

Selective catalytic reduction of nitric oxide over cerium-doped activated carbons



Annappabha Athappan^a, Melanie L. Sattler^{a,*}, Sumathi Sethupathi^b

^a Department of Civil Engineering, University of Texas at Arlington, Arlington, TX, USA

^b Department of Environmental Engineering, Universiti Tunku Abdul Rahman, Malaysia

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ABSTRACT

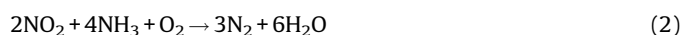
An affordable selective catalytic reduction (SCR) catalyst for nitrogen oxides (NO_x) from diesel engines is needed, which is effective at low as well as high temperatures. The contribution of this study was to directly compare the effectiveness of cerium-doped activated carbons as potential diesel SCR catalysts, via testing under similar conditions. Unmodified and cerium-doped granular activated carbon (GAC), activated carbon fiber (ACF), and multiwall carbon nanotubes (MWCNTs) were tested in a fixed bed column from 100–400 °C for 150 and 500 ppm concentration NO. For 150 ppm NO, CeGAC (with the highest cerium surface weight percent) achieved the highest reduction efficiencies over all temperatures. It maintained these efficiencies over 12 h of durability testing. However, CeGAC was only thermally stable to 310 °C, and its reduction efficiency did not increase at 500 ppm NO, due to limited accessibility of internal pore space. For high NO_x conditions, CeMWCNTs (thermally stable until 412 °C) achieved the highest efficiencies above 280 °C (85% at 300 °C). Additional research is needed to extend the thermal stability of CeGAC or CeACF to higher temperatures, or increase the reduction efficiencies of CeMWCNTs at lower temperatures.

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Introduction

The environmental effects of nitrogen oxides (NO_x) include formation of ground-level ozone, acid precipitation, and fine particles, as well as reductions in visibility. The adverse health effects of NO₂ include airway inflammation and aggravation of asthma. 90–95% of NO_x is emitted in the form of NO from stationary sources and mobile sources burning fossil fuels. In the United States, mobile sources contribute over half of NO_x emissions [1].

The 3-way catalytic converters that have substantially reduced NO_x emissions from gasoline vehicles operate optimally at stoichiometric conditions; thus, they do not work well for diesel engines, which operate in oxygen-rich fuel lean conditions [2]. Exhaust gas recirculation can be used to reduce NO_x in diesel engines, but only achieves reductions of around 50% [3]. Another alternative, selective catalytic reduction (SCR), involves adding a reducing agent (such as ammonia or urea) to reduce NO_x in the exhaust stream, as shown in Eqs. (1) and (2) [2].



Traditional SCR catalysts are based on an active metal oxide phase (usually V₂O₅ or WO₃–V₂O₅) supported on a high surface area metal oxide support (e.g., TiO₂). Typical NO_x reduction efficiencies are around 80% [2].

Although SCR has been widely used for reducing NO_x from stationary sources like coal-fired boilers, challenges still remain in identifying appropriate catalysts for diesel engines, due in part to their wide range of operating temperatures (100–400 °C) [3–6]. Following EPA's 2010 regulation of heavy-duty highway compression-ignition engines and urban buses, selective catalytic reduction became available in most light-duty diesel engines. Although SCR based on zeolites significantly reduces NO_x from these engines, the effective operating temperature is above 300 °C [7]. Pt-based catalysts can be used for low temperatures (150–300 °C), but are expensive [8].

Thus, an SCR catalyst for NO_x from diesel engines is needed, which is effective over the range of 100–400 °C and affordable. This research aims to address that need.

Granular activated carbon (GAC) is one of the most widely-used and cost-effective kinds of carbon. A number of previous studies

* Corresponding author. Fax: +1 817 272 2630.

E-mail addresses: annaathappan@providenceeng.com (A. Athappan), sattler@uta.edu (M.L. Sattler), sumathi@utar.edu.my (S. Sethupathi).

have evaluated the effectiveness of GAC in removing NO_x. Activated carbon-supported metal catalysts (Pt, Pd, Fe, Co, Ni and Cu) have higher NO_x conversions at lower temperatures [9,10]. Among several metals tested (Fe, Co, Ni, V, Mn, Cu, Ce), Ce was reported to have the most promising future due to its nontoxicity and high activity. Peanut shell activated carbon doped with 10 wt% cerium showed better performance in removal of SO₂ and NO_x compared to other metal dopants at temperatures above 300 °C [11]. Cerium has high capacity in storing and releasing oxygen in the surface due to the presence of cerium in two different valance states, namely Ce⁴⁺ and Ce³⁺ [12–14].

Activated carbon in a cloth structure, known as activated carbon fiber (ACF), has a surface area of 1000–2000 m²/g, higher than many traditional activated carbons [15]. ACF has evenly distributed micropores, which gases can access more easily than GAC micropores. ACF also has advantages of low weight, high adsorption capacity, and high regeneration capacity. ACF impregnated with ammonia has achieved 70% NO oxidation at room temperature [16]. The ability of vanadium oxide loaded ACF to reduce NO_x at temperatures ranging from 100 to 250 °C has been examined [17]. No studies, to our knowledge, have evaluated the capacity of Ce-doped ACF for NO_x reduction.

Carbon nanotubes, formed by rolling a graphite sheet into a tube-shaped structure, have received much attention for their potential applications in pollution control. SCR of NO using NH₃ over cerium oxide-doped MWCNTs has shown reduction efficiencies ranging from 70% to 90%, depending on Ce/C ratio, in the temperature window of 250–450 °C [18].

The aforementioned studies have each looked at NO_x reduction using one kind of AC catalyst, under conditions of temperature and NO_x concentration that vary from study to study. The contribution of this study is to directly compare the effectiveness of cerium-doped activated carbons (granular activated carbon, activated carbon fiber, and multiwall carbon nanotubes) as potential diesel SCR catalysts, via testing under similar conditions.

Ce was chosen as a dopant in particular due to its ability to reduce NO_x, non-toxic properties, and relatively low cost. The temperature range tested was based on typical diesel engine exhaust temperatures [19]. Typical concentrations of NO_x in diesel exhaust range from 50 to 700 ppm [20]; a low concentration (150 ppm) and high concentration (500 ppm) were tested in this research.

Material and methods

Catalyst preparation

Activated carbon fiber (ACF) and granular activated carbon (GAC) with mesh size 4x6 were purchased from Calgon Corporation. Catalytic multi-walled nanotubes (MWCNTs) produced by chemical vapor deposition (CVD) were purchased from Materials and Electrochemical Research (MER) Corporation. The nanotubes were 20–25 nm in diameter and 1–5 μm in length. According to manufacturer data, impurities present in the MWCNTs were 1.8 wt

% iron (Fe), 2.6 wt% alumina (Al), and traces (~0.02%) of cobalt (Co), with the rest carbon.

The catalyst impregnation procedure was adapted from previous work by Sumathi et al. [21] which found 10 wt% Ce loading to be optimum for flue gas control. 0.1 g cerium as cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O) was mixed with 100 ml deionized water. Cerium (III) nitrate hexahydrate was chosen because it is water soluble and it is a type of anhydrous salt which does not react with the carbon.

1 g ACF, GAC, or MWCNT was added, and the solution was mixed for 5 h. The solution was then heated to 70 °C and constantly mixed until the water completely evaporated. The wet sample was oven dried for 12 h in a muffle furnace at 110 °C to remove excess water. Finally, the sample was calcined in a tube furnace (Lindberg, type TF55035A) at 500 °C in the presence of Argon (Ar) for 4 h. The metal-doped activated carbon was then designated as CeACF, CeGAC, or CeMWCNTs.

Catalyst characterization

Characterization is important in understanding and analyzing the catalyst. Methods used to characterize the catalyst are described below.

Carbon–hydrogen–nitrogen (CHN) analysis was conducted using a PerkinElmer 2400 Series II CHNO/S analyzer. Samples encapsulated in an aluminum vials were combusted completely in a pure oxygen environment and reduced to the elemental gases CO₂, H₂O, and N₂. The thermal conductivity detector in the instrument detects the percentage of C, H, and N present in the combustion product.

Surface area and pore volume was measured using Micromeritics, ASAP 2000 Series by N₂ adsorption at 77 K. The BET (Brunauer–Emmett–Teller) surface area (S_{BET}) and pore volume were calculated using Brunauer–Emmett–Teller and *t*-plot equation, respectively. Prior to analysis, each sample (about 0.1 g) was placed in an analysis tube and degassed at 300 °C for at least 5 h to remove any adsorbed species from the surface. After degassing, the sample was transferred to the analysis station, where it was cooled in liquid N₂ environment at temperature 77 K. The adsorption–desorption processes were done automatically by software linked to the analyzer.

Bulk density of the activated carbons and catalysts were measured approximately in the laboratory. Each sample was filled up to 1 ml in the small vial after taring and weighed in a digital weighing machine with 4 significant digits. Three replicate density measurements were made and averaged.

Scanning electron microscope (SEM) imaging and energy dispersive spectroscopy (EDS) analysis were obtained using A HitachiS-3000 N integrated with EDS. A small amount (less than 100 mg) of sample was loaded into the specimen chamber. Secondary electron images with high vacuum, 25 kV magnification and working distance 15–25 mm were used to capture high resolution images in sub-micron and nanometer range. EDS with same 25 kV magnification, zero tilt, detention time of 20–40% was

Table 1
CHN and EDS analyses.

Types of sample	CHN analysis		EDS analysis	
	Carbon (wt%)	Hydrogen (wt%)	Cerium (wt%)	Oxygen (wt%)
GAC	83.0	0.31	0	0
CeGAC	80.1	0.86	84.2	1.4
ACF	71.5	2.14	0	4.7
CeACF	56.6	1.47	12.2	10.3
MWCNTs	94.4	1.07	0	4.5
CeMWCNTs	85.9	0.67	2.7	6.8

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