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Development of surface functionalized activated carbon fiber for control of NO and particulate matter

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ABSTRACT

This study investigates the development and potential application of activated carbon fibers (ACF) functionalized with ammonia for control of NO and particulate matter (PM) in diesel engine exhaust. A tubular reactor packed with ACF was used to experimentally study the oxidation of NO at room temperature. Tests were conducted at ACF functionalized with three aqueous ammonia concentrations (3, 5, 10 M), three basic reagents (ammonia, pyridine, amine) and three NO concentrations (100, 300, 500 ppm). After offline investigation, the ACF-packed tubular reactor was installed downstream of the engine's exhaust to ascertain the PM capturing efficiency of ACF. The experimental conditions for PM removal included three weights of ACF (2, 3.5, 4.5 g), three engine loads (0, 25, 50 Nm) and three temperatures (150, 300, 450 °C). The maximum 70% conversion for NO was obtained at NO concentration of 300 ppm for ACF functionalized with 5 M ammonia, whereas maximum 90% reduction in PM was observed at engine load of 25 Nm and 450 °C. The study shows significant potential for the ACF based filters in capturing both homogeneous and heterogeneous pollutants emitted from automobiles. Our previously developed transport model incorporating the mechanism for the oxidation of NO was also used to explain the experimental data.

1. Introduction

The adverse impact of nitrogen oxide (NO) and particulate matter (PM) emitted from diesel engines on atmospheric air quality and human health is well recognized [1,2]. The selective catalyst reduction (SCR) of NO using ammonia, and oxidation at room temperature are the two widely used techniques to control emission of NO from flue gases. V_2O_5 supported on TiO_2 catalyst and other noble metals are preferred for SCR. However, these catalysts may be prohibitively expensive. Majority of PM emitted from diesel engines are nanoparticles, largely consisting of carbon soot, condensed ash from the lubricating oil, condensate of HC and sulfuric acid, and also substantial amount of metallic compounds [3–5]. With regard to the control of PM emitted from diesel engines, a variety of diesel particulate filters (DPF) have been developed in the last decade which essentially rely on the basic principle of collection of the particles on a substrate and their simultaneous oxidation [6–8]. Yet, there are concerns regarding particulate capturing efficiency and regeneration of these filters.

The focus of the present study is on the development of activated carbon fiber (ACF) for the combined removal of NO and PM emitted from the diesel engine. In recent times, ACF has been the interest of a numerous research studies due to the recognition of its multi-facet roles as an adsorbent, a catalyst as well as support to metallic catalyst in the context of air pollution control [9–13]. In the present study, the surface of ACF was modified by incorporating basic functional groups with a view to improving its affinity towards NO for the subsequent oxidation to NO_2. In this context, there are also a number of studies pertaining to the surface functionalization of ACF or active carbons (AC) by using basic agents such as NH_3 and amines, either in liquid or vapor phase [14–17]. The surface functionalization yields in the incorporation of many functional groups such as C=N, C—N, cyclic amide and nitrile group, which is shown to significantly improve the adsorption capacity of the functionalized ACF in comparison to that of the untreated ACF. Nitrogen doping of ACF by the chemical vapor deposition (CVD) of pyridine has also been carried out [18]. The equilibrium NO concentration on the nitrogen-doped ACF is observed to significantly increase in comparison to the untreated ACF.

From the literature survey, it may also be inferred that most of the studies pertain to the applicability of surface functionalized ACF under equilibrium conditions. The present study envisages the development of functionalized ACF for control of NO under dynamic

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(flow) conditions. In our previous studies, it has been experimentally demonstrated that the true performance of an adsorbent for a gaseous species is reflected under flow conditions taking into considerations different mass transfer and kinetic rates, which are absent during equilibrium conditions [9–12].

In the following section, the experimental set-up and procedure used in the study for the preparation of surface functionalized ACF are described. The discussion of the data pertaining to the NO oxidation is presented next. The description of the experimental set-up for ascertaining the efficiency of the prepared ACF in capturing PM from the exhaust of a diesel engine and the data thereof are discussed in the subsequent section. Finally, conclusions are made.

2. NO oxidation

2.1. Experimental

2.1.1. ACF preparation (activation and carbonization)

The raw carbonaceous fibers based on the phenolic resin precursor were procured from Nippon Kynol Inc., Japan. The ACFs were prepared first by carbonizing the raw fibers in an inert atmosphere and then by activation using steam as an oxidizing agent. The details of the experimental set-up and procedure used for activation and carbonization may be obtained from our previous work and are not reproduced here for brevity [11]. In brief, the set-up mainly consisted of the two co-axially mounted tubes made of inconel, which were horizontally placed in a ceramic furnace at a high temperatures ($T \sim 1373$ K). The inner tube ($L = 32$ cm, I.D. = 0.8 cm) was circumferentially perforated with holes of 0.05 mm diameter and 1 cm apart. ACF was wrapped over the perforated section of the inner tube, one end of which was connected to the gas inlet, while the other end was closed, so that the incoming gas flowed into the tubes radially outward through the perforations, the wrapped fiber, and then the outer tube before exiting through the vent.

For carbonization, the raw samples were pyrolyzed at 1273 K. The samples were slowly heated upto the desired temperature at a constant rate of ~3 °C/ min under a small N_2 flow rate (300 sccm). Carbonization was carried out for 90 min. Following carbonization, activation was carried out for 120 min. After activation, the samples were cooled to the room temperature at a rate of 3 °C/ min under a small N_2 flow rate (300 sccm).

2.1.2. ACF surface functionalization

The surface of the ACF samples was functionalized by impregnating them with several basic reagents (ammonia, pyridine, amine, etc.), either in the liquid or vapor phase. Fig. 1a is the schematic of the experimental set-up used in the study of liquid phase impregnation. ACF was wrapped over a perforated glass tube, which in turn was mounted inside a conical flask with provisions made for the water inlet and outlet. One end of the tube was closed. The outer surface of the tube was perforated with holes of diameter 0.1 mm at the center-to-center distance of 4 mm. With the aid of a peristaltic pump, the alkaline solution in a glass container was continuously re-circulated to the inlet of the tube, as shown in the schematic (Fig. 1a). It was observed that this method (impregnation under flow condition) resulted in uniform dispersion of the reagents in ACF as compared to other traditional methods like impregnation by continuously stirring ACF in solution or leaving ACF in the solution under batch condition without stirring. Additionally, the total time of impregnation was considerably reduced (approximately 12 h) as against 20–24 h in other arrangements.

The aqueous solutions of three different basic reagents (ammonia, pyridine, and amine) were used for impregnation in the study. The impregnation time was 12 h, whereas the temperature of the impregnating solution was set between 60 and 80 °C. Tests were conducted at three different aqueous ammonia concentrations (3, 5, and 10 M). The weight of ACF wrapped over the perforated tubular reactor was approximately 5 g during each impregnation run. The flowrate of the reagents was set constant at 20 cm^3 per min by setting the speed of the pre-calibrated peristaltic pump.

Fig. 1b is the schematic of the arrangement used for the vapor phase impregnation of ACF. Nitrogen as a carrier gas was bubbled through a bubbler containing the aqueous alkaline solution of the reagent for impregnation. The temperature of the bubbler was set constant at 40–60 °C with the aid of a Freon refrigeration unit, depending upon the required concentration of the vapor in the carrier gas. The concentration of the aqueous solution was the same as that used in the liquid phase impregnation. Thus, the vapor phase concentration in the carrier gas was set by the saturation vapor pressure of the liquid. For example, 5 M liquid ammonia concentration at 40 °C corresponds to approximately 15% (v/v) vapor phase concentration in nitrogen. The reagent laden nitrogen was passed at a constant flowrate of 100 sccm (cc per min measured at standard conditions) through a perforated tubular reactor wrapped with ACF. The weight of ACF was approximately 5 g. The geometrical configuration of the reactor is similar to that used for activation step. The contact (impregnation) temperature was set at 750 °C, whereas contact time was one hour. The vapor–solid contact resulted in the attachment of N-containing functional groups over the ACF surface. After impregnation, the system was allowed to cool down to room temperature while being purged with nitrogen.

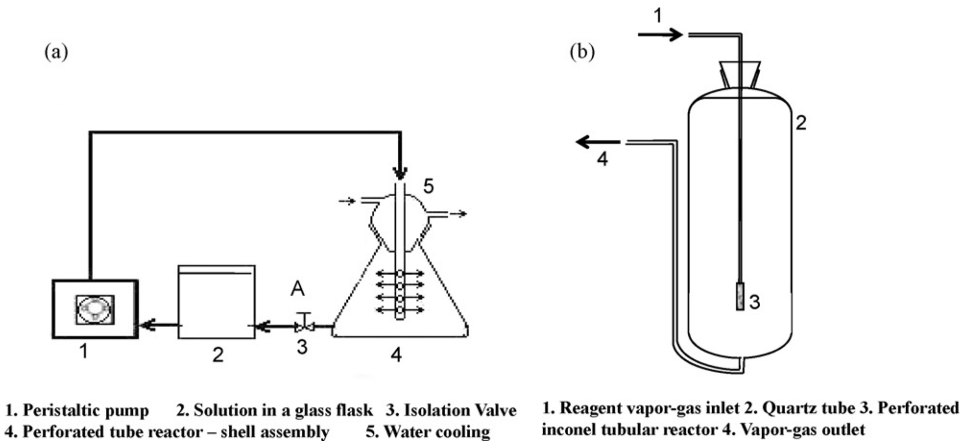

Fig. 1. (a) Schematic of the experimental set-up for aqueous phase surface functionalization of ACF. (b) Schematic of the experimental set-up for vapor phase surface functionalization of ACF.