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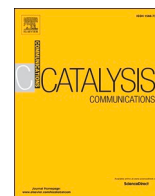Part of the Biochemical and Biomolecular Engineering Commons

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Short communication

The effects of ceria loading on three-way catalysts for passive SCR operation

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A B S T R A C T

Passive SCR systems, which employ both a three-way catalyst and SCR catalyst, are effective for the reduction of nitrogen oxide (NO_x) emissions from lean burn gasoline engines. However, questions remain regarding the effect of three-way catalyst formulations on their performance in these systems. Here, $Pd/CeO_x/Al_2O_3$ catalysts with variable CeO_x loading were synthesized, characterized, and evaluated to determine the effects of CeO_x on catalyst performance. While a small amount of ceria was beneficial for promoting essential reactions, excess ceria was detrimental due to the increase in oxygen storage capacity. Additionally, insights into potential reaction pathways for NH_3 production were determined.

1. Introduction

Passive selective catalytic reduction (pSCR) is a potential approach for controlling nitrogen oxide (NO_x) emissions from lean burn gasoline engines [1]. These engines are more efficient than conventional, stoichiometrically operated engines [2]. However, because of the excess oxygen in the exhaust, while the engine is operating lean, it is not possible to reduce NO_x in the exhaust with a traditional three-way catalyst (TWC). Passive SCR employs both a close coupled TWC and a downstream SCR catalyst. The system works by periodically operating the engine in a fuel-rich regime. This provides the TWC with enough reductants to reduce the NO_x in the exhaust to ammonia (NH_3). This NH_3 is stored on a downstream SCR catalyst, typically a Cu-exchanged zeolite. During fuel-lean operation, the stored NH_3 is used to reduce the NO_x in the exhaust. This approach avoids the need for additional hardware typically used in diesel SCR applications, which require urea storage tanks and injectors.

While much research has been conducted to optimize TWC activity for traditional stoichiometric operation, commercially available formulations have not yet been designed around the needs of a pSCR system. Three-way catalyst components can have a significant effect on the production of NH_3 in a pSCR system. Many of these differences have been investigated in previous literature. Adams et al. [3] investigated the differences in NH_3 production when adding barium or ceria to the catalyst formulation, showing that ceria addition is useful when CO is used as a reductant in NH_3 production. Another study by Adams et al.

[4] investigated the effectiveness of Pd-based vs. Pt-based catalysts for the operation of pSCR, showing that Pd was more effective due to its increased activity for the water-gas shift reaction at lower temperatures. Water-gas shift is important for pSCR since it converts the criteria pollutant CO to CO_2 and H_2, mitigating CO emissions during fuel-rich operation.

Ceria is often used in commercial TWCs for several beneficial attributes [5–7], including oxygen storage and promotion of the water-gas shift reaction. Oxygen storage is a beneficial attribute of TWCs on stoichiometrically operated gasoline engines because it allows for the oxidation of CO and HCs during brief oscillations into rich operation. Ceria loading also promotes water-gas shift, which is highly beneficial in a pSCR system because it aids in the production of NH_3 and, as previously mentioned, mitigates CO emissions [8,9]. This increase in water-gas shift reaction activity should plateau at fairly low ceria loading because the reaction occurs at the interface between the ceria and precious metal [10]. However, in a pSCR system, high levels of oxygen storage inhibit the reduction of the catalyst at the beginning of the rich phase, preventing NH_3 formation for a significant portion of the rich phase, as shown in a previous work [11]. This effect should scale with the amount of ceria in the formulation. To balance these effects, there will likely be an optimum ceria loading for NH_3 production. No research to date has isolated these individual effects of ceria on TWC performance in pSCR.

In the present work, model $Pd/CeO_x/Al_2O_3$ catalysts have been synthesized to investigate the effects of variable ceria loading on TWC

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performance in pSCR. Pd was used as the PGM due to its high pSCR performance as reported in previous evaluations [12]. The catalysts have been characterized using BET analysis and x-ray diffraction (XRD), and have been evaluated for their catalytic activity in a flow reactor. The activity measurements were focused on the production of NH_3 using H_2 or CO as a reductant, as well as the production of H_2 from the water-gas shift reaction under cycling conditions. These measurements allowed us to directly track the multiple effects ceria has on the performance of TWCs in pSCR systems.

2. Experimental

2.1. Catalysts preparation

Several model $Pd/CeO_x/Al_2O_3$ catalysts were synthesized to investigate the effects of Ce loading on several reactions in a pSCR system. The formulations are shown in Table 1. The $Pd/CeO_x/Al_2O_3$ samples were synthesized with 1 wt% Pd and 0–10 wt% Ce. The model catalysts were synthesized via sequential wet impregnation of Ce then Pd onto a γ-Al_2O_3 support. After each impregnation, the catalysts are calcined in air for 3 h at 650 °C.

2.2. Catalysts characterization

Powder XRD was used to characterize the catalysts synthesized via wet impregnation and identify what crystalline phases were present in each sample. The instrument was a Rigaku Mini Flex II diffractometer using Cu Kα radiation. The calcined powdered catalyst samples were scanned at 2θ values between 10° and 80° to capture all observable peaks in the samples. Additionally, the crystallite size was estimated using the Scherrer equation (Eq. (1)). This equation allows for the estimation of the crystallite size (τ) from the x-ray wavelength (λ), the full width at half maximum of the peak (β), and the Bragg angle of the peak (θ), and K the crystallite geometrical shape (K = 0.9 for sphere).

$$\tau = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

Additionally, surface area ($m^2\ g^{-1}$) measurements were conducted on the calcined catalyst samples using a Autosorb-1-C analyzer produced by Quantachrome. Samples were outgassed at 180 °C overnight before analysis. Physisorption isotherms were collected under N_2 gas flow and the surface areas were determined through a multipoint BET analysis.

2.3. Catalysts performance evaluation

The powder catalysts were evaluated in a flow reactor (quartz U-tube). The introduction of gases into the reactor was controlled through several mass flow controllers. Water was introduced into the apparatus through a temperature-controlled bubbler. The temperature of the catalyst was controlled through a furnace surrounding the quartz tube. During the reaction, the catalyst effluent gas was analyzed with an MKS MultiGas 2030HS gas phase Fourier transform infrared (FTIR) spectrometer.

The catalysts were pre-reduced at 550 °C in 1% H_2 and 5% H_2O before being evaluated using the cycling reactive conditions outlined in Table 2. These reactions were used to evaluate each catalyst for the production of NH_3 when H_2 was used as a reductant (H_2 + NO + H_2O), the production of H_2 from the water-gas shift reaction (CO + H_2O), and the production of NH_3 when CO was used as the reductant

Table 1
Model $Pd/CeO_x/Al_2O_3$ formulations.

Catalyst	1Pd	1Pd 0.5Ce	1Pd 1Ce	1Pd 2Ce	1Pd 5Ce	1Pd 10Ce
Pd Loading	1.0%	1.0%	1.0%	1.0%	1.0%	1.0%
Ce Loading	None	0.5%	1.0%	2.0%	5.0%	10.0%

Table 2
Various feed gas compositions under Rich and Lean reaction conditions.

	H_2 + NO + H_2O		CO + H_2O		CO + NO + H_2O	
Phase	Rich	Lean	Rich	Lean	Rich	Lean
O_2 (%)	0	10	0	10	0	10
H_2 (%)	1	1	0	0	0	0
CO (%)	0	0	1	1	1	1
NO (%)	0.05	0.05	0	0	0.05	0.05
H_2O (%)	5	5	5	5	5	5

(CO + NO + H_2O). In each case, 100 mg of catalyst was evaluated using 333 S cm^3 min^{-1} (evaluated at 0 °C, 1 atm) feed gas volume flow rate balanced by Ar. During each reaction, the catalyst was exposed to 5 min of rich operation, where no O_2 was present, and 5 min of lean operation, where there was 10% O_2 in the reactive gas mixture. The effluent gas was diluted to 1 S L min^{-1} (evaluated at 0 °C, 1 atm) with Ar to improve the time resolution of the FTIR measurements. The performance metrics were calculated during rich operation and averaged across six cycles. Because the system was cycled between lean and rich conditions, the influence of oxygen storage appeared as a delay in the NH_3 production.

3. Results and discussion

The XRD spectra for the $Pd/CeO_x/Al_2O_3$ catalysts after impregnation and calcination are shown in Fig. 1. The catalysts show diffraction peaks corresponding to PdO, CeO_2, and γ-Al_2O_3. From these diffraction patterns, both PdO and CeO_2 are highly crystalline. At low Ce loadings (0.5–1 wt%), the characteristic peaks of CeO_2 are too broad and their magnitude is too low to determine meaningful crystallite size. As the Ce loading is increased, the CeO_2 diffraction pattern becomes dominant, and the CeO_2 particles become larger, up to a maximum of 11.2 nm for the 1Pd10Ce sample (determined from the peak at 2θ = 29 degrees). However, despite the changing relative magnitude of the Pd diffraction pattern, the crystallite size of Pd does not change significantly as more ceria is added, and the Pd maintains a crystallite size of 20–25 nm for all samples (determined from the peak at 2θ = 34 degrees).

The surface areas of the catalyst samples determined from BET measurements are shown in Table 3. Overall, the surface areas of the catalysts did not significantly change based on Ce loading, with all samples showing values in the 47–58 m^2 g^{-1} range. This indicates that the Ce loading does not significantly affect the surface area, and the minor changes in surface area are unlikely to play a large role in catalyst activity.

The rich phase production of NH_3 during H_2 + NO + H_2O exposure over each Ce loading is shown in Fig. 2. Each catalyst shows between 84% and 87% NH_3 yield regardless of temperature or ceria loading. The reason there is little change with respect to ceria loading is likely because the ceria does not play a large role in the reduction of NO by H_2 to form NH_3. This reaction has been shown to occur primarily on the noble metal surface [13]. Because each of these catalysts have sufficient Pd surface area to allow for the reduction to occur, they show similar activity.

Fig. 3a shows the production of H_2 from CO + H_2O exposure. The H_2 production is measured based on the disappearance of H_2O, tracked by gas phase FTIR. Here, there is a significant dependence of H_2 production on the ceria loading, which is consistent with previous literature [10,14]. At 350 °C, the 1Pd catalyst has no discernible activity for the water-gas shift reaction. As more ceria is added to the formulation, there is a significant increase in H_2 production at 350 °C, resulting in a H_2 yield of ~ 0.7 at 10 wt% ceria. However, at elevated temperatures of 450–550 °C, increasing the ceria loading beyond 1–2 wt% has a negative effect on the cycle-averaged production of H_2. This is because, at these temperatures, ceria is highly active for oxygen storage [7]. This leads to an inhibition in the reduction of the catalyst, which is a necessary step for H_2 production to begin. This effect is shown in Fig. 3b, which shows
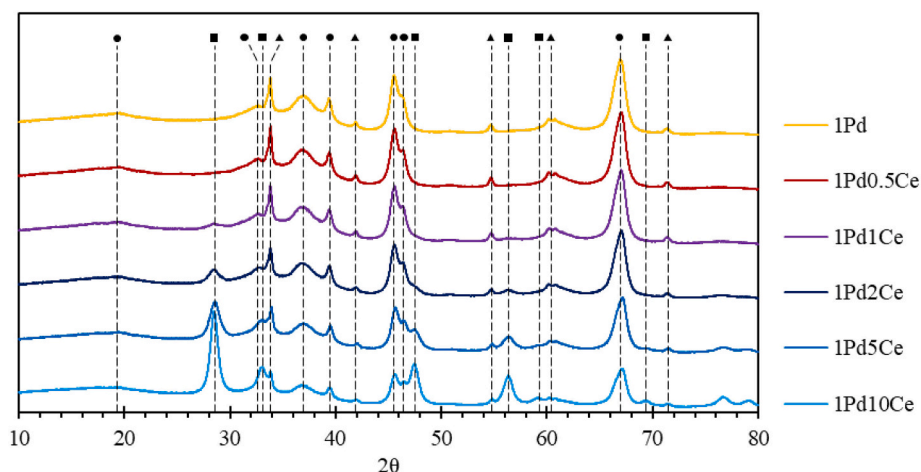
Fig. 1. Powder XRD for $Pd/CeO_2/Al_2O_3$ catalysts. Diffraction peaks for $\gamma\text{-}Al_2O_3$ (●), CeO_2 (■), and PdO (▲) are identified and labeled in the diffraction patterns.

Table 3
Catalyst surface areas determined by BET analysis.

Sample	Surface area m^2 g^{-1}
1 Pd	58.1
1Pd-0.5Ce	52.2
1Pd-1Ce	54.9
1Pd-2Ce	54.1
1Pd-5Ce	47.0
1Pd-10Ce	47.6
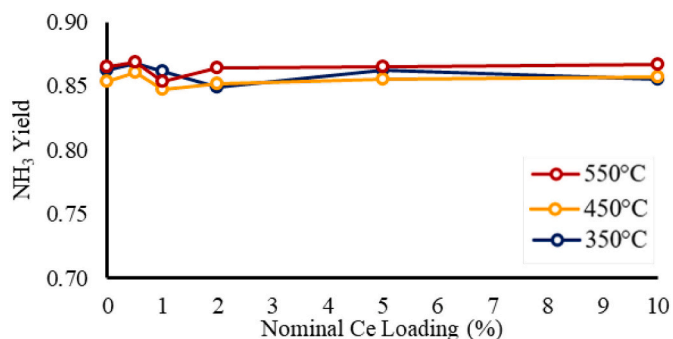
Fig. 2. Rich phase production of NH_3 from $NO + H_2 + H_2O$ during lean/rich cycling operation.

the rate of H_2 production as a function of time since the beginning of rich operation. The 1Pd—10Ce catalyst sample takes ~20 s longer to begin producing H_2 than the 1Pd—1Ce catalyst sample at 550 °C. Because of this delay, the presence of excess oxygen storage beyond 1–2 wt% ceria has a negative effect on the overall generation of H_2 from the water-gas shift reaction on a TWC.

Fig. 4 shows the production of NH_3 during exposure to $CO + NO + H_2O$. The trends in this reaction mirrored those of H_2 production quite closely. However, at 350 °C, on the 1Pd catalyst, with no ceria loading, there was still a fractional NH_3 yield of 0.72, when there was negligible water-gas shift activity. Looking at these two reactions together leads to the conclusion that the formation of molecular H_2 is not a necessary step in the production of NH_3 over Pd catalysts. This means that, at least under some conditions, NH_3 production likely occurs through the isocyanate hydrolysis pathway discussed in the literature [15,16]. However, as the ceria content of the catalyst was increased, leading to higher production of H_2, the NH_3 yield also increases notably. Therefore, while it is not strictly necessary to produce H_2, catalysts that enhance the production of molecular H_2 in WGS have a positive impact on the reduction of NO to NH_3. This is further illustrated by looking at higher temperature experiments, where the 1Pd catalyst showed activity for the water-gas shift reaction, and the NH_3 yield increased accordingly. In this reaction, the same detrimental effect of excess oxygen storage was seen at 450 and 550 °C, where ceria content in excess of 2 wt% prevented the reduction of the catalyst and outweighed the beneficial effects.
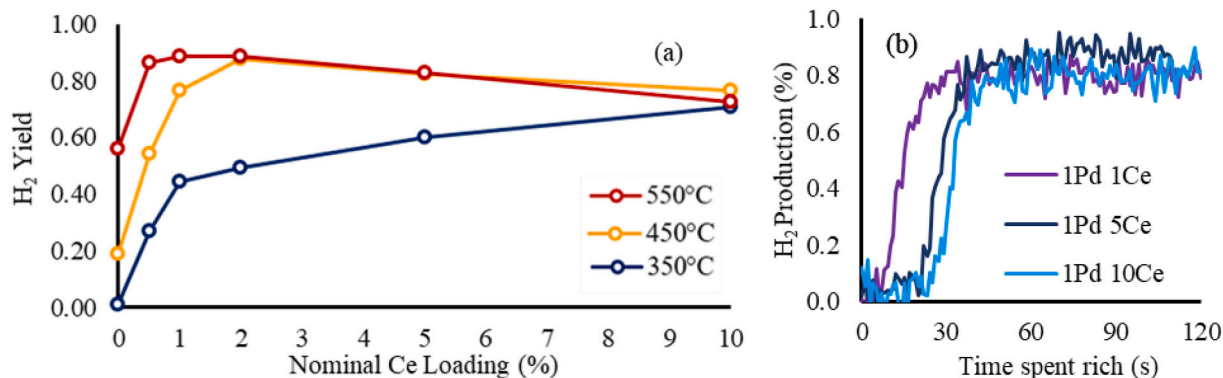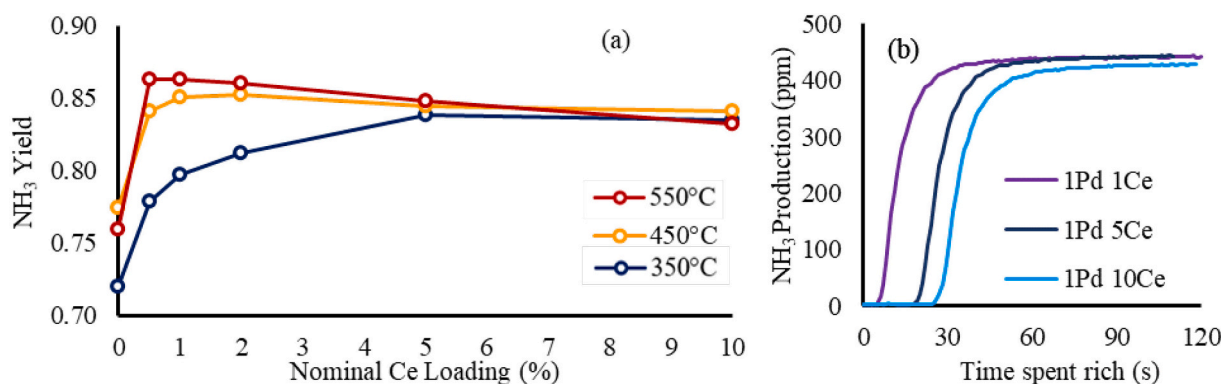

Fig. 3. (a) Rich phase production of H_2 from $CO + H_2O$ during lean/rich cycling operation, (b) time delay in H_2 production at 550 °C after switching to rich operation.

Fig. 4. (a) Rich phase production of NH_3 from $CO + NO + H_2O$ during lean/rich cycling operation, (b) time delay in NH_3 production at 550 °C after switching to rich operation.

4. Conclusions

Understanding the fundamental role(s) of each component and promoter in commercially formulated automotive catalysts is an ongoing challenge. This is particularly relevant in the implementation of pSCR, where a catalyst must operate under several reactive conditions effectively. In this work, it was shown that ceria loading does not have a significant effect on the NH_3 production when H_2 is used as a reductant. However, the loading of ceria did have a large impact on the production of H_2 from the water-gas shift reaction. The ceria-free 1Pd catalyst showed no H_2 production at 350 °C, while adding even 0.5 wt% ceria increased the H_2 yield to 25%. Still, the 1Pd catalyst showed high activity to produce NH_3 at 350 °C when CO was used as a reductant despite showing no activity for the water-gas shift reaction at the same temperature. This indicates that it is possible to produce NH_3 over Pd without the formation of molecular H_2, which suggests that, at these low operating temperatures, the isocyanate hydrolysis pathway illustrated in previous literature might play a role. Adding 0.5 wt% Ce allowed for the catalyst to be active for the water-gas shift reaction and greatly improved the NH_3 yield, showing that the production of molecular H_2 is still greatly beneficial to the production of NH_3. However, when more than 2 wt% ceria was added to the catalyst formulation, the overall cycling activity began to suffer at elevated temperatures. This is because the oxygen storage provided by ceria inhibits the reduction of the catalyst, which prevents the formation of NH_3 for a longer period of rich operation under cycling conditions. Based on these results, a ceria loading of 0.5–2 wt% appears to be optimal for TWC formulations intended for use in pSCR applications.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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