



In Situ Investigations on the Facile Synthesis and Catalytic Performance of CeO₂-Pt/Al₂O₃ Catalyst

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Abstract: Ceria-modified Pt/Al₂O₃ catalyst has been commonly prepared by the impregnation of platinum on ceria-modified alumina and widely applied in the chemical industry and automotive industry. The in situ diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS), and thermogravimetric (TG) analysis techniques were employed to investigate the typical mechanisms of the bis(ethanolammonium)hexahydroxyplatinate(IV) and cerium nitrate decomposition catalyzed by Pt^{δ+} species for the facile synthesis of CeO₂-Pt/Al₂O₃ catalyst. It was found that Pt⁴⁺-catalyzed decomposition of cerium nitrate leads to the higher dispersity of ceria and forming more active oxygen species, on the basis of X-ray diffraction (XRD) and H₂ temperature-programmed reduction (H₂-TPR) results. The in situ activity measurements were also performed to investigate the reaction mechanisms and the specific activities for the catalytic CO, NO, C_3H_6 and C_3H_8 co-oxidation. The results indicate that undesirable N₂O by-product is formed by the selective catalytic reduction (SCR) of NO by C_3H_6 below 350 °C. The cerium addition effectively improves the activity of catalytic oxidation, but exhibits an increased N₂O yield, due to the increased reducibility.

Keywords: platinum; ceria; in situ characterization; catalytic oxidation

1. Introduction

Platinum-based catalysts have been widely used in the chemical industry for the catalytic dehydrogenation of light alkanes, such as ethane and propane [1,2], as well as the automotive industry to catalytically oxidize harmful pollutants, including CO, NO, and hydrocarbons [3–6]. Ceria has been used in automotive catalysts, due to its oxygen storage capacity and the ability to stabilize active metals [7–9]. The recognized ability of ceria to undergo rapid reduction/oxidation cycles ($4\text{CeO}_2 \Rightarrow 2\text{Ce}_2\text{O}_3 + \text{O}_2$) plays a significant role in providing oxygen mobility and oxygen storage/release [8]. In our previous investigations, it was reported that the synergy between ceria additive and active Pt species has a positive impact on the stability of coordinately unsaturated Pt²⁺ and Pt⁴⁺ species, thereby drives C–C and C–H bonds activation and promotes low-temperature oxidation of propane [10]. Ceria can also stabilize atomically dispersed ionic platinum (Pt²⁺ species) to accelerate CO oxidation at low temperature [11]. The shape-dependent ability to anchor single Pt²⁺ species increases in the order: Ceria cubes < ceria nanorods < polyhedral ceria [9]. Bruix [12] et al. suggested that the unsaturated Pt²⁺ species is effectively stabilized by bonding to O^{2–} sites in square pockets of CeO₂ surfaces.



The ceria addition into Pt-based diesel oxidation catalyst (DOC) showed the positive impact on the improvement of platinum dispersion, and generation of more active oxygen species and oxygen vacancies over the catalyst, which strengthens the interactions between NO molecules and the catalyst surfaces to promote NO oxidation into NO₂ and form nitrate species [13]. The introduction of cerium into Pt/Al₂O₃ catalyst leads to enhancing the dispersity of active Pt nanoparticles and reducibility of catalyst, which was reported by Ma et al. [14]. They also found that the Ce-containing Pt/Al₂O₃ catalyst exhibits more active for propane dehydrogenation and higher coking-resistant ability than Ce-free Pt/Al₂O₃ catalyst. As a doping element, cerium addition to alumina increases the thermal stability of alumina and improves the ability to remove carbon species during partial oxidation of methane [15]. Improved effectiveness of the carbon cleaning promotes the reactivity of partial oxidation of methane. Promotion of Pt/Al₂O₃ by cerium for CO oxidation was also found by Son and his co-workers [16,17], due to the enhanced oxygen supply to the Pt sites.

Some methods for cerium addition into Al_2O_3 supported catalyst have been reported, for instance, incipient wetness impregnation [10], controlled surface reaction (CSR) technique [18], and atomic layer deposition (ALD) technique [19]. The latter two methods can effectively improve the dispersity of ceria, but the use of expensive organometallics, such as Ce(acac)₃ (cerium acetylacetonate) and Ce(TMHD)₄ (tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)cerium) is required to prepare the CeO_{2-x}/Pt/Al₂O₃ catalyst. By contrast, the incipient wetness impregnation method was considered as the most practical method, resulting from requiring the use of low-cost inorganic precursors, such as Ce(NO₃)₃ (cerium nitrate) and (NH₄)₂[Ce(NO₃)₆] (diammonium hexanitrate cerate) [10,20]. The cerium addition by incipient wetness impregnation using Ce(NO₃)₃ has been successfully employed to prepare the highly-efficient automotive catalysts [13]. However, the structure evolution of precursors is still unknown during the process for preparing the cerium-modified Pt/Al₂O₃ catalyst.

It is worth mentioning that the choice of platinum precursors is also very important for the preparation of Pt catalysts by the incipient wetness impregnation method [21]. The typical Pt-precursors, such as H_2PtCl_6 (hexachloroplatinic(IV) acid), Pt(NO_3)₂ (platinum(II) nitrate) and Pt(NH₃)₄(NO₃)₂ (tetraammineplatinum(II) nitrate), were used to prepare those Pt-supported catalysts [22,23]. However, the use of H_2PtCl_6 as a precursor will lead to the introduction of chlorine, although the tetravalent state of platinum readily interacts with non-stoichiometric oxides. By contrast, using a new [HOCH₂CH₂NH₃]₂Pt(OH)₆ (bis(ethanolammonium)hexahydroxyplatinate(IV)) as the Pt-precursor can refrain from chlorine incorporation and its hydroxyls can bond to the surface of oxide support with hydrogen bonds to strengthen the interactions between platinum precursors and support. In the work, therefore, some in situ characterization techniques were used to investigate the facile synthesis of CeO₂-Pt/Al₂O₃ catalyst by impregnation method using Ce(NO₃)₃ and [HOCH₂CH₂NH₃]₂Pt(OH)₆

2. Results and Discussion

2.1. Thermogravimetric Results

The thermogravimetric (TG) analysis of the different samples was carried out, and the results were displayed in Figure 1. The pure Al₂O₃ sample shows a slight, but consecutive weight loss up to 550 °C, which can be ascribed to the dehydration of sample and the decomposition of chemically adsorbed hydroxyl species [24]. By contrast, the introduction of Pt-precursor induces the additional weight loss that is reasonably related to the decomposition of chemical fragments from [HOCH₂CH₂NH₃]₂Pt(OH)₆. As for the Ce-containing samples, the weight loss is largely higher compared to those of Ce-free samples, which can be assigned to the transformation and thermal decomposition of nitrate precursors.



Figure 1. Thermogravimetric (TG) curves of the different samples at a heating rate of 10 °C/min in N₂ steam.

2.2. Decomposition of Pt-Precursor

The TG curve for the decomposition of Pt-precursor on Al₂O₃ powder was achieved through subtracting TG data of pure Al₂O₃ (Figure 1) from the data of the pristine Pt/alumina powder without calcination. The obtained TG curve and the corresponding derivative thermogravimetric (DTG) curve were displayed in Figure 2a. The TG curve can be divided into three weight loss steps according to the DTG curve. Step 1 with weight loss of 0.41 mg per 100 mg sample, where a temperature ranges from 50 °C to 135 °C, represents the weight loss by the removal of physically adsorbed water [25]. Step 2 removes H₂O molecules from Pt(OH)₆^{2–} species [26]. In the TG experiment, the theoretical weight loss for the complete decomposition of Pt(OH)₆^{2–} species is 0.27 mg. However, the actual weight loss in this step reaches to 0.51 mg, indicating that partial HOCH₂CH₂NH₃⁺ species starts to be transformed in the step. Increasing the temperature to 482 °C, the total weight loss reaches 1.16 mg. However, no significant change in weight loss was observed with the further temperature increments. It is assumed that Pt-precursor was completely decomposed into PtO₂ and gas; the total weight loss would be 1.38 mg. The gapped results between actual and theoretical weight loss can be contributed to the formation of coke during decomposition of Pt-precursor, as well as some errors during the data processing.



Figure 2. TG and derivative thermogravimetric (DTG) curves (**a**) and diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS) spectra (**b**) collected during thermal decomposition of Pt-precursor on Al_2O_3 powder at a heating rate of 10 °C/min in N₂ steam.

Further evidence for the transformation of Pt complexes during the programmed temperature procedure in N_2 steam was provided by diffuse reflectance infrared Fourier transformed spectroscopy

(DRIFTS), as displayed in Figure 2b. The band centered at 1454 cm⁻¹ can be assigned to deformation vibration of the methylene group $\delta(CH_2)$ from HOCH₂CH₂NH₃⁺ species, and the corresponding symmetric and asymmetric vibrations were respectively observed at 2888 cm^{-1} , $v_s(CH_2)$, and 2950 cm^{-1} , v_{as} (CH₂) [27]. The shoulder at 1533 cm⁻¹ should be related with O–H bending mode in water [28]. The local peak centered at 1587 cm^{-1} corresponds to the bending mode of the Pt–NH₃ species [29]. Increasing temperature from 100 °C to 200 °C only led to a significant decrease in the intensity of the bending vibration hydroxyl group δ (OH) in water, which illustrates water loss in the catalyst sample. Carbonyl (bands at 2070 ~ 2040 cm⁻¹, linear bonded Pt–CO species) and isocyanate surface complexes (bands at 2150 ~ 2100 cm⁻¹, Pt–NCO species) [30,31] first clearly appeared at 250 °C. With further increments in temperature, the Pt-NCO vibrational bands showed an increase in intensity and a shift towards higher wavenumbers, reaching 2150 cm⁻¹ at 500 °C, while the band at 2048 cm⁻¹ assigned to Pt-CO species shifted toward 2040 cm⁻¹ at 450 °C and disappeared at 500 °C. The blue-shift of $v_{\rm s}$ (NCO) reflects increasing NCO coverage, due to the further transformation of HOCH₂CH₂NH₃⁺ species. In addition, three were also the formation of some surface oxy-carbon species, including enolates (1392 cm⁻¹, v_s (CH₂=CH–O)) [32], and formates (1377 cm⁻¹, v_s (COO)) [33] in the temperature regions of 250 ~ 400 °C. According to TG and in situ DRIFTS results, the thermal decomposition process of Pt-precursor can be summarized as the following reaction (I):

$$[HOCH_2CH_2NH_3]_2Pt(OH)_6 \rightarrow Pt-CO + Pt-NCO + oxy-carbon \rightarrow Pt-NCO + Pt sites.$$
(I)

2.3. Decomposition of Ce-Precursor

In Figure 3a,c, the weight loss at the temperature range of 50 ~ 138 °C is assigned to the removal of physically adsorbed water, while the other weight loss at higher temperature corresponds to removing chemically bound water and NO_3^- species [24]. As showed in Figure 3a, a significant weight loss of 10.54 mg was observed in the temperature regions of 138 ~ 296 °C, primarily, due to the transformation and decomposition of NO_3^- species. The TG curve showed in Figure 3c exhibited a total weight loss of 11.06 mg up to 248 °C and a maximum weight loss rate of 0.243 mg/°C at 195 °C. The decomposition temperature of Ce-precursor on Pt/alumina was lower, and the maximum weight loss rate was higher compared to that of Ce-precursor on Al₂O₃, which indicates the occurrence of Pt-catalyzed decomposition of cerium nitrate. The total weight losses in Figure 3a,c were 14.03 mg and 15.11 mg per 100 mg sample, respectively, showing the weight gap of 1.08 mg that is closely related to the decomposition of Pt-precursor.

From Figure 3b, it can be seen that Ce-precursor on Al₂O₃ started to transform bridging nitrates $(1650 \sim 1600 \text{ cm}^{-1}, (Ce-O)_2=NO)$ and monodentate nitrates $(1530 \sim 1480 \text{ cm}^{-1}, Ce-ONO_2)$ into chelating bidentate nitrates (bands at 1585 ~ 1530 cm⁻¹, Ce-O₂NO) [34–36] above 150 °C, and the vibrational bands of nitrates disappeared with the temperature increment up to 450 °C. This indicates that the following reactions for the thermal decomposition of cerium(III) nitrate are accomplished, as showed in the reaction (II) reported by Wendlandt et al. [37]. Compared with the DRIFTS spectra for the thermal decomposition of bridging nitrates at lower wavenumber (centered at 1616 cm⁻¹) and bands in the 2200 ~ 2100 cm⁻¹ region assigned to N₂O, N₂, NO₂⁺, and NO⁺ [36]. In addition, the DRIFTS spectrum at 400 °C in Figure 3d exhibits a significantly weaker intensity in Ce–O₂NO mode at 1552 cm⁻¹ than the decomposition of Ce-precursor on Al₂O₃. The results can be ascribed to Pt-catalyzed decomposition of nitrates that promotes the removal of NO₃⁻ species and the formation of CeO_{2-x}. These promotional effects would be conducive to the enhancement of Pt–CeO_{2-x} interactions, due to the in situ reduction of Pt^{\delta+} species by Ce³⁺ ions in an inert atmosphere,

$$Ce(NO_3)_3 \cdot xH_2O(s) \to Ce(NO_3)_3(s) \to CeONO_3(s) \to CeO_{2-x}(s). \tag{II}$$

Weight loss (mg)

16

14

12

4



2 0.025 DTC 0 0.000 2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 100 150 200 250 300 350 400 450 500 550 50 Wavenumber (cm⁻¹) Temperature (°C)

2123

Figure 3. TG and DTG curves (a,c) and DRIFTS spectra (b,d) collected during thermal decomposition of Ce-precursor on Al₂O₃ (**a**-**b**) and Pt/Al₂O₃ (**c**-**d**) powders at a heating rate of 10 °C/min in N₂ steam.

2.4. Catalytic Performance

The activities of catalytic CO, NO, C_3H_6 and C_3H_8 co-oxidation over the Pt-supported catalysts were performed on a continuous flow fixed-bed micro-reactor. The results of activity measurements were showed in Figure 4, and the corresponding characteristic temperatures were summarized in Table 1. The activity of different reactions over the Pt/Al₂O₃ catalyst was easily distinguished, decreasing in the order: CO oxidation > C_3H_6 oxidation > NO oxidation > C_3H_8 oxidation according to the light-off curves (showed in Figure 4a). The catalytic oxidation of hydrocarbons required the higher reaction temperature than CO oxidation, in particular for C_3H_8 oxidation, owing to the higher reactivity of CO oxidation on Pt active sites compared to that of hydrocarbons [3]. The activity of C_3H_6 oxidation is higher than NO oxidation, due to the NO oxidation inhibition by C₃H₆ over the Pt/Al₂O₃ catalyst [38].



Figure 4. Conversion (**a**,**c**) and yield (**b**,**d**) curves during catalytic oxidation reactions over the Pt/Al₂O₃ (**a**,**b**), CeO₂-Pt/Al₂O₃ (**c**,**d**) and reference (**e**,**f**) catalysts.

In the case of NO conversion, no NH₃ product was detected, but significant N₂O (below 350 °C) and NO₂ (above 250 °C) products were formed. NO molecule started to be consumed when CO oxidation reached near to complete conversion, showing the maximum NO conversion rate of 83% at 289 °C, maximum N₂O yield of 32% at 260 °C and maximum NO₂ yield of 38% at 340 °C. The results indicate that NO was transferred into undesirable N₂O via the selective catalytic reduction (SCR) of NO by C_3H_6 at low temperature and oxidized into desirable NO₂ in the higher temperature regions. The related reactions include:

$$2NO + C_3H_6 + 4O_2 \rightarrow N_2O + 3CO_2 + 3H_2O,$$
 (III)

$$2NO + O_2 \rightarrow 2NO_2. \tag{IV}$$

Samples	СО		NO		C ₃ H ₆		C ₃ H ₈	
	T ₅₀ ^a	T ₉₀ b	T_{50}	T ₉₀	T_{50}	T ₉₀	T_{50}	T ₉₀
Pt/Al ₂ O ₃	210.6	241.3	262.2	nd ^c	243.3	252.0	384.0	456.8
CeO2-Pt/Al2O3	177.7	200.1	209.5	nd	208.8	217.6	335.5	364.8
Reference catalyst	201.2	244.7	nd	nd	245.2	264.0	329.1	390.4
Δ_1^{d}	32.9	41.2	52.7	nd	34.5	34.4	48.5	92.0
Δ_2^{e}	23.5	44.6	nd	nd	36.4	46.4	-6.4	25.6

Table 1. The characteristic temperatures for catalytic oxidation of CO, NO, C_3H_6 and C_3H_8 over the Pt/Al_2O_3 and CeO_2-Pt/Al_2O_3 catalysts.

^a T_{50} is the specific temperature reached the conversion of 50%, so-called "light-off temperature". ^b T_{90} is the specific temperature reached the conversion of 90%. ^c nd = no data. ^d Δ_1 represents the characteristic temperature gap between Pt/Al₂O₃ and CeO₂-Pt/Al₂O₃ catalyst. ^e Δ_2 represents the characteristic temperature gap between the reference catalyst and CeO₂-Pt/Al₂O₃ catalyst.

By comparison with Pt/Al₂O₃, the NO conversion curve almost entirely overlapped with the one of C₃H₆ with a higher N₂O yield over the CeO₂-Pt/Al₂O₃ catalyst up to 210 °C, illustrating that the low-temperature C₃H₆-SCR activity was improved, due to the increased reducibility by the addition of ceria [39]. In addition, the CeO₂-Pt/Al₂O₃ catalyst exhibited a lower temperature to achieve the maximum NO conversion rate, N₂O and NO₂ yield. From Table 1, it can also be observed that the ceria addition led to a significant T_{50} decrease of 32.9 °C, 52.7 °C, 34.5 °C, 48.5 °C, respectively, for the CO, NO, C₃H₆ and C₃H₈ conversion. The T_{90} gaps between Pt/Al₂O₃ and CeO₂-Pt/Al₂O₃ catalyst for CO and C₃H₈ conversions are higher than the corresponding T_{50} gaps, reaching 41.2 °C and 92.0 °C, respectively. These results indicate that the ceria addition significantly promotes low-temperature catalytic oxidation of CO, NO, C₃H₆ and C₃H₈, which agree well with the literature [10,13,16,20]. In addition, the CeO₂-Pt/Al₂O₃ catalyst showed the lower characteristic temperatures for CO, NO and C₃H₆ conversion than that of the reference catalyst, although there was no obvious superiority for catalytic oxidation of C₃H₈. Particularly, the activity for catalytic NO oxidation into NO₂ was significantly improved by using [HOCH₂CH₂NH₃]₂Pt(OH)₆. This indicates that [HOCH₂CH₂NH₃]₂Pt(OH)₆ is a better Pt-precursor compared to Pt(NH₃)₄(NO₃)₂.

2.5. XRD and H₂ Temperature-Programmed Reduction (H₂-TPR) Analysis

Figure 5a showed the XRD patterns of the different catalyst samples. The diffraction peaks associated with ceria in the CeO₂/Al₂O₃ and CeO₂-Pt/Al₂O₃ catalysts can be easily observed and exhibited well-crystallized fluorite-type phase [40]. The characteristic peaks appeared at $2\theta = 28.54^{\circ}$, 33.16°, 47.58° and 56.52° are respectively assigned to the (111), (200), (220) and (311) surfaces of ceria nanocrystals. The domain size was calculated using the Scherrer Equation based on XRD line-width broadening data of the (111) surface. The average sizes of CeO₂ nanoparticles in the CeO₂/Al₂O₃ and CeO₂-Pt/Al₂O₃ catalysts were 7.0 nm and 4.1 nm, respectively, indicating that the catalytic decomposition of cerium nitrate by Pt^{δ +} species show a positive impact on promoting the dispersity of ceria. Co-existence of Pt⁴⁺ and Pt²⁺ species in Pt/alumina powder using [HOCH₂CH₂NH₃]₂Pt(OH)₆ as the Pt-precursor has been confirmed in our previous investigations [10]. The average size of CeO₂ nanoparticles in the reference catalyst was bigger by comparison with the CeO₂-Pt/Al₂O₃ catalyst, reaching 5.4 nm. The results illustrate that the presence of Pt⁴⁺ species has a better promotional effect on improving the dispersity of ceria than Pt²⁺ species. Besides, the ceria addition resulted in a significant decrease in the intensity of the peaks assigned to alumina supports, which can be ascribed to the Ce-promoted stability of alumina structures [16,19].



Figure 5. XRD patterns (**a**) and H₂ temperature-programmed reduction (H₂-TPR) profiles (**b**) of the different catalyst samples.

The reducibility of the catalysts was also investigated by the H₂-TPR measurement, and the results were shown in Figure 5b. In the case of the Pt/Al_2O_3 catalyst, three H_2 consumption peaks appeared at 111 °C, 154 °C and 214 °C, respectively. The slight peaks centered at 111 °C and 154 °C are closely related to the reduction of adsorbed oxygen on Pt nanocrystals and O²⁻ species bonded to surface platinum atoms, whereas, the peak centered at 214 °C should be assigned to the reduction of oxygen species that are adjacent to active Pt sites. As for the CeO_2/Al_2O_3 catalyst, the reduction peaks at 100 °C and 139 °C correspond to adsorbed oxygen species on ceria nanocrystals. The peaks at 252 °C and higher temperatures are respectively associated with the reduction of activated surface oxygen species and shallow lattice oxygen in ceria by the following reaction (V) [10,40]. By contrast, the intensity of H₂ consumption peaks below 250 °C strongly increased, and the peaks showed an obvious shift toward lower temperature, which indicates the significant increments of activated surface oxygen species and the increased reducibility of the CeO₂-Pt/Al₂O₃ catalyst. The H₂-TPR profile of the reference catalyst exhibits the lower intensity of H_2 consumption peaks below 200 °C, and these peaks appeared at higher temperature compared with the CeO₂-Pt/Al₂O₃ catalyst, suggesting that the choice of Pt-precursors plays an important role in the reducibility of Ce-containing catalysts and [HOCH₂CH₂NH₃]₂Pt(OH)₆ is an optimal precursor,

$$2\text{CeO}_2 + \text{H}_2 \rightarrow \text{Ce}_2\text{O}_3 + \text{H}_2\text{O}.$$
 (V)

3. Materials and Methods

3.1. Materials and Catalyst Preparation

Bis(ethanolammonium)hexahydroxyplatinate(IV), [HOCH₂CH₂NH₃]₂Pt(OH)₆, was supplied by Sino-platinum metals Co., Ltd., Kunming, China. The nano-alumina was purchased from Aladdin, Shanghai, China. Cerium nitrate and aluminium nitrate were purchased from Xilong Chemical Co., Ltd., Guangzhou, China.

The Pt/alumina powder with the target Pt loading of 1.176% was prepared by incipient wetness impregnation of nano-alumina with an aqueous solution of $[HOCH_2CH_2NH_3]_2Pt(OH)_6$, followed by dry at 50 °C under vacuum condition overnight and calcination at 200 °C in 10%O₂/N₂ stream for 30 min. The Pt/Al₂O₃ catalyst was prepared by incipient wetness impregnation of the collected Pt/alumina powder. 17 g of the as-prepared Pt/alumina powder was added into Al(NO₃)₃ aqueous solution containing 29.42 mmol Al under magnetic stirring at room temperature for 2 h. The obtained slurries were dried at 50 °C under vacuum condition overnight and calcined at 550 °C in 10%O₂/N₂ stream for 2 h with a heating rate of 10 °C/min in N₂ stream to obtain the Pt/Al₂O₃ sample. To synthesize the CeO₂-Pt/Al₂O₃ catalyst, 17 g of the prepared Pt/alumina powder was dispersed in an aqueous solution of Ce(NO₃)₃ containing 17.43 mmol Ce, and then the obtained slurries were stirred, dried

3.2. Characterization

 CeO_2 -Pt/Al₂O₃ catalyst.

The in situ diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS) spectra were collected on a Nicolet 6700 FT-IR spectrometer equipped with an MCT detector. As for in situ detection of the thermal decomposition process of Pt-precursor and Ce-precursor, 2 g of the pristine sample without calcination was firstly pretreated at 50 °C under vacuum condition for 10 h. Then, background spectra were collected at every 50 °C from 100 °C to 500 °C in a flow of nitrogen (50 mL/min) with a heating rate of 10 °C/min. After cooling to room temperature, 100 mg of as-pretreated catalyst sample was placed in the in situ cell, and each transient experiment was measured in N₂ stream with a total flow rate of 50 mL/min. The same methods were taken with the background spectrum collection procedure to acquire DRIFTS spectra.

The thermal decomposition characteristics of Pt-precursor and Ce-precursor in N₂ stream with a heating rate of 10 °C/min were examined by thermogravimetric (TG) analysis, using an STA 449 F3 thermoanalyzer. The pristine samples without calcination were firstly pretreated at 50 °C under vacuum condition for 10 h. 100 mg of as-pretreated sample was immediately placed in the pot of thermoanalyzer and heated at a rate of 10 °C/min from 50 °C to 550 °C in a flow of nitrogen (50 mL/min).

X-ray diffraction (XRD) patterns were recorded on a Philips X'pert Pro diffractometer in the 2θ range of 5–90° with an increment step of 0.02°, using a Ni filtered Cu K α radiation (λ = 0.15418 nm) source. The X-ray tube was operated at 36 kV and 30 mA.

 H_2 temperature-programmed reduction (H_2 -TPR) was carried out on CHEMBET 3000 automated chemisorption instrument equipped with a thermal conductivity detector (TCD). 100 mg of sample was placed in a quartz U-tube reactor and pretreated in an airstream with a total flow rate of 50 mL/min at 450 °C for 30 min. After cooled to room temperature, H_2 -TPR experiments were performed in an H_2 -Ar (9.91% of H_2 by volume) stream with a total flow rate of 50 mL/min from 50 °C to 620 °C at a heating rate of 10 °C/min.

3.3. Catalytic Performance Tests

The catalytic oxidation activity of the catalysts was performed under atmospheric pressure in a continuous flow fixed-bed micro-reactor system. 500 mg of the catalyst sample with an average diameter of 40–60 mesh was placed in a quartz tube with an inner diameter of 8 mm for activity measurements. The total flow rate was 500 mL/min to make the gas hourly space velocity of (*GHSV*) value of 60,000 mL/(g·h). The outlet concentrations of reaction gases and gaseous products were analyzed online using a 2030DBG2EZKS13T MultiGas FT—IR Analyzer purchased from MKS Instruments, Inc. Prior to the activity measurement, each catalyst sample was pretreated at 500 °C in a flow of O_2 -N₂ (10% of O_2 by volume) mixture for 30 min. The catalytic performance was tested in a continuous flow of the reaction mixture gas. The inlet composition of the reaction mixture gas was 500 ppm CO, 200 ppm NO, 660 ppm C₃H₆, 290 ppm C₃H₈, 10 vol.% O_2 , 8 vol.% CO₂, 5 vol.% H₂O and ~77 vol.% N₂. NO conversion, α (NO, %), was calculated by the following Equation (1):

$$\alpha(\text{NO},\%) = \frac{C_{\text{NO},in} - C_{\text{NO},out}}{C_{\text{NO},in}} \times 100\%,$$
(1)

$$Y(NH_3,\%) = \frac{C_{NH_3,out}}{C_{NO,in}} \times 100\%,$$
(2)

$$Y(N_2O,\%) = \frac{2 \times C_{N_2O,out}}{C_{NO,in}} \times 100\%,$$
(3)

$$Y(NO_2, \%) = \frac{C_{NO_2,out}}{C_{NO,in}} \times 100\%,$$
(4)

where, $C_{\text{NO},in}$ and $C_{\text{NO},out}$ represent the concentrations of the inlet and outlet NO gas, respectively. The NH₃, N₂O and NO₂ yields were calculated according to the Equations (2–4) on the basis of the outlet concentrations of NH₃, N₂O and NO₂ products, respectively. The values of CO, C₃H₆ and C₃H₈ conversion rate were calculated by the same method associated with the calculation for NO conversion.

4. Conclusions

It was observed that Pt-catalyzed decomposition of cerium nitrate effectively increases the dispersity of ceria and significantly promotes the formation of activated surface oxygen species. The presence of Pt^{4+} species effectively improve the dispersity of ceria and readily increases the reducibility of Ce-containing catalysts. The undesirable N₂O by-product was formed, due to the selective catalytic reduction of NO by C₃H₆ below 350 °C, according to the results of in situ activity measurements. The N₂O yield was increased by the addition of ceria, resulting from the increased reducibility of Ce-containing catalysts. The improved activity of CeO₂-Pt/Al₂O₃ catalyst for the catalytic CO, NO, C₃H₆ and C₃H₈ co-oxidation were attributed to its high reducibility and the high surface concentrations of activated oxygen species from the interactions between active Pt sites and ceria.

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