Efficient low temperature lean NO_x reduction over Ag/Al_2O_3—A system approach

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ABSTRACT

This study focuses on lean NO_x reduction (LNR) by n-octane using silver–alumina based catalysts, with the addition of hydrogen. The work takes a system approach, where parameters such as temperature, reformate gas composition, fuel penalty and realistic monolith samples are considered. The LNR catalyst samples were prepared by impregnation and sol–gel methods and the NO_x reduction performance was characterized by flow-reactor experiments, where realistic engine-out gas compositions were used. The hydrogen feed over the LNR catalyst samples was determined via data achieved by autothermal reforming experiments over a rhodium based catalyst, using real diesel as feedstock. The LNR catalyst samples generally show an enhanced NO_x reduction when hydrogen is added to the gas feed. In particular, a 2 wt% silver–alumina sample with the addition of minute amounts of platinum, shows a high increase in NO_x reduction when hydrogen is added to the feed. The addition of CO, a potential poison in the reaction and a by-product from the reforming, did not show any significant effect on the LNR catalyst performance at the conditions used. This is beneficial, since it renders a CO clean-up step in the reformer system unneeded. Ammonia formation is discussed in terms of a possible dual-SCR system. Finally, the fuel penalty for hydrogen production and hydrocarbon addition is taken into consideration. It is found that an addition of 1000 ppm H_2 leads to unacceptable fuel penalties.

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1. Introduction

Combustion in excess oxygen, as in diesel- and lean-burn engines, can significantly improve the fuel economy for automotive engines, thus reducing the formation of CO_2. However, the lean environment in the exhaust gas obstructs the ability of the conventional three-way catalyst to reduce NO_x. New strategies for efficient lean NO_x reduction must therefore be developed. In connection to this, fuel cell auxiliary power (FC-APU) and hydrocarbon selective catalytic reduction (HC-SCR or LNR) units are proposed as two major strategies as ground for introducing hydrogen in the transport sector to reduce emissions.

A promising catalyst for HC-SCR is silver–alumina [1–7], over which high conversion of NO_x to N_2 with hydrocarbons as reductant has been demonstrated [2,7–13]. However, poor performance at low temperatures, typically 150–300 °C, is a drawback since efficient NO_x abatement at these temperatures is required e.g. diesel engine exhausts. By using long-chained hydrocarbons the SCR reaction has previously been shown to

proceed at lower temperatures and with wider activity window, compared to using shorter hydrocarbons [11,14,15]. The reason for this effect is suggested to be related to the lower activation (i.e. partial oxidation) temperature for longer hydrocarbons, compared to shorter ones [15,16]. Furthermore, results show that the addition of small amounts of hydrogen drastically improves the low-temperature activity, first reported by Satokawa [17] in 2000.

On-board fuel processing of liquid hydrocarbon fuels is a way to supply hydrogen to a vehicle by using the existing fuel infrastructure. The hydrogen can be used either for avoiding operation of a truck engine at stand-still by using an APU system, or to increase the low-temperature activity of silver-based NO_x reduction catalysts. The latter option will be discussed in this paper. An FC-APU system could also be used in marine applications or as a range extender in a fuel cell vehicle. The critical step in the reforming process is the evaporation and catalytic conversion of the hydrocarbon fuel into a hydrogen-rich reformate. Rh-based monolithic catalysts have proven to be very active for autothermal reforming (ATR) of diesel [18]. Furthermore, these catalysts have shown a high selectivity and a good durability while using commercial diesel fuels.

Limited number of studies can be found in the open literature where the performance of a HC-SCR catalyst has been investigated using both diesel reformate and exhaust gas as feedstocks [19,20].

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Table 1
Washcoat properties for the powder support and catalyst (ATR) used in this study. For the powder catalyst, the subscripts in the molecular formula reveal the nominal weight loading of the active metals and promoters on the alumina support. The surface area and porosity were measured by N_2-BET while the crystallite size of ceria was measured by XRD using the Scherrer equation at Bragg angle $2\theta = 28.5°$.

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)	$d_p(CeO_2)$ (nm)
δ-Al_2O_3	105	0.92	349	–
$Rh_{1.0}Pt_{1.0}Ce_{10}La_{5.0}/\delta$-$Al_2O_3$	88	0.60	270	8.0

Along with hydrogen production also carbon monoxide is formed in the reformer system. For use in e.g. a polymer electrolyte fuel cell (PEFC) based APU system, high CO levels (>10 ppm) is a major drawback since it poisons the electrodes in the fuel cell [21]. In the NO_x reduction, however, the effect of CO is not necessarily negative. Furthermore, production of hydrogen in a fuel reformer causes a fuel penalty, which, together with the need for a reducing agent in the LNR unit (*i.e.* fuel), should be minimized in order to maintain high fuel economy. Many studies in the literature reports on the effect of hydrogen on the NO_x reduction over the silver–alumina system, and often the hydrogen concentration is high (ranging between 1000 ppm and 1 vol.%) [22]. One possible side effect of hydrogen addition to the silver–alumina catalyst is the formation of ammonia, which is mainly considered as negative, as ammonia is harmful for the environment. However, attempts have been made in order to use the formed ammonia in a NH_3-SCR catalyst after the HC-SCR catalyst. The concept has been shown by DiMaggio et al. [23], where remaining NO_x species are reduced by the ammonia formed over the HC-SCR catalyst.

The aim of the present study is to investigate how various parameters, such as hydrogen and carbon monoxide concentration, affects the NO_x reduction over the silver–alumina system. This work takes a system approach where parameters as temperature and fuel penalty are considered. Furthermore, realistic gas mixtures from exhaust and reformer are used in the experiments and the catalysts are coated on monolith samples to mimic a real system.

2. Experimental

2.1. ATR catalyst preparation

Table 1 shows the washcoat properties of the support and the RhPt-based catalyst used for the ATR experiments. The metal precursors used for the catalyst preparation were Rh nitrate ($Rh(NO_3)_3$, Rh 8–10% (w/w), Sigma–Aldrich), Pt nitrate (($NH_3)_4Pt(NO_3)_2$, Pt 3–4% (w/w), Alfa Aesar), Ce nitrate ($Ce(NO_3)_3\cdot 6H_2O$, 99.99%, Alfa Aesar)) and La nitrate ($La(NO_3)_3\cdot 6H_2O$, 99.9%, Alfa Aesar) solutions. The catalyst was supported on δ-alumina. The δ-alumina was made by calcining γ-alumina (PURALOX HP-14/150, Sasol Germany GmbH) at 1000 °C for 1 h with little loss of surface area. The alumina powder was impregnated with the metals by the incipient wetness (IW) technique in accordance with the nominal weight loading presented in Table 1. The resulting powders were calcined at 800 °C for 3 h and deposited via ethanol-slurry dip-coating procedure onto 400 CPSI cordierite monoliths, with dimensions OD = 17.8 mm, l = 30.5 mm (Corning).

2.2. ATR catalyst characterization

Fresh powder samples of $Rh_{1.0}Pt_{1.0}Ce_{10}La_{5.0}/\delta$-$Al_2O_3$, taken from the catalyst preparation prior to the deposition on the monoliths, were characterized by using the following instruments: surface area and pore size distribution were measured by nitrogen sorption at 77 K using a Micromeritics ASAP 2010 instrument. Approximately 0.4 g powder was used and degassed at 250 °C for 3 h prior to analysis.

The crystal phases were determined by X-ray diffraction (XRD), using a Siemens Diffraktometer D5000 scanning 2θ from 10° to 90° in the scan mode (0.02°, 1 s), using Ni filtered Cu Kα radiation.

Temperature programme reduction (TPR) was performed at 30–1000 °C, 10 °C/min, with hydrogen as adsorbate using a Micromeritics Autochem 2910 equipped with a TCD. Approximately 0.1 g powder was used for the analysis.

The surface composition and chemical state of the deposited additives and loaded active metals were determined using X-ray photoelectron spectroscopy (XPS). The XPS studies were performed in a Phi Quantum 2000 system.

2.3. ATR experiments

The diesel reforming experiments were carried out at reactor inlet temperature of 650 °C and atmospheric pressure. A standard diesel fuel ($\sim$C/H = 6.43 (weight ratio), $\sim$6 ppm S,) whose physical and chemical properties are in close correlation to Swedish Environmental Class 1 diesel (MK 1) [24], was used as feedstock. The following operating parameters were employed: H_2O/C = 3.0, O_2 = 0.49 (λ = 0.33), GHSV $\sim$ 17,700 h^{-1} and time on stream (TOS) $\sim$3 h. The experiments were carried out in a vertically mounted stainless steel tubular reactor with ID = 23.7 mm equipped with three thermocouples. The product gases were analyzed using a Gasmet Cr-200 Fourier Transform Infrared Spectroscopy (FTIR) and a Maihak modular system S710 equipped with non-dispersive infrared sensor (NDIR) and thermal conductivity detector (TCD).

2.4. LNR sample preparation

The LNR catalyst samples were prepared via wet impregnation and two single step sol–gel methods, as described previously [25]. The wet impregnation was performed by adding an Ag/EDTA-complex solution to a water based γ-Al_2O_3 slurry (SBa200, Sasol), which was kept under stirring for 2 h ($AgNO_3$ ($\geq$99%, Sigma–Aldrich) as precursor) while the pH was kept at 6.3 by nitric acid (10%, Fluka) addition. The slurry was subsequently freeze-dried and calcined at 600 °C. In the sol–gel methods, aluminum isopropoxide (AIP; 98+%, Aldrich) and silver nitrate were used as precursors. The formed gel was subsequently dried (thermally at 100 °C or by freeze-drying) followed by calcination at 600 °C, and was then crushed to a fine powder. All samples were washcoated onto monoliths (400 CPSI, length 20 mm, 21 mm OD), using 20 wt% boehmite as binder. Further details about the preparation methods and the washcoating have been presented previously [25].

To activate the hydrocarbon for NO_x reduction in the SCR reaction, it is necessary to partially oxidize the hydrocarbon [12]. Platinum is a known oxidation catalyst, and can thus act as oxidation sites on the catalyst. However, the oxidation must be mild enough not to combust the reductant, but high enough to partially oxidize the hydrocarbon, preferably at low temperatures (below 300 °C). To achieve these properties of the catalyst, a minute amount of Pt (100 ppm by weight) was added to a catalyst containing 2 wt% Ag (nominal) prepared by sol–gel with freeze-drying. The platinum was added as a diluted (1000 ppm Pt by weight) platinum