarized in Fig. S1(d). The performance of the degreened (DG) catalysts is shown in Fig. 1. DG and fresh catalysts have a similar performance, suggesting that the studied catalysts are stable when exposed to the DG conditions. The DG $Pt/xCeO_2$-AlNS (x = 10-80%) and DG Pt/CeO_2 catalysts show a similar performance, and they are both outperforming Pt/AlNS. Moreover, DG $Pt/xCeO_2$-AlNS (x = 10-80%) and DG Pt/CeO_2 outperform the state-of-the-art DG Rh/TiAl catalyst in CO and THC conversions, while they are comparable in NO reduction performance. The $T_{50,90}$'s of all studied DG catalysts are summarized in Fig. 1(d).

The redox hydrothermal stability is a key parameter for TWCs, as the catalyst lifetime needs to be maintained after prolonged vehicle usage (> 150,000 miles of driving). The catalyst performance after redox hydrothermal aging (HTA) is shown in Fig. 2. Pt/CeO_2 and Pt/AlNS deactivated significantly after the redox HTA, as the light-off curves for CO, THC, and NO are shifted to higher temperatures compared to their DG state. The state-of-the-art Rh/TiAl catalyst is able to maintain its activity before and after redox HTA. Interestingly, incorporating CeO_2 in AlNS improved the catalytic performance after redox HTA significantly compared to Pt/CeO_2 and Pt/AlNS. The $T_{50,90}$'s of those catalysts for CO, THC, and NO conversions were summarized in Fig. 2d. The optimal CeO_2 loading for the Pt/Ce-AlNS catalysts is 50-60 wt.%. Moreover, 1 wt.% Pt/60%Ce-AlNS has lower T_{90}'s for THCs and NO ($T_{90(THC)}$ = XXX, $T_{90(CO)}$ = YYY) compared to Rh/TiAl ($T_{90(THC)}$ = XXX, $T_{90(CO)}$ = YYY) after redox HTA. Furthermore, 1% Pt/60%Ce-AlNS shows the lowest ΔT_{50} ($\Delta T_{50} = T_{50}(HTA) - T_{50}(DG)$) for CO, THC, and NO conversions compared to Pt/AlNS and Pt/CeO_2 (Fig. S2), suggesting the improved durability of the catalysts when CeO_2 is incorporated into AlNS.

The surface area and pore volume of fresh/HTA catalysts were measured by N_2 adsorption/desorption isotherms to investigate the effect of CeO_2 deposition over AlNS. As shown in Table. 1, fresh Pt/AlNS has the highest surface area (197.9 m^2/g), while fresh Pt/CeO_2 shows the lowest surface area (69.9 m^2/g) of all measured fresh catalysts. Incorporation of CeO_2 onto AlNS leads to a decrease in the surface area. Specifically, increasing the CeO_2 loading from 20 wt.% to 80 wt.% led to a decrease in the surface area from 149 to 97 m^2/g. The pore volume of those catalysts follows a similar trend as the surface area. The surface areas of the studied samples decreased after redox HTA, that can be attributed to the growth of the CeO_2 and Al_2O_3 crystalline size during HTA. Specifically, the surface area of Pt/CeO_2 decreased from 70 (fresh) to 2.0 (HTA) m^2/g, while the surface area of Pt/AlNS decreased from 198 (fresh) to 68 (HTA) m^2/g. Incorporation of CeO_2 onto AlNS improves the surface area after HTA compared to Pt on bare CeO_2. For example, the surface area of Pt/60%Ce-AlNS (20 m^2/g) is about 10 times higher than Pt/CeO_2 (2.0 m^2/g) after HTA.

The XRD patterns of fresh and HTA Pt/xCe-AlNS (x = 0, 20, 40, 60, 80 %) and Pt/CeO_2 catalysts are shown in Fig. 3. CeO_2 has a cubic fluorite phase (JCPDS 34-0394) over CeO_2 containing samples,[42] with the peaks at 28.3°, 32.8°, 47.0°, and 55.8° corresponding to CeO_2 (111), (200), (220), and (311) facets, respectively. The crystallite size of CeO_2 over Pt/xCe-AlNS (x = 0, 20, 40, 60, 80 %) and Pt/CeO_2 is shown in Table. 1. The CeO_2 crystallite size of fresh Pt/CeO_2 is 9.2 nm, while depositing CeO_2 onto AlNS leads to smaller CeO_2 crystallite sizes. The crystallite size of CeO_2 increased from 5.5 to 7.5 nm, when increasing the CeO_2 loading from 20 to 80 wt.% over the fresh Pt/Ce-AlNS catalysts. Smaller CeO_2 crystallites have a bigger surface for Pt deposition, and they have more reactive surface oxygen species due to the presence of more stepped/edge sites compared to larger CeO_2 crystallites. Pt is well dispersed over the fresh Pt/Ce-AlNS and Pt/CeO_2 samples as barely any Pt(111) peak ($2\theta = 39.8°$) is observed over their XRD pattern.[43] The CeO_2 crystallite size of Pt/CeO_2 increased from 9.2 to 22 nm (Table 1) after redox HTA, suggesting severe CeO_2 sintering. This observation is consistent with the surface area and pore volume loss of Pt/CeO_2 after HTA. However, Pt/Ce-AlNS catalysts show a smaller growth of the CeO_2 crystallite size (6.1 – 9 nm CeO_2 growth) compared to Pt/CeO_2 (13.2 nm CeO_2 growth) after redox HTA, indicating that the interaction between CeO_2 and AlNS can improve the redox hydrothermal stability of CeO_2 nanocrystals. Moreover, the metallic Pt(111) peak can be observed over fresh/HTA Pt/AlNS, HTA Pt/Ce20%-AlNS, and HTA Pt/Ce40%-AlNS. A sharp peak at

39.8° shows up over Pt/AlNS after HTA, suggesting that severe Pt sintering occurred. Interestingly, the Pt (111) peak becomes less intense with increasing CeO_2 loading, indicating that CeO_2 retards Pt sintering. A possible explanation for this behavior is that when the CeO_2 loading/coverage is low, the Pt species can detach from the CeO_2 surface and migrate onto the surface of AlNS. However, the detached Pt species tend to aggregate to large particles since Pt interacts weakly with AlNS. On the contrary, when the CeO_2 loading increases, the possibility that the detached Pt species migrate back to the CeO_2 surface during redox HTA increases that can lead to diminishing of Pt sintering. An ideal catalyst would be able to suppress the Pt sintering and thus the catalyst deactivation during redox HTA, by tuning the occurrence of the following two phenomena: 1) Pt detaching from CeO_2 followed by sintering on AlNS surface and 2) Pt re-dispersion/migration back to CeO_2 surface.

H_2-TPR experiments were conducted over CeO_2 and Ce-AlNS to understand the origin of the improved redox hydrothermal stability of CeO_2 nanocrystals over AlNS (Fig. 4). AlNS show no H_2 consumption peaks at the temperature range of 100-1000 °C. Pure CeO_2 shows multiple H_2 consumption peaks. Specifically, the peaks from 300-550 °C can be attributed to the reduction of surface and sublayer Ce^{4+}, and the peak from 550-800 °C is associated with the reduction of bulk Ce^{4+}. Introducing CeO_2 onto AlNS leads to the appearance of a new H_2 consumption peak at c.a. 880 °C, in addition to the peaks that are similar to the ones of pure CeO_2 (300-800 °C). Increasing the CeO_2 loading from 20-60 wt.% leads to an increase in H_2 consumption at ~880 °C, while 80 wt.%Ce-AlNS shows a decreased H_2 consumption compared to 60 wt.% Ce-AlNS due to the decreased amount of AlNS as a platform. The 880 °C peak is not present in pure CeO_2 and AlNS, suggesting that it is associated with the interfacial sites of CeO_2 and AlNS. The H_2 consumption for the peaks at c.a. 880 °C is summarized in Fig. 4c and Table S1.

The Pt species over fresh and HTA Pt/xCe-AlNS (x = 0 – 80 wt.%) and Pt/ CeO_2 catalysts were characterized by CO-DRIFTS (Fig. 5). A broad peak centered at 2097 cm^{-1} along with smaller shoulder peaks at 2030-2070 cm^{-1} are observed over fresh Pt/AlNS (Fig. 5a). The peak at 2097 cm^{-1} can be attributed to CO adsorbed on coordinatively saturated Pt sites of extended (100) facets, suggesting the presence of large Pt particles.[44] The shoulder peaks at 2030-2070 cm^{-1} are associated with bridged CO adsorbed on Pt nanoparticles. Introducing CeO_2 onto Pt/AlNS shifts the peaks to lower wavenumbers (e.g. 2097 cm^{-1} is shifted to 2088 cm^{-1}), suggesting the formation of new Pt species. All studied CeO_2 containing catalysts show similar Pt species with the 2088

cm^{-1} peak assigned to CO adsorbed on Pt nanoclusters on CeO_2.[23] Pt deposition on CeO_2 is also confirmed by Raman spectroscopy (Fig. S3), as the peak associated with Pt-O-Ce (672 cm^{-1}) is observed over both Pt/CeO_2 and Pt/60%Ce-AlNS. The 2087 cm^{-1} peak is shifted to a slightly higher wavenumber (2092 cm^{-1}) in fresh Pt/CeO_2 compared to the fresh Pt/xCe-AlNS samples (Fig. 5a), indicating the presence of ionic Pt species.[35] The CO-DRIFTS spectra over the same samples after redox HTA are shown in Fig. 5b. The 2097 cm^{-1} peak intensity of HTA Pt/AlNS increased substantially compared to its fresh state, suggesting that severe Pt sintering occurred after redox HTA. This observation is consistent with the XRD results (Fig. 3). Two peaks, at 2095 and 2072 cm^{-1}, are observed over redox HTA Pt/CeO_2, that are attributed to CO adsorbed on Pt(100) facets and bridged CO on Pt nanoparticles, respectively. The peak at 2097 cm^{-1} is also present over the HTA Pt/xCe-AlNS samples. However, a peak at 2087 cm^{-1} associated with CO on Pt nanoclusters is present over both fresh and HTA Pt/xCe-AlNS, indicating that incorporating CeO_2 nanocrystals in AlNS can slow down Pt sintering. Furthermore, the majority of Pt species over Pt/60%Ce-AlNS are Pt nanoclusters even after harsh redox HTA as the intensity of the 2087 cm^{-1} peak is greater than the intensity of the 2097 cm^{-1} shoulder peak. The Pt particle sizes of HTA Pt/AlNS, Pt/60%Ce-AlNS, and Pt/CeO_2 are also confirmed by STEM images (Fig. 6). Large Pt (> 20 nm) particles were observed over HTA Pt/AlNS with an average Pt size of c.a. 32.0 nm (Fig. 6a). Both small Pt nanoclusters (< 2 nm) and Pt nanoparticles (2-20 nm) were observed over Pt/CeO_2 with an average Pt size of 5.4 nm. On the contrary, much smaller Pt nanoclusters (avg. ~1.5 nm) were observed over Pt/60%Ce-AlNS than Pt/CeO_2 and Pt/AlNS, which is consistent with its high TWC activity (Fig. 2).

The performance of 1 wt.% Pt/60%Ce-AlNS is compared to 1 wt.% Pt/60%Ce-AlCom and a physical mixture of 1.67 wt.% Pt/CeO_2 and AlNS (the composition is equal to 1 Pt/CeO_2-AlNS) to verify the importance of AlNS (Fig. S4). 1 wt.% Pt/60%Ce-AlNS outperforms both 1% Pt/60%Ce-AlCom and 1.67 wt.% Pt/CeO_2 + AlNS physical mixture. Specifically, the 1 wt.% Pt/60%Ce-AlNS had a lower T_{90} for CO, THC, NOx conversions compared to the physically mixed sample (1.67 wt.% Pt/CeO_2 + AlNS) by 50, 37, and 39 ºC, respectively. This observation confirms the importance of anchoring the CeO_2 nanocrystals on the AlNS surface. Moreover, 1 wt.% Pt/60%Ce-AlNS outperforms 1 wt.% Pt/60%Ce-AlCom suggesting the benefit of using penta-site rich AlNS instead of commercial Al_2O_3. This observation is supported by H_2-TPR results (Fig. S6) that show that Pt/60%Ce-AlNS has more penta-sites (606.3 μmol/g) compared to

Pt/60%Ce-AlCom (187.5 μmol/g). It is also worth noting that the physically mixed sample does not have a H_2 consumption peak at c.a. 880 °C. This observation further confirms that the H_2 consumption peak at 880 °C originates from interfacial CeO_2. The 1% Pt/60%Ce-AlNS shows the least deactivation for CO, THC, and NOx conversions after redox HTA compared to Pt/60%Ce-AlCom and 1.67 wt.% Pt/CeO_2 + AlNS (Fig. S5). For instance, the THC conversion at 225 °C decreased by only 21% over Pt/60%Ce-AlNS, compared to 66% and 63% over Pt/60%Ce-AlCom and 1.67 wt.% Pt/CeO_2 + AlNS, respectively. Moreover, smaller CeO_2 crystallites are formed over Pt/60%Ce-AlNS (15.3 nm) compared to Pt/60%Ce-AlCom (19.6 nm), Pt/CeO_2 (22.4 nm), and the physically mixed sample (22.3 nm) (Fig. S7) after HTA, suggesting that the impregnation of $Ce(NO_3)_3$ onto AlNS is necessary for obtaining strong CeO_2-AlNS interaction. Most Pt species over HTA Pt/60%Ce-AlNS and Pt/60%Ce-AlCom are nanoclusters based on CO-DRIFTS (Fig. S8). Therefore, the improved activity of Pt/60%Ce-AlNS compared to Pt/60%Ce-AlCom can be attributed to the formation of smaller CeO_2 crystallites (less active surface oxygen species). Severe Pt sintering can also be observed over the Pt/CeO_2+AlNS sample as the dominant peak in CO-DRIFTS is 2097 cm^{-1}, which is associated with CO adsorbed on large Pt particles.

4. Conclusions

In conclusion, a series of Pt/Ce-AlNS catalysts were synthesized with CeO_2 nanocrystals anchored on γ-Al_2O_3 nanosheets and Pt deposited on CeO_2. In the DG state, those catalysts show a similar activity with Pt/CeO_2 when evaluated under TWC conditions, indicating that the Pt was deposited on CeO_2. After redox HTA, 1 %Pt/60%Ce-AlNS shows reactivity comparable to the state-of-the-art Rh-based catalyst. The XRD and N_2 adsorption/desorption results showed that incorporation of CeO_2 on the surface of AlNS can slow down CeO_2 crystallite size growth. Moreover, CO-DRIFTS and TEM results confirm that optimizing the CeO_2 coverage/loading (60 wt.%) results in the majority of the Pt being present as nanoclusters even after harsh redox HTA, whereas severe Pt sintering is observed over Pt/CeO_2 and Pt/AlNS catalysts.

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