

Self-propagating Synthesis of Pd–CeO₂/Al₂O₃ Automotive Monolith Catalysts

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Abstract—Pd–CeO₂ catalysts on a monolith support with a honeycomb structure have for the first time been prepared by surface self-propagating thermal synthesis (SSTS). Decomposition routes for the cerium precursors are deduced from TG–DTA data and from the mass spectra of decomposition intermediates. The Pd–CeO₂/Al₂O₃ monoliths prepared by SSTS are more active in CO oxidation, total hydrocarbon oxidation, and nitrogen oxide reduction than the catalysts obtained by conventional impregnation. This is explained by the fact that the SSTS products have a larger specific surface area and their active component has a smaller particle size.

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Current catalytic converters are typically composed of a noble metal (Pt, Pd, Rh), a promoter (CeO₂, CeO₂–ZrO₂), and a monolith support with a honeycomb structure (alumina or cordierite) [1, 2].

Cerium oxide is widely used as a promoter in three-way catalysts owing to its ability to bind or release oxygen, depending on the air : fuel ratio in the exhaust gas [3, 4]. The unique redox properties of CeO₂ are due to the fact that cerium can readily change its oxidation state (Ce⁴⁺/Ce³⁺). As this takes place, the oxide retains its stable fluorite structure, which includes mobile O^{2–} ions [5, 6]. Furthermore, cerium admixtures prevent γ -Al₂O₃ from sintering at high temperatures, reduces the particle size of the noble metals, and enhances their thermal stability [7].

In recent years, cerium-containing catalysts have been prepared not only by conventional methods, such as impregnation and coprecipitation, but also by the initiation of a very exothermic redox reaction between powdered precursors of the active component (combustion synthesis). Noble-metal-containing cerium oxide thus synthesized is very active in CO oxidation, in the total oxidation of hydrocarbons, and in the reduction of nitrogen oxides [3, 8, 9]. However, this method affords only monolith catalysts and generally requires subsequent calcination.

The surface self-propagating thermal synthesis (SSTS) method was developed to synthesize a variety of supported oxide catalysts active in CO oxidation and in the total oxidation of hydrocarbons [10, 11]. The principle of this method is that an exothermic reaction

between precursors of the active component is carried out immediately on the surface of a support of a given nature and shape. The main advantage of this method is that it produces nonequilibrium phases with structure defects, which can serve as active sites in the resulting catalyst [12, 13]. Another advantage is the high rate of the reaction. Due to intensive heat transfer from the support surface, the highest SSTS temperature does not exceed 500°C and the sintering of the active component can, therefore, be avoided [14, 15].

Here, we consider Pd–CeO₂/Al₂O₃ catalysts prepared by SSTS from various precursors and compare their performances in CO oxidation, in the total oxidation of methane and propane, and in the reduction of nitrogen oxides with propane.

EXPERIMENTAL

The support was a γ -Al₂O₃ monolith with a honeycomb structure, a granule diameter of 20 mm, a channel size of 1.5 × 1.5 mm, a pore volume of 0.34 cm³/g, and a specific surface area of 150 m²/g. The catalysts prepared by different methods had the same composition, specifically, 10 wt % CeO₂ and 0.5 or 1.0 wt % Pd. The catalysts were synthesized as follows.

Procedure 1a: SSTS from a mixture of (NH₄)₂Ce(NO₃)₆ and Pd(NO₃)₂. For loading the γ -Al₂O₃ support with cerium and palladium precursors, the support was impregnated with a mixed solution of stoichiometric amounts of (NH₄)₂Ce(NO₃)₆ (C_{Ce} = 100 mg/ml) and Pd(NO₃)₂ (C_{Pd} = 6.8 mg/ml). The chemicals were purchased from Merck. The subsequent

Table 1. Observed and calculated weight loss data for the thermal decomposition of bulk cerium ammonium nitrate

Temperature range, °C	Weight loss, %		Decomposition step
	observed	calculated	
30–100	1.3	1.3	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6 \cdot 0.4\text{H}_2\text{O} \longrightarrow (\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$
100–235	16.6	17.2	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6 \longrightarrow \text{Ce}(\text{NO}_3)_4 \cdot \text{HNO}_3$
235–260	14.6	14.5	$\text{Ce}(\text{NO}_3)_4 \cdot \text{HNO}_3 \longrightarrow \text{Ce}(\text{NO}_3)_3(\text{NO}_2)$
260–450	35.8	36.1	$\text{Ce}(\text{NO}_3)_3(\text{NO}_2) \longrightarrow \text{CeO}_2$

synthetic procedure is detailed in an earlier publication [15]. The average combustion front temperature was 390°C. The heat wave velocity calculated as the ratio of the sample length to the combustion front traveltime was 0.08 mm/s.

Procedure 1b: SSTS of monolith-supported ceria from (NH₄)₂Ce(NO₃)₆ followed by the introduction of palladium. The monolith support was impregnated with a cerium ammonium nitrate solution with $C_{\text{Ce}} = 100$ mg/ml and was dried. Thereafter, SSTS [15] was carried out. Ce/Al₂O₃ was loaded with palladium by impregnating it with an aqueous palladium nitrate solution ($C_{\text{Pd}} = 6.8$ mg/ml) taken in excess. The excess solution was removed from the support channels by drying at 90°C for 12 h and calcination at 550°C for 3 h.

Procedure 2: SSTS of ceria from a mixture of Ce(NO₃)₃ and citric acid followed by supporting palladium. This procedure included impregnating the monolith support with precursors from a cerium nitrate–citric acid (1 : 5 mol/mol) redox mixture, drying, and SSTS. Palladium was supported as described above. The combustion front temperature was 382°C, and the thermal wave velocity was 0.06 mm/s.

Procedure 3: standard procedure. Pd–Ce/Al₂O₃ catalysts were prepared by impregnating the monolith support with an excess of an aqueous cerium nitrate solution ($C_{\text{Ce}} = 100$ mg/ml) followed by drying at 90°C and calcination at 600°C for 4 h. Ce/Al₂O₃ was loaded with palladium by impregnating it with an aqueous palladium nitrate solution ($C_{\text{Pd}} = 6.8$ mg/ml) followed by drying at 90°C for 12 h and calcination at 550°C for 3 h.

X-ray diffraction patterns from the catalysts were obtained on a DRON-3 diffractometer (monochromated CuK_α radiation; $2\theta = 20^\circ$ – 60°). The active component content was determined by atomic absorption spectroscopy. The BET surface areas of the catalysts were determined from thermal nitrogen desorption data obtained on a Sorpty gas adsorption system (Carlo Erba, Italy). The thermal decomposition of the precursors of the active component was studied by thermal analysis of intermediates on an STA-449C Jupiter thermanalytical system (Netzsch) attached to a QMS-403C Aeolos quadrupole mass spectrometer via a heated capillary.

Catalytic activity was measured in CO oxidation, in the total oxidation of hydrocarbons, and in the reduction of nitrogen oxides with propane in a flow reactor using 1 cm³ of a monolith catalyst. The oxidation of CO, a model reaction, was carried out in a stoichiometric mixture containing 1 vol % CO, 0.5 vol % O₂, and nitrogen as the balance gas in the temperature range 20–400°C at a constant flow rate of 10000 h^{–1}. Catalytic activity was estimated as the temperature at which 50% of the CO was converted (T_{50}). The reaction products were analyzed by gas chromatography using a column packed with Porapak Q and a thermal-conductivity detector. The total oxidations of methane and propane were carried out at 200 to 700°C at a flow rate of 1000 h^{–1}. The hydrocarbon concentration in the initial hydrocarbon–air mixture was 1 vol %. The selective catalytic reduction of NO with propane was studied between 70 and 550°C at a gas flow rate of 11500 h^{–1}. The standard reaction mixture consisted of 0.2 vol % NO, 0.1 vol % C₃H₈, 5.0 vol % O₂, and nitrogen as the balance gas.

RESULTS AND DISCUSSION

Thermal Decomposition of Pure and γ-Al₂O₃-Supported Cerium Precursors

Cerium ammonium nitrate contains both oxidizing and reducing ligands, so SSTS using this precursor does not require any reducing agent. Table 1 lists thermanalytical data for the thermal decomposition of (NH₄)₂Ce(NO₃)₆ in an inert medium. The overall weight loss for this salt is 68.3%.

The first decomposition stage, which takes place in the temperature range 30–100°C, is the single-step loss of weakly bound, physically adsorbed water. This is indicated by the presence of lines at m/z 18, 17, and 16 in the mass spectrum. The rate-limiting step in the decomposition of most ammonium salts is proton transfer from the ammonium cation to the complex anion, which results in ammonia evolution [16]. This process occurs between 100 and 235°C. The wide variety of products (NH₃, NO, NO₂, O₂, N₂O, and N₂) resulting from the decomposition of cerium ammonium nitrate at 235–450°C is possibly due to the interaction between

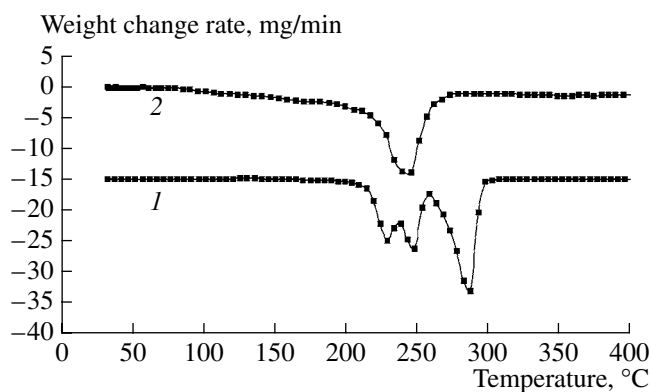


Fig. 1. Decomposition of (1) pure and (2) γ - Al_2O_3 -supported cerium ammonium nitrate in an inert medium. The supported salt content is 10 wt %.

the NH_4^+ and NO_3^- ions on the surface or in the gas phase.

Enumerating chemically plausible mechanisms of cerium ammonium nitrate decomposition, we simulated the weight loss sequence in terms of the chemical equations of individual decomposition steps. The mechanism that provided the best fit to the weight loss in each step was taken to be the best description of the decomposition process (Table 1). This procedure led us to the following probable mechanism for bulk cerium ammonium nitrate decomposition in an inert medium:

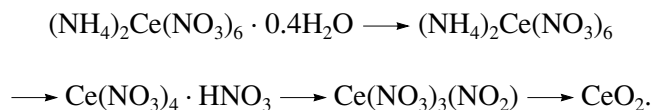


Figure 1 shows the DTG curve for the decomposition of pure and γ - Al_2O_3 -supported cerium ammonium nitrate. Clearly, the decomposition of the supported salt is simpler and is complete at a lower temperature than the decomposition of the pure salt. This can be due to the fact that the $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ particles are smaller on the support surface than in the bulk salt, since it was demonstrated that the cerium ammonium nitrate decomposition mechanism depends strongly on the particle size [17].

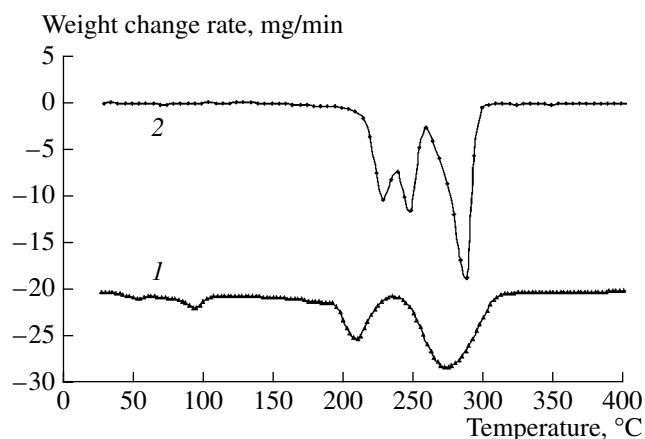
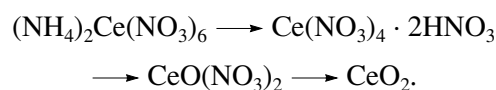


Fig. 2. Decomposition of bulk cerium precursors in an inert medium: (1) $\text{Ce}(\text{NO}_3)_3$ and (2) $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$.

Table 2 presents the data obtained by simulating the decomposition of γ - Al_2O_3 -supported cerium ammonium nitrate. According to these data, the decomposition of the supported salt is likely to proceed as follows:



A comparative study of cerium ammonium nitrate decomposition in inert and oxidizing media has demonstrated that the precursor decomposition mechanism is almost independent of the atmosphere.

Comparing the DTG curves for the cerium precursors, namely, cerium ammonium nitrate and cerium nitrate (Fig. 2), shows that the decomposition of these salts is complete at the same temperature. Since $\text{Ce}(\text{NO}_3)_3$ decomposes at a lower rate, the final temperature of CeO_2 formation from this salt is 15–20°C higher. The maximum decomposition rate is 23.5%/min for $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and 8.4%/min for $\text{Ce}(\text{NO}_3)_3$.

The thermal decomposition curves for the cerium precursors $\text{Ce}(\text{NO}_3)_3$ and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ supported on Al_2O_3 are shown in Fig. 3. The decomposition of supported $\text{Ce}(\text{NO}_3)_3$ comes to completion at a considerably lower temperature than the decomposition of the bulk salt.

Table 2. Observed and calculated weight loss data for the thermal decomposition of γ - Al_2O_3 -supported cerium ammonium nitrate

Temperature range, °C	Weight loss, %		Decomposition step
	observed	calculated	
140–185	2.2	2.0	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6 \longrightarrow \text{Ce}(\text{NO}_3)_4 \cdot 2\text{HNO}_3$
185–285	13.2	13.5–13.4	$\text{Ce}(\text{NO}_3)_4 \cdot 2\text{HNO}_3 \longrightarrow \text{CeO}(\text{NO}_3)_2$
285–510	5.5	5.9	$\text{CeO}(\text{NO}_3)_2 \longrightarrow \text{CeO}_2$

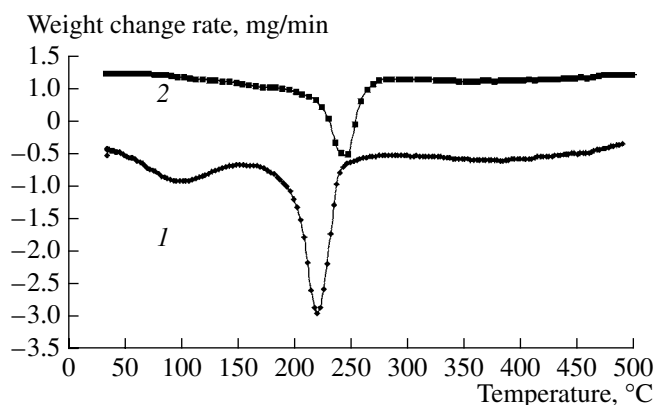


Fig. 3. Decomposition of γ -Al₂O₃-supported cerium precursors: (1) Ce(NO₃)₃/Al₂O and (2) (NH₄)₂Ce(NO₃)₆/Al₂O₃. The supported salt content is 10 wt %.

Properties of Catalysts Prepared by Different Procedures

X-ray diffraction demonstrated that the SSTS of ceria and palladium on the γ -Al₂O₃ surface exerts no effect on the structure of the support. The CeO₂ particle size in the Pd-CeO₂/Al₂O₃ catalyst prepared by the standard procedure was 15–20 nm. The diffraction patterns from all samples obtained by SSTS from cerium ammonium nitrate and a cerium nitrate–citric acid mixture showed no reflections from CeO₂ even when the active component content was as high as 10 wt %. Apparently, most of the cerium oxide in these samples was amorphous to X-rays. It is possible that the violent gas evolution during the self-propagating reaction between the precursors of the active component caused CeO₂ dispersion of on the support surface. The palladium content of all samples was below the detection limit of the X-ray powder diffraction method.

According to the data presented in Table 3, the specific surface area of the Pd-CeO₂/Al₂O₃ catalysts depends strongly on the preparation procedure. For the catalysts prepared by SSTS procedures 1a, 1b, and 2, S_{sp} is 34–36 m²/g larger than S_{sp} for the sample synthesized by standard procedure 3 and is nearly equal to the specific surface area of γ -Al₂O₃ (150 m²/g).

Activity of the Catalysts in the Conversion of Toxic Components of the Exhaust Gas

The temperature dependences of NO conversion into N₂ on the catalysts prepared using the above procedures are plotted in Fig. 4. The 1% Pd–10% CeO₂/Al₂O₃ catalyst prepared using SSTS procedure 1b is the most active; the 50% conversion of NO to N₂ is reached at 237°C. At 285°C, the NO conversion is 87%.

The 50% conversion of NO on the catalyst prepared by procedure 1a is reached at a higher temperature than the same NO conversion on the catalyst prepared by

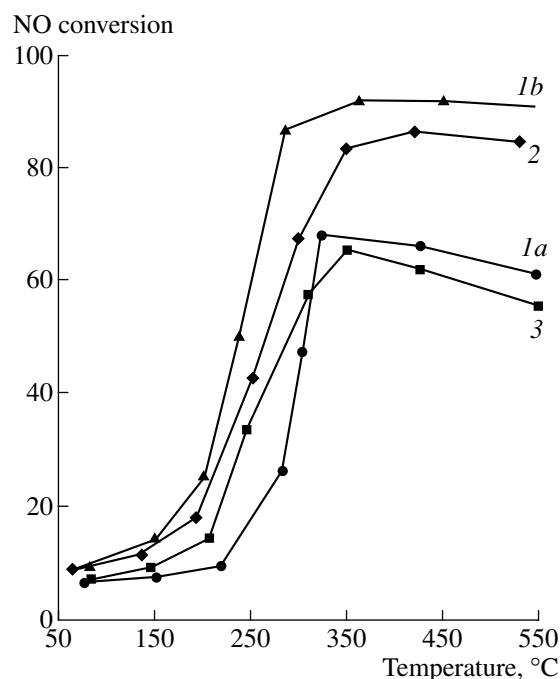


Fig. 4. Temperature dependence of the NO conversion in N₂ on catalysts prepared by different procedures. The curves are numbered in the same way as the synthetic procedures.

conventional procedure 3. However, above 310°C, the activities of these catalysts are nearly equal. A possible explanation for the higher activity of the sample prepared by procedure 1b is that, in the sequential synthesis, palladium is more finely dispersed on the CeO₂ surface and is more efficiently involved in the catalytic process.

As is clear from Fig. 5, the highest activity in the total oxidation of methane and propane is again shown by the catalyst obtained by SSTS procedure 1b. The complete conversion of methane and propane on this catalyst is reached at 435 and 330°C, respectively.

The 50 and 100% CO conversion temperatures for the catalysts containing 0.5 and 1.0 wt % Pd are listed in Table 4. In CO oxidation, a model reaction, complete CO conversion on the catalysts prepared by SSTS procedures 1b and 2 is reached at much lower temperatures than complete CO conversion on the catalyst synthe-

Table 3. Specific surface area of catalysts prepared by different procedures

Preparation procedure	S_{sp} , m ² /g
1a	143
1b	142
2	144
3	108

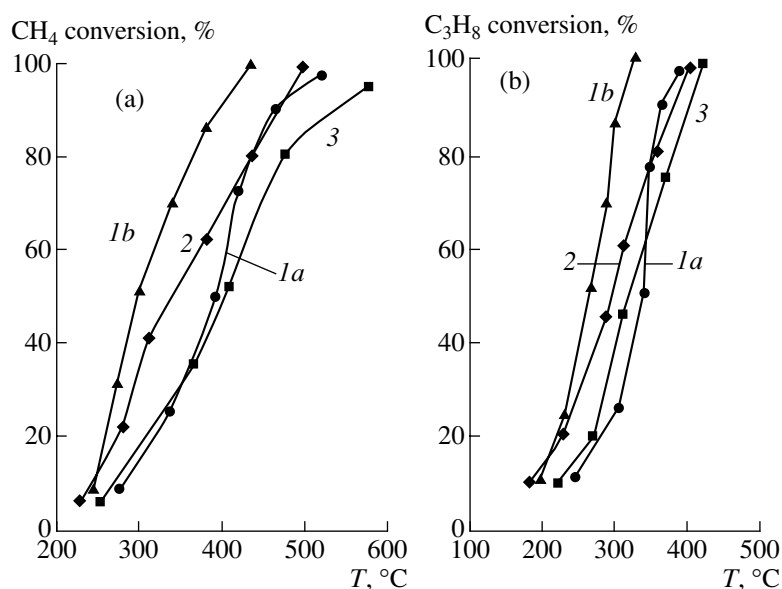


Fig. 5. Temperature dependence of the extent of the total oxidation of (a) methane and (b) propane on catalysts prepared by different procedures. The curves are numbered in the same way as the synthetic procedures.

sized by conventional procedure 3. In all cases, raising the palladium content from 0.5 to 1.0 wt % increases the activity of the catalyst. Note that the 100% conversion of CO on the 0.5% Pd–10% CeO₂/Al₂O₃-1b catalyst prepared using procedure 1b is reached at approximately the same temperature as complete CO conversion on the 1% Pd–10% CeO₂/Al₂O₃-3 catalyst, whose palladium content is twice as high.

Thus, the highest activity in all four reactions examined is exhibited by the Pd–CeO₂/Al₂O₃ monolith catalysts prepared by the SSTs of ceria from cerium ammonium nitrate (procedure 1b). Next in activity are the catalysts prepared by SSTs using a supported mixture of cerium nitrate and citric acid (procedure 2) followed by

modifying the product with palladium by conventional impregnation.

Thus, this study resulted in self-propagating synthetic procedures for obtaining automotive monolith Pd–CeO₂/Al₂O₃ catalysts from different precursors, namely, (NH₄)₂Ce(NO₃)₆ and a mixture of Ce(NO₃)₃ and citric acid.

The decomposition of the cerium precursors was studied in detail by the TG–DTA method in combination with mass spectrometric analysis of intermediate products. Decomposition routes were suggested to explain the thermal behaviors of bulk and γ -Al₂O₃-supported cerium ammonium nitrate.

Finely dispersed ceria obtained by self-propagating synthesis on the support surface has a larger specific surface area than the sample obtained by the conventional procedure. The catalysts prepared by SSTs are much more active in the reactions involved in automotive emission mitigation than their counterparts obtained by the conventional method. The 100% conversion of NO on the SSTs catalysts is reached at 350–400°C; 100% CO conversion, at 110–125°C. The temperatures of complete methane and propane conversion on these catalysts are 430–520 and 330–380°C, respectively.

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Table 4. Temperatures of 50 and 100% CO conversion on palladium containing catalysts prepared by different procedures

Catalyst	Preparation procedure	$T_{50}, ^\circ\text{C}$	$T_{100}, ^\circ\text{C}$
0.5% Pd–10% CeO ₂ /Al ₂ O ₃	1a	121	160
1% Pd–10% CeO ₂ /Al ₂ O ₃	1a	90	125
0.5% Pd–10% CeO ₂ /Al ₂ O ₃	1b	98	131
1% Pd–10% CeO ₂ /Al ₂ O ₃	1b	73	110
0.5% Pd–10% CeO ₂ /Al ₂ O ₃	2	105	144
1% Pd–10% CeO ₂ /Al ₂ O ₃	2	80	119
0.5% Pd–10% CeO ₂ /Al ₂ O ₃	3	117	165
1% Pd–10% CeO ₂ /Al ₂ O ₃	3	88	132

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