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Effect of water vapor on the activity and stability of Pd/SZ and Co/ZrO_2 in dual-catalyst treatment of simulated exhaust from lean-burn natural gas engines

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ABSTRACT

A dual-catalyst system, consisting of an NO oxidation catalyst component (Co/ZrO_2) and a NOx reduction catalyst component (Pd/SZ) was investigated for selective catalytic reduction of NOx under lean conditions. The integrated catalyst system is capable of performing three-distinct catalytic functions, namely, NOx reduction, combustion of unburned hydrocarbons and oxidation of carbon monoxide. The hydrothermal stability of the dual-catalyst system was investigated through steady-state and time-on-stream measurements. Water vapor was found to inhibit the NOx reduction activity of Pd/SZ, whereas it had no effect on NO oxidation over Co/ZrO_2. The dual-catalyst system was capable of retaining stable catalytic activity during simulated lean exhaust treatment in the presence of 7% H_2O.

1. Introduction

Lean-burn natural gas reciprocating engines constitute a well-understood, simple and inexpensive technology that reaches higher efficiencies and produces significantly cleaner exhaust emissions than the rich-burn alternatives [1]. These engines are increasingly popular for distributed power generation. Lean-burn operation results in cleaner engine-out exhaust, but the exhaust stream still contain significant levels of carbon monoxide, unburned hydrocarbons and nitrogen oxides (NOx). The current aftertreatment technologies for emissions abatement from stationary sources utilize NH_3 as the reducing agent, but these technologies have several drawbacks concentrated around ammonia slip and direct oxidation, corrosion of the downstream equipment due to ammonium salts, and infrastructure requirements [2]. The three-way catalyst technology used in mobile applications is unsuitable for lean-burn natural gas engines since it is ineffective under lean-burn conditions [3]. Significant research efforts have been devoted to the development of aftertreatment technologies that would utilize unburned hydrocarbons that are available in the exhaust stream as the reducing agents for NOx reduction. Methane has attracted particular attention as the reducing agent since it is readily available as the major component of natural gas and it is the least expensive lower hydrocarbon. Although methane is readily available, effective utilization of methane as the reducing agent in a hydrocarbon–SCR system is a significant challenge due to the difficulty of activating methane and the competition from combustion of the hydrocarbon in the presence of excess oxygen [4,5].

Palladium-based catalysts supported on zeolites and other acidic supports are among the most widely studied catalysts for selective catalytic reduction of NOx with CH_4 under lean conditions [6]. Nishizaka and Misono [7,8] were the first to report a link between the acidity of the support and activity in NOx reduction. Later it was established by a number of studies that Pd^{2+} ions were the active sites for the NOx reduction reaction [9] whereas, PdO aggregates showed activity for CH_4 combustion [10,11]. The role of acidic supports in stabilizing palladium in the form of Pd^{2+} ions was shown by Resasco and coworkers [9]. Further work by Resasco and coworkers [12] showed that protons associated with surface sulfate groups served as anchoring sites for Pd^{2+} ions over Pd/SZ. Although zeolite-supported Pd catalysts showed high CH_4–SCR activity, the major drawback of these catalysts was their poor stability under reaction conditions. Studies on the deactivation of zeolite-supported Pd catalysts showed agglomeration of bulky PdO particles outside the zeolite pores by hydrothermal treatment [13,14] and by extended time-on-stream [11,15,16]. On most of the zeolite systems, leaching of aluminum under hydrothermal conditions from tetrahedral sites within the zeolite framework to locations in zeolite pores was reported to result in the formation of PdO aggregates and loss of metal dispersion [17]. Sulfated zirconia (SZ) supported palladium catalysts showed better hydrothermal

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stability than their zeolite-based counterparts [18]. Quincoces et al. [19] reported a reversible decrease in both NO reduction and CH_4 combustion activity of Pd–Co/SZ in the presence of water vapor accompanied with a shift in the optimum operating temperature to higher temperatures. Figueras et al. [20] showed that water resulted in a reversible decrease in the NOx reduction activity of Cu/SZ, but these authors did not observe a change in the optimum operating temperature window. Further work on the effect of water vapor on NOx reduction over SZ [21,22] showed leaching of sulfate during reaction in the presence of water vapor and Resasco and coworkers [21] reported that this sulfate leaching resulted in a permanent loss in the selectivity of Pd/SZ. Bimetallic palladium catalysts were also investigated for improving NOx reduction activity and hydrothermal stability. Platinum incorporation into Pd/SZ [18,23] and Pd/MOR [24] has been shown to improve both the hydrothermal stability and the catalytic activity. Similar synergistic effects were reported on Co-promoted Pd catalysts supported on MFI [25], MOR [26], ferrierite [27], ZSM-5 [28] and SZ [29]. The improved activity was associated with the activity of the second metal ion in catalyzing NO oxidation to NO_2 in a reaction scheme where Pd ions served as sites for NO_2 reduction [23,28].

Previously, we have reported a novel integrated oxidation/selective catalytic reduction approach to combine three-distinct catalytic functions, namely NOx reduction, CO oxidation and hydrocarbon combustion in a single unit to be utilized for treatment of lean-burn natural gas engine exhaust, without the need for additional fuel injection [30,31]. This approach aims to take advantage of the stronger oxidizing potential of NO_2 relative to NO by utilizing two separate catalytic systems for oxidizing NO to NO_2, and then reducing NO_2 to N_2 with unburned methane available in the lean-burn engine exhaust. NO oxidation to NO_2 is an exothermic and reversible reaction that is thermodynamically limited at high temperatures [32], however, when this reaction takes place in close proximity to a reduction catalyst, NO_2 is removed from the system through SCR reaction, pushing the thermodynamic limitations posed on the system by shifting the equilibrium towards products. The oxidation catalyst also serves to replenish NO_2 that is converted to NO through partial reduction, leading to significantly higher N_2 yields than utilization of an SCR catalyst alone. The oxidation catalyst further takes part in the combustion of excess hydrocarbons and oxidation of carbon monoxide that have not been consumed during the selective catalytic reduction reaction [30]. The dual-catalyst approach has focused on simultaneous development of two separate catalytic systems, which will be physically mixed together. Through this approach, Co-based oxidation catalyst formulations which are able to achieve equilibrium conversions at temperatures as low as 250 °C and gas hour space velocities (GHSV) of 35,000 h^{-1} were developed [33]. Palladium catalysts supported over sulfated zirconia prepared by impregnation of commercial monoclinic zirconia (SZ) support has been reported to give good NO_2 reduction activity with CH_4 around 375–400 °C [34]; however, addition of water vapor to the feed stream resulted in suppression of both NOx reduction and hydrocarbon oxidation activities of the dual-catalyst bed tested under simulated lean exhaust conditions [30]. In a later contribution, we have reported a 'one-pot' sol–gel Pd/SZ catalyst which exhibited significant NO_2 reduction activity around 400–450 °C [35]. As a continuation of our earlier work on dual-catalyst approach for aftertreatment of lean-burn natural gas engine exhaust, in this contribution, we examine the interaction of water vapor with the oxidation and reduction catalyst components of the dual-catalyst scheme, namely Co/ZrO_2 and Pd/SZ, and its implications on the activity and hydrothermal stability of a dual-catalyst bed comprised of these catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

NOx reduction catalyst component (0.3% Pd/SZ) was prepared using a single-step sol–gel procedure which was described in detail earlier [35]. The procedure uses acetic acid as a controlled hydrolysis agent to slow down hydrolysis of zirconium and promote anchoring of sulfur into the zirconium network. Palladium acetate (Aldrich), zirconium propoxide (70% solution in n-propanol, Aldrich) and sulfuric acid (Fisher Sci.) were used as the precursors. A calculated amount of palladium acetate, to give 0.3% Pd loading in the final catalyst, is dissolved in n-propanol and calculated amounts of zirconium propoxide and sulfuric acid were added under constant stirring to achieve final concentrations of 1 M and 0.5 M, respectively. After 30 min of stirring, acetic acid in the amount to give a hydrolysis ratio of 4 is added using a syringe pump, set to deliver 0.2 ml/min of acetic acid. Gelation occurred during the course of 1 h and the gel was dried overnight in a convection oven at 110 °C. The dried gel was ground and calcined at 700 °C for 4 h under continuous flow of oxygen and then, ground to a fine powder before being transferred into vials for storage.

The NO oxidation catalyst (10% Co/ZrO_2) was prepared through an incipient wetness impregnation route using commercial monoclinic zirconia (m-ZrO_2) supplied by Saint-Gobain. The support material, which was received in pelletized form, was ground and sieved to save the 100/150 mesh cut (0.149–0.105 mm). The support was then calcined in air for 3 h at 500 °C. Cobalt nitrate hexahydrate (Aldrich) was used as the precursor. A calculated amount of cobalt precursor to yield 10% loading was dissolved in water and m-ZrO_2 support was impregnated with this solution in two steps. After each impregnation, the catalyst was dried at 110 °C overnight. After the second drying, the catalysts were calcined in air at 500 °C for 3 h. The oxidation catalyst used in this study have been characterized using BET surface area measurements, temperature-programmed techniques, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), laser Raman spectroscopy and diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) and the characterization results have been reported previously [33].

Surface area and pore volume measurements were done on a Micromeritics ASAP 2010 accelerated surface area and porosimetry instrument, using nitrogen adsorption/desorption isotherms collected at liquid nitrogen temperature. BJH pore size distributions (PSD) were determined using the desorption branch of the isotherm. Before measurement, samples were degassed overnight at 130 °C under a vacuum of 3 μmHg. Nitrogen physisorption measurements indicate a BET surface area of 67 m^2/g for Pd/SZ and the BJH pore size distribution calculations are in line with that of a mesoporous material with pore size distribution centered at 4 nm.

The chemical states of zirconium, sulfur and oxygen in Pd/SZ were investigated on a Kratos AXIS Ultra X-ray photoelectron spectrometer, using monochromatized Al Kα (1486.7 eV) X-ray source operated at 13 kV and 10 mA. Sample was supported on a double-sided carbon tape for analysis. For studying the variation of sulfur concentration with information depth, spectra were collected before and after etching the surface with 3 kV Ar^+ ion beam for 3 minutes in two cycles, to remove several layers from the surface at a time. X-ray photoelectron spectrum of Pd/SZ was collected in the Zr 3d, S 2p, O 1s and C 1s regions. Collected data were corrected for charge shifting using standard C 1s binding energy of 284.5 eV. Data analysis with background subtraction and curve fitting was done on XPS Peak 4.1. For quantitative comparison of the variation of surface composition with the removal of surface layers,