NO Oxidation by Activated Carbon Catalysts: Impact of Carbon Characteristics, Pressure, and the Presence of Water

Seyed A. Dastgheib,* Hafiz Salih, Tina Ilangovan, and Justin Mock

ABSTRACT: Nitric oxide can be removed from flue gas by catalytic oxidation of NO to NO2, followed by dissolution of NO2 in water. The work presented here includes catalytic NO oxidation by activated carbons (ACs) at atmospheric and elevated pressures under dry and wet conditions at ambient temperature. The AC samples had different physicochemical characteristics including surface areas of ∼400–1600 m²/g and micropore volumes of ∼0.2–0.6 cm³/g while having different surface chemistries. Dry tests indicated that introducing nitrogen functionalities or coating with pyrolytic carbon could enhance the catalytic activity of AC for NO oxidation. Nitric oxide concentration profiles from the oxidation experiments under dry conditions showed maximum values after 5–15.5 h of testing and a steady-state condition after ∼12–30 h and that a major release of NO2 began after reaching the maximum values in the NO concentration. Adsorption profiles showed a high rate of NOx adsorption during the early hours of these experiments, and this rate decreased almost exponentially to a near-zero value. A near-complete catalytic conversion was achieved for NO oxidation at 120 psig under dry conditions, substantially higher than the 62% value of the noncatalytic NO oxidation at 217 psig. The wet trickle-bed experiments revealed that an inert packing material with a high external surface was a more suitable option than the ACs for NO oxidation in a wet trickle-bed system, even for ACs that exhibited high catalytic reactivity under dry conditions. Noncatalytic NO oxidation in the trickle-bed system was enhanced by the higher gas–liquid contact surface of the packing material for NO2 dissolution in water. Complete wetting of the hydrophilic AC or the presence of water vapor in the gas in contact with the surface of the superhydrophobic AC could eliminate or drastically reduce the catalytic activity of the AC for NO oxidation.

1. INTRODUCTION

Nitrogen oxides (NOx) are harmful air pollutants in industrial flue gases, including in flue gas generated from coal combustion. Nitrogen oxides are commonly removed and converted to nitrogen by selective catalytic reduction at high temperatures (300–400 °C) with ammonia or similar reducing agents. A comprehensive review of NOx control strategies for coal-fired power plants is given by Srivastava. The selective catalytic reduction process is a proven technology, but it requires a high temperature and has challenges associated with the use and handling of ammonia or other reducing chemicals. Another approach to NOx abatement is through the oxidation pathway, in which NO is oxidized to NO2 in the presence of a catalyst, after which the NO2 is removed by dissolution in water. The oxidation of NO to NO2 can be carried out at ambient temperatures because NO oxidation is more thermodynamically favorable at lower temperatures and NO2 is more stable at <200 °C. Additionally, unlike the selective catalytic reduction approach, the oxidation option requires no additional chemicals that could add to the overall process cost and create other operational and environmental issues.

Several catalysts, including precious metals and activated carbons (ACs), can effectively catalyze the oxidation of NO. Nitric oxide oxidation by ACs with the suitable physicochemical characteristics is a cost-effective solution for NOx removal. In addition to oxidizing NO, AC catalysts can oxidize other pollutants to states that are more soluble in water and more easily removable, resulting in a multipollutant removal strategy. This includes conversion of SO2 to SO3 or elemental mercury to ionic mercury, which can be removed by dissolution in water.

A recent review article reported several studies that demonstrated effective oxidation of NO on active sites of AC catalysts or similar carbon materials. Several studies of NO oxidation on carbon catalysts have been conducted under...
dry conditions at atmospheric pressure but at different temperatures and oxygen concentrations. These works investigated the impact of the physicochemical characteristics and operational conditions of the ACs (e.g., oxygen concentration and temperature) on NO oxidation. Among the physical properties, microporosity, particularly the volume of smaller micropores, was found to have a critical role in NO oxidation. This observation was based on the proposed mechanism that the reaction of NO with oxygen occurs in the small micropores on the carbon surface. The catalytic activity of the AC materials for NO oxidation also depends on the availability and abundance of active catalytic sites, which in turn depend on the surface chemistry of the ACs. The introduction of nitrogen functionalities to the surface, the doping of ACs with metal catalysts, the deposition of carbon nanoparticles on the carbon surface, and heat treatment of the ACs have all been shown to substantially enhance the catalytic activity of ACs for NO oxidation.

Several other works conducted under different relative humidity conditions have demonstrated the negative impact of water vapor on NO oxidation at the temperature range of 125 °C. Mochida et al. reported that the addition of moisture reduced NO conversion by a heat-treated AC fiber from 82% under dry conditions to 21% under 100% relative humidity. Other researchers have reported that because the adsorbed water molecules deactivate the catalytic sites, the presence of moisture, even at a 50% relative humidity level, can eliminate the catalytic activity of the tested ACs for NO oxidation. Based on the data reported in these works, heat treatment of the AC (i.e., by making the surface more hydrophobic by removing the surface oxygen functionalities) or enhancing surface hydrophobicity can make moisture less harmful to the catalytic activity of ACs for NO oxidation. For practical applications, the main question is whether superhydrophobic ACs (i.e., those with a water contact angle of ≥145°) can catalyze NO oxidation in the presence of water.

If this is the case, the NOx removal process could be achieved in a more effective manner by integrating the NO oxidation (gas–solid) and NOx dissolution (gas–liquid) processes into a single three-phase system, such as a trickle-bed reactor. In this system, the NO2 resulting from NO oxidation on an AC catalyst is removed by a continuous flow of water that is injected on top of the AC catalyst bed. The feasibility of a trickle-bed reactor system for NO oxidation depends on the performance of the superhydrophobic ACs in the presence of liquid water. To the best of our knowledge, no previous reports on this process have been identified in the literature.

Nitric oxide oxidation can be substantially enhanced at pressures up to 15 bar; however, noncatalytic NO oxidation may require a considerable time to achieve high conversion at this pressure. An AC catalyst could potentially improve the performance of high-pressure NO oxidation, but a data gap exists in the literature that could confirm its expected performance.

The work presented in this article includes an evaluation of several commercial ACs and two surface-modified ACs for NO oxidation, an assessment of the impact of pressure on NO oxidation, and a side-by-side comparison and analysis of NO oxidation by selected hydrophilic and superhydrophobic ACs and an inert packing material under dry and wet trickle-bed conditions. The impact of carbon characteristics, pressure, and the presence of water on NO oxidation is discussed, and the feasibility of using hydrophilic and superhydrophobic ACs for catalytic NO oxidation in a trickle-bed system is evaluated.

2. EXPERIMENTAL SECTION

2.1. Materials. The AC materials used in this work included four commercial and two modified ACs. The commercial ACs were (1) F400, a bituminous coal-based, microporous AC manufactured by Calgon Carbon (Pittsburgh, PA); (2) Nuchar, a wood-based mesoporous AC, previously obtained from MeadWestvaco (Richmond, VA); (3) GC, a coconut shell-based microporous AC; and (4) GC-S, which is GC impregnated with elemental sulfur. Both GC and GC-S were obtained from General Carbon (Paterson, NJ). The AC samples were crushed and sieved, and particles with mesh sizes between 12 and 16 (1.68 and 1.19 mm) were collected, washed with deionized water, dried at 105 °C for 24 h, and stored in air-tight containers.

Two modified ACs were also prepared from F400 in our laboratory. Activated carbon F400-N was prepared by introducing nitrogen functionalities onto the carbon surface through treatment with melamine, which was performed in a manner similar to the method of Bagreev et al. The melamine treatment was conducted by stirring 2 g of F400 in 100 mL of an 80% ethanol solution containing 1.3% w/v melamine at room temperature for 5 h. The suspension was then boiled to obtain a dry solid, which was heated at a heating rate of 10 °C/min to 600 °C under nitrogen, held at this temperature for 50 min, and finally cooled under nitrogen to ambient temperature.

The superhydrophobic AC, F400-C2H2, was prepared by the deposition of pyrolytic carbon on F400 through acetylene pyrolysis at 500 °C. Two grams of the F400 sample was first heated under 500 cm3/min of argon at 900 °C for 1 h to remove the majority of the hydrophilic oxygen functionalities and to prepare the active sites for carbon deposition. The sample was then cooled to 500 °C, at which time argon was switched to 100 cm3/min of acetylene for 30 min and finally cooled to an ambient temperature under argon.

An inert packing material was also used in some experiments. A stainless steel (SS) distillation packing material was obtained from the Cannon Instrument Company (State College, PA). This packing material had a half-cylinder shape with equal lengths and diameters of 4.1 mm, thicknesses of 0.08 mm, and an external surface area of approximately 1890 m2/m3.

2.2. NO Oxidation. The NO oxidation experiments were performed at the ambient temperature under dry or wet conditions by using AC catalysts. Baseline tests were also performed with an empty bed (i.e., without placing any material in the reactor). The majority of the experiments were performed at the ambient pressure; however, some experiments were also performed at elevated pressures. For the experiments conducted at atmospheric pressure, a fixed-bed glass tube reactor with a 1 cm internal diameter was used, and for the high-pressure experiments, a stainless steel 1 cm column was used. A back-pressure gas regulator was placed after the reactor to control the pressure in the high-pressure experiments. A gas flow rate of 50 standard cm3/min was used for both the dry and wet tests. The NO inlet concentration was 1000 ± 50 ppm (in nitrogen) in the presence of ~4% oxygen. The AC catalyst mass was fixed at 0.5 g, corresponding to a bed height of 1.3–2.8 cm. For the SS inert material, a similar bed height was used that was equal to ∼2 g of the packing
material. The treated gas mixture was analyzed for NO, NO\textsubscript{2}, and NO\textsubscript{x} with a chemiluminescence CLD 64S NO\textsubscript{x} analyzer (Eco Physics, Ann Arbor, MI).

Experiments were performed in the presence of water in the trickle-bed mode (i.e., water dripping from the catalyst bed), with a gas flow rate of 50 cm\textsuperscript{3}/min and a water injection rate of 0.5 mL/min. The trickle-bed experiments were conducted under co-current conditions in which water was injected to the gas inlet at the top of the reactor and wash water was collected in a flask at the bottom of the column. For the selected experiments, the wash water was collected and titrated with 0.1 N NaOH to quantify the amount of dissolved acid.

2.3. Characterization of Carbon Catalysts. The surface area and porosity of materials were characterized by nitrogen adsorption isotherms at 77 K at a relative pressure ($P/P_0$) of 10\textsuperscript{-5} to 1 by using a Gemini VII instrument (Micromeritics, Norcross, GA). Samples were degassed in a vacuum for 2 h at 200 °C prior to nitrogen adsorption. The surface area was calculated from the linear range of the Brunauer−Emmett−Teller (BET) equation from a relative pressure of 0.03−0.3.

The total pore volume was calculated from the adsorbed volume of nitrogen near the saturation point ($P/P_0 = 0.99$). The micropore volume (volume of pores with a diameter of <2 nm) was calculated from the Dubinin−Radushkevich equation in the $P/P_0$ range of 0−0.1. The cumulative meso- and macropore volumes were estimated by subtracting the micropore volume from the total pore volume. This cumulative volume is mostly representative of the sample mesoporosity since the macropore volume (volume of pores with a diameter of >50 nm) is negligible compared to the mesopore volume (volume of pores with a diameter of 2−50 nm).

Hydrophobicity was characterized by measuring the water contact angles of water droplets placed on the surface of finely ground samples. Image J software was used to process the digital photographs of water droplets on the samples.

3. RESULTS AND DISCUSSION

3.1. Physicochemical Characteristics of the ACs. As outlined in Table 1, among the four commercial ACs, Nuchar

| activated carbon | BET surface area (m\textsuperscript{2}/g) | total pore volume (cm\textsuperscript{3}/g) | micropore volume (cm\textsuperscript{3}/g) | meso + macropore volume (cm\textsuperscript{3}/g) | water contact angle (°) |
|------------------|-----------------------------------------|------------------------------------------|------------------------------------------|-----------------------------------------------|------------------------|
| F400             | 1118                                    | 0.643                                    | 0.442                                    | 0.201                                         | 0                      |
| GC               | 1022                                    | 0.451                                    | 0.413                                    | 0.038                                         | 0                      |
| GC-S             | 436                                     | 0.253                                    | 0.170                                    | 0.083                                         | 0                      |
| Nuchar           | 1596                                    | 1.248                                    | 0.593                                    | 0.655                                         | 0                      |
| F400-C\textsubscript{2}H\textsubscript{2} | 689                                     | 0.321                                    | 0.279                                    | 0.042                                         | 145                    |
| F400-N           | 420                                     | 0.252                                    | 0.170                                    | 0.082                                         | 0                      |

Figure 1. Concentration profiles of nitric oxides during NO oxidation by different activated carbons under dry testing conditions at ambient temperature and pressure. Catalyst mass = 0.5 g; total gas flow rate = 50 cc/min; inlet [NO] = 1000 ppm (in nitrogen); and [O\textsubscript{2}] = ∼4%. (a) NO, (b) NO\textsubscript{2}, (c) NO\textsubscript{x}, and (d) NO\textsubscript{x} removed by adsorption. The profile of NO\textsubscript{x} removed by adsorption was determined by subtracting the NO\textsubscript{x} outlet from the NO inlet at each given time. The NO oxidation conversion percentage vs the time-on-stream can be calculated from the NO concentration (a) and is equal to 100 × ((1000 − [NO])/1000).
is a primarily mesoporous material with the highest specific surface area, \( \sim 1600 \text{ m}^2/\text{g} \), and a large micropore volume. GC, a microporous AC, has a surface area of \( \sim 1000 \text{ m}^2/\text{g} \) and a total pore volume of 0.451 cm\(^3\)/g with negligible mesoporosity. GC-S is the GC carbon impregnated with \( \sim 13\% \) elemental sulfur in the S\(_2\) form. Sulfur impregnation of the GC carbon (i.e., GC-S) results in a significant reduction of its surface area to 436 m\(^2\)/g, mainly because the carbon micropores are obstructed by elemental sulfur. F400 has a surface area of \( \sim 1100 \text{ m}^2/\text{g} \) and a total pore volume of 0.643 cm\(^3\)/g and is \( \sim 70\% \) microporous. F400 and GC have similar surface areas and micropore volumes, but F400 has additional mesoporosity, whereas Nuchar has a substantially larger surface area and higher pore volumes. These three ACs are manufactured from different raw materials (i.e., F400 from coal, GC from coconut shells, and Nuchar from wood) and were prepared through physical activation by steam (F400 and GC) or chemical activation by phosphoric acid (Nuchar). Therefore, they are expected to have different surface chemistries.

F400-N was prepared by treatment of the F400 AC with melamine at 600 °C to attach nitrogen functionalities to the surface. The total nitrogen content of F400-N was not measured, but based on a nitrogen content of 18.4% reported for similar materials prepared by a similar method,\(^a\) it was expected to be at a substantial level of \( >10\% \). The introduction of nitrogen functionalities to the F400 surface by the melamine treatment resulted in a more than 60% reduction in the surface area and pore volume of the AC.

F400-C\(_2\)H\(_2\), prepared by the deposition of pyrolytic carbon on the F400 surface, had an \( \sim 40\% \) less surface area and an \( \sim 50\% \) less total pore volume compared with its precursor. However, the deposited carbon had a greater impact on reducing the mesopore volume than the micropore volume. The micropore volume was reduced by only 37%, whereas the volume of larger pores was reduced by 80%. Coating the F400 AC with pyrolytic carbon resulted in a superhydrophobic surface, as indicated by the measured water contact angle of 145°, whereas the other AC materials were hydrophilic and exhibited complete wetting, with a water contact angle of 0° (Table 1).

The SS packing material had a relatively large external surface (i.e., \( 1890 \text{ m}^2/\text{m}^3 \)), but according to data from a surface area analysis (not included in Table 1), it had no measurable internal surface area or porosity.

3.2. NO Oxidation under Dry Conditions. The goal of this work was to perform a fundamental study looking at the catalytic and adsorptive properties of different activated carbons for NO oxidation and removal at the ambient temperature. These simplified conditions are much different from the real flue gas conditions that have different compositions and impurities and are at different pressures and temperatures. However, these conditions enable us to simplify a complex system to better understand NO oxidation.

Concentration profiles of NO, NO\(_2\), and NO\(_3\) during NO oxidation by different ACs under dry conditions at ambient temperature and pressure are shown in Figure 1a–c. The NO oxidation conversion percentage vs the time-on-stream can be also calculated from the NO concentration (Figure 1a) and is equal to \( 100 \times ((1000 – [\text{NO}])/1000) \). The difference between the NO inlet and NO\(_3\) outlet concentrations at each given time was also calculated and is shown as the amount of NO\(_3\) removed by adsorption (Figure 1d). The baseline test represents the test conducted under the same conditions by using an empty bed without any AC catalyst. The steady-state NO conversion rate, the cumulative amount of NO\(_3\) adsorption (calculated from the integration of NO\(_3\) adsorption profiles), and the time required to reach the maximum NO concentration or a sudden release of the adsorbed NO\(_3\) to the outlet stream were also obtained from the concentration profiles and are listed in Table 2.

The NO concentration profiles of different ACs showed continuous increases in the NO concentration until the maximum values were reached after 5–15.5 h of testing, and then a steady-state condition was approached after \( \sim 12–30 \) h (Figure 1a). In contrast, the measured concentration of NO\(_3\) in the outlet stream was negligible during the first hours of the experiments, and a substantial release of NO\(_3\) began after reaching the maximum values on the NO profiles (Figure 1 and Table 2). The adsorption profiles (Figure 1d) showed a high rate of NO\(_3\) adsorption during the early hours of the experiments. This rate decreased almost exponentially as the testing progressed and finally approached zero by the late stage of experiments when the total NO\(_3\) concentration in the output approached the NO input concentration of 1000 ppm (Figure 1c). The general trend of reaching maximum values in the NO concentration profiles and the delay in NO\(_3\) release is consistent with other reports.\(^9,16\) As proposed by Mochida et al.,\(^5\) NO\(_2\) generated from NO oxidation was initially adsorbed in the carbon micropores, reducing the available adsorption sites for NO and leading to a continuous increase in the NO concentration until a certain near-saturation condition was reached. At this point, the adsorbed NO\(_3\) was released and the NO concentration was reduced. The cumulative amount of NO\(_3\) adsorbed during the 40 h period of the experiments with different ACs varied in a range of 0.8–2.4 mmol/g. The highest value was observed for Nuchar, with the largest micropore volume, and the lowest value was observed for GC-S, with the smallest micropore volume (Table 2). A similar correlation was also observed for GC and F400, which had similar moderate micropore volumes of \( \sim 0.4 \text{ cm}^3/\text{g} \) and exhibited a similar cumulative NO\(_3\) adsorption of \( \sim 2 \text{ mmol/g} \). For F400-N and F400-C\(_2\)H\(_2\), the total NO\(_3\) adsorption observed was much higher than expected, based on their relatively low micropore volumes. The enhanced adsorption of these modified ACs was likely due to their more favorable...
surface chemistry, which resulted in a higher affinity for NO\textsubscript{x} adsorption.

The baseline NO oxidation results showed an \sim 10\% NO conversion in the absence of a catalyst, whereas a conversion of 47--81\% was observed when an AC catalyst was used (Figure 1 and Table 2). Among the tested commercial ACs, F400 showed a 74\% conversion for NO oxidation, significantly higher than the 47--59\% conversion observed for the other tested commercial ACs. The NO oxidation performance of F400 was increased to \sim 80\% by introducing nitrogen functionalities (F400-N) or coating the carbon surface with pyrolytic carbon (F400-C\textsubscript{2}H\textsubscript{2}). Other researchers reported NO conversion values of \sim 20--90\% for different virgin or modified carbon catalysts tested under the similar or different operational conditions (i.e., \sim 400--1000 ppm NO\textsubscript{x}, \sim 4--5\% oxygen, sorbent mass of 0.2--1.0 g, gas flow rate of 100 mL/min, near-ambient temperature, atmospheric pressure, and dry condition).\textsuperscript{5,10,15}

As stated previously, the catalytic activity of an AC for NO oxidation depends on a combination of its physical and chemical properties. However, the results shown in Table 2 suggest that favorable surface chemistry had a dominant impact compared with the micropore volume under the experimental conditions used in this study. Activated carbons exhibiting the highest and lowest conversion rates (i.e., F400-N and GC-S) had the same micropore volumes. In contrast, F400-N and F400-C\textsubscript{2}H\textsubscript{2} had lower micropore volumes than most of the other materials but exhibited the best performance for NO oxidation (Table 2). It is likely that all of the tested ACs had sufficient micropore volumes to accommodate NO oxidation but that their overall catalytic activities were dominated by their more favorable surface chemistry or the availability of suitable catalytic sites. The superior performance of F400-N and F400-C\textsubscript{2}H\textsubscript{2} is also consistent with reports indicating that nitrogen functionalization, carbon coating, or the development of a more hydrophobic surface can enhance the catalytic activity of ACs for NO oxidation.\textsuperscript{6,7,15}

### 3.3. NO Oxidation at an Elevated Pressure

The impact of pressure on the catalytic NO oxidation was examined by comparing the NO oxidation profiles of F400 at atmospheric and elevated (i.e., 120 psig) pressures at ambient temperature and under dry conditions. To compare catalytic with noncatalytic NO oxidation in the absence of a catalyst, baseline tests were also conducted by using an empty bed or a bed filled with an inert SS packing material. Additional baseline tests with F400 at atmospheric or high pressure with 0\% oxygen were also performed. The high-pressure tests were conducted for a short period of time (i.e., 2 h), mainly because of operational issues (such as fluctuation of gas flow rate and stability of mass flow controller) associated with conducting longer-duration high-pressure testing.
Concentration profiles of NO, NO<sub>2</sub>, NO<sub>x</sub>, and NO<sub>x</sub> adsorbed for the baseline F400 tests in the absence of oxygen at atmospheric or elevated pressure confirmed that no NO<sub>2</sub> formation or considerable NO adsorption occurred even at an elevated pressure of 200 psig (Figure 2). Other researchers also reported no NO adsorption on AC catalysts in the absence of oxygen, but the high-pressure result presented in this work suggests that NO could not be physisorbed on the AC surface, even at 200 psig, and also oxygen presence was essential to facilitate NO chemisorption on the chemisorbed oxygen sites.

Noncatalytic NO oxidation (empty bed) at atmospheric pressure in the presence of oxygen resulted in an ∼10% conversion, whereas increasing the pressure to 217 psig substantially increased NO conversion to 62%. The reaction of NO with oxygen results in the generation of 1 mol of the NO<sub>2</sub> product from 1.5 mol of the reactant (i.e., NO + 1/2O<sub>2</sub> → NO<sub>2</sub>); therefore, based on Le Chatelier’s principle, an increase in pressure is expected to increase the oxidation of NO.

The catalytic conversion of NO by F400 at atmospheric pressure was 74%, but a near-complete conversion could be achieved by increasing the pressure to 120 psig, as the NO concentration profile for F400 at 120 psig approaches zero after ~1 h (Figure 2a). The NO and NO<sub>x</sub> profiles show a near-complete NO conversion at elevated pressure, in which about 94% of NO<sub>x</sub> is removed by adsorption into the carbon pores. These results demonstrate that under dry conditions, a near-complete NO conversion at ambient temperature can be achieved by using a carbon catalyst at a moderate pressure.

The complete NO conversion is likely due to the contribution of both catalytic oxidation and noncatalytic high-pressure oxidation.

3.4. NO Oxidation under Dry and Wet Trickle-Bed Conditions. A side-by-side comparison of NO, NO<sub>2</sub>, and NO<sub>x</sub> profiles for NO oxidation by F400, F400-C<sub>2</sub>H<sub>2</sub>, and an inert SS packing material under dry and wet trickle-bed conditions at ambient pressure and temperature is shown in Figure 3. The inert SS packing material had no catalytic reactivity and was expected to exhibit a noncatalytic conversion rate of ∼10%, whereas steady-state conversion rates of 74% for F400 and 79% for F400-C<sub>2</sub>H<sub>2</sub> were observed for their catalytic NO oxidation runs under dry conditions (Figure 1a). Figure 3a shows a noncatalytic conversion rate of ∼55% with a continuous flow of water on the SS packing material in the trickle-bed configuration. The SS packing material, because of its high external surface, which created a high gas−liquid contact surface, could substantially enhance NO<sub>2</sub> dissolution in water. Unlike NO, which had a low solubility of <1 mg/L in water, NO<sub>2</sub> was highly soluble in water and reacted with water to produce nitrous and nitric acids. Figure 3b also confirms the low NO<sub>2</sub> concentration in the gas phase for all of the trickle-bed experiments. According to Le Chatelier’s principle, the continuous removal of NO<sub>2</sub> from the gas phase by dissolution in the water stream can force the NO oxidation reaction to proceed, resulting in a higher NO oxidation conversion.

Figure 3a shows the initial conversion rates of 49% for F400 and 54% for F400-C<sub>2</sub>H<sub>2</sub> at ~7 h, each decreasing by ~12−14%.
by the end of the trickle-bed experiments. These rates are considerably lower than the average conversion rate of ~55% for the SS packing material. Furthermore, the wet conversion rates of these ACs are substantially lower than the rates under dry conditions. These observations can be further analyzed in the light of two important factors, namely, the external surface of the materials for enhancing the gas−liquid contact surface (which increases the NO2 dissolution rate) and the detrimental effect of water vapor and liquid water on the catalytic activity of ACs for NO oxidation.

The external surface of the AC materials was estimated at 2091 m2/m3, based on their average particle diameter of 0.1435 cm, their approximation of spherical geometry, and a void volume of ~0.5. This value is similar to the external surface of 1890 m2/m3 for the SS packing material. The external surface of the SS packing material was expected to be almost completely available for gas−liquid mass transfer for dissolution of NO2 in the water film. However, because of the small particle sizes of the ACs and a water tension effect, some interparticle voids might have been filled with water, and the theoretical external surface of the AC particles might not have been fully available for the formation of liquid water films on the particles. Therefore, a lower external surface for NO2 dissolution was available for the ACs compared with that of the SS packing material. The hydrophobicity of the ACs was also expected to affect the available surface for gas−liquid mass transfer. The F400 could be completely wetted with water, but the F400-C2H2 had a superhydrophobic surface and repelled liquid water. Therefore, in the trickle-bed system, the water stream was expected to be forced through the voids in the F400-C2H2 bed without wetting the individual particles.

As described briefly above, different researchers have reported that water vapor has a detrimental effect on NO oxidation, resulting in a significant reduction or even complete elimination of the catalytic activity of ACs owing to the adsorbed water molecules deactivating the catalytic sites.14−17 Previous studies have been conducted in the gas phase with the addition of water vapor at different relative humidity levels; however, the trickle-bed testing condition in this work provided a gas phase that was saturated with water vapor in addition to a liquid water stream that continuously dissolved and removed the NO2 product from NO oxidation. The liquid water fully wet the hydrophilic F400 AC, but the superhydrophobic F400-C2H2, which was not wetted with water, was exposed only to the water vapor. It is likely that by wetting the F400 AC, the catalytic activity of F400 was eliminated and that the mechanism for NO2 removal was based on noncatalytic NO oxidation and dissolution of the NO2 product in water. For the superhydrophobic F400-C2H2, the catalytic activity appeared to be significantly reduced by the presence of water vapor, and NO2 removal was controlled by the diminished catalytic NO oxidation of AC, noncatalytic NO oxidation, and NO2 dissolution in water.

The NOx concentration in the outlet gas for the trickle-bed experiments was substantially lower than the inlet NO concentration of 1000 ppm (Figure 3c), which was primarily due to the removal of NO2 by dissolution in water or by adsorption onto the AC (Figure 3d). After the trickle-bed experiments with ACs, the wash water was collected and titrated with 0.1 N NaOH. A mass balance was performed based on the cumulative amount of the NO gas input during the experiments, the quantity of dissolved NO2 measured by acid titration, and the cumulative amount of NOx measured in the outlet gas (Table 3). The cumulative amount of NOx in the outlet stream was estimated based on the integration of NOx concentration profiles shown in Figure 3c. For F400, an interpolation was performed for the initial portion of the data that was not available because of measurement issues during that period.

The amount unaccounted for NOx for the F400 test was about −3%, suggesting no adsorption onto the F400 AC. For F400-C2H2, the sum of the total NOx output in the gas phase and the NOx dissolved in water was ~25% less than the total NO input (Table 3). The mass balance results suggest that F400-C2H2 catalysts adsorbed a significant amount of NOx, whereas almost no adsorption occurred on the F400 AC surface. This might be explained by the wettability of these materials, whereby F400-C2H2 could not be wetted by the injected water and NO2 in the gas phase had access to the carbon surface and could be adsorbed and accumulate in the carbon pores. However, F400 was completely wetted with a water film, which prevented direct access of gas-phase NO2 to the carbon pores. The injected water stream continuously dissolved and removed NOx from the gas phase.

Overall, a high-surface-area packing material appeared to be a more suitable option than ACs for NO oxidation in a wet trickle-bed system, even if the ACs showed high catalytic reactivities under dry conditions. Complete wetting of hydrophilic F400 or the presence of water vapor for the superhydrophobic F400-C2H2 eliminated or drastically reduced the catalytic activity of ACs.

## Table 3. Mass Balance of the Total NO Input and NOx Output during Trickle-Bed Experiments with Activated Carbons

| activated carbon | total NO input (mmol) | NOx dissolved in water (mmol) | total NOx output in the gas phase (mmol) | NOx adsorbed (mmol) | NOx adsorbed (%) |
|------------------|-----------------------|-------------------------------|-------------------------------------------|---------------------|-----------------|
| F400             | 9.286                 | 3.542                         | 5.994                                     | −0.250              | −2.7            |
| F400-C2H2        | 5.671                 | 1.151                         | 3.100                                     | 1.420               | 25.0            |

**Note:** The mass balance was performed for the total time of the experiments (74.5 h for F400 and 45.5 h for F400-C2H2).

4. CONCLUSIONS

The goal of this work was to perform a fundamental study about the catalytic and adsorptive properties of different ACs for NO oxidation and removal at the ambient temperature. The work presented in this article includes an evaluation of several commercial ACs and two-surface-modified ACs for NO oxidation, an assessment of the impact of pressure on NO oxidation, and a side-by-side comparison and analysis of NO oxidation by selected hydrophilic and superhydrophobic ACs and an inert packing material under dry and wet trickle-bed conditions.

Nitric oxide concentration profiles from the catalytic oxidation experiments under dry conditions showed that maximum values were reached after 5−15.5 h of testing and a steady-state condition was achieved after ~12−30 h, whereas a substantial release of NOx began after reaching the maximum values in the NO concentration profiles. Results indicate that introducing nitrogen functionalities or coating the carbon surface with pyrolytic carbon can enhance the catalytic activity of AC for NO oxidation. The cumulative amount of adsorbed NOx during the NO oxidation experiments was quantified as...
being in a range of 0.8−2.4 mmol/g, which depended on the total micropore volume and surface chemistry of the ACs.

The noncatalytic NO oxidation at atmospheric pressure in the presence of oxygen resulted in an ~10% conversion, whereas increasing the pressure to 217 psig substantially increased the NO conversion to 62%. In comparison, the catalytic conversion of NO by the F400 AC at atmospheric pressure under dry condition was 74%, but a near-complete conversion was achieved by increasing the pressure to 120 psig.

A side-by-side comparison of the results from F400, F400- C₃H₄, and an inert SS packing material for NO oxidation under dry and wet trickle-bed conditions at ambient pressure and temperature showed that the packing material was a more suitable option than ACs for NO oxidation in a wet trickle-bed system, even for the ACs that exhibited high catalytic reactivity under dry conditions. Noncatalytic NO oxidation in a trickle-bed system was enhanced through a higher gas−liquid contact surface of the packing material for NO₃ dissolution in water. Complete wetting of the hydrophilic AC or the presence of water vapor in the gas in contact with the surface of the superhydrophobic AC resulted in a drastic reduction or elimination of the NO oxidation capability of the AC. Overall, a packing material with a high external surface area appears to be a more suitable option than ACs for NO oxidation in a wet trickle-bed system, even if the ACs show high catalytic reactivity under dry conditions.

The simplified conditions assumed in this work are much different from the real flue gas conditions that have different compositions and impurities and are at different pressures and temperatures. However, these conditions enable us to simplify a complex system to better understand NO oxidation. A coal-derived flue gas is a complex gas mixture, containing numerous species as well as great variability due to the many different coals that are burned, and the various power plant configurations employed.25 As an example, the following composition for an untreated flue gas from burning a low-sulfur bituminous coal has been reported: 15−16% CO₂; 5−7% H₂O; 3−4% O₂; 100 ppm HCl; 800 ppm SO₂; 10 ppm SO₃; 500 ppm NO₂; 20 ppm CO; 10 ppm hydrocarbons; 1 ppb Hg; fine particulates as fly ash; and N₂. Future work can include the evaluation of the impacts of some of the acid gases such as HCl, SO₂, and SO₃ upon both the homogeneous and heterogeneous oxidations of NO.

### ACKNOWLEDGMENTS

This work was partially supported by the U.S. Department of Energy, National Energy Technology Laboratory (Cooperative Agreement DE-FE0029161). This document does not necessarily reflect agency views. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use. Neither the United States Government, nor any agency thereof, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.

### REFERENCES

(1) Gutberlet, H.; Schallert, B. Selective catalytic reduction of NOx from coal fired power plants. Catal. Today 1993, 16, 207−235.
(2) Srivastava, R. K.; Hall, R. E.; Khan, S.; Culligan, K.; Lani, B. W. Nitrogen oxide emission control options for coal-fired electric utility boilers. J. Air Waste Manage. Assoc. 2005, 55, 1367−1388.
(3) Després, J.; Elesner, M.; Koebel, M.; Kröcher, O.; Schnyder, B.; Wokaun, A. Catalytic oxidation of nitrogen monoxide over Pt/SiO₂. Appl. Catal., B 2004, 50, 73−82.
(4) Shen, Y.; Ge, X.; Chen, M. Catalytic oxidation of nitric oxide (NO) with carbonaceous materials. RSC Adv. 2016, 6, 8469−8482.
(5) Mochida, I.; Shirahama, N.; Kawano, S.; Korai, Y.; Yasutake, A.; Tanoura, M.; Fuji, S.; Yoshikawa, M. NO oxidation over activated carbon fiber (ACF). Part 1. Extended kinetics over a pitch based ACF of very large surface area. Fuel 2000, 79, 1713−1723.
(6) Sousa, J. P. S.; Pereira, M. F. R.; Figueiredo, J. L. Modified activated carbon as catalyst for NO oxidation. Fuel Process. Technol. 2013, 106, 727−733.
(7) Talukdar, P.; Bhaduri, B.; Verma, N. Catalytic oxidation of NO over CNF/ACF-supported CeO₂ and Cu nanoparticles at room temperature. Ind. Eng. Chem. Res. 2014, 53, 12537−12547.
(8) Adapa, S.; Gaur, V.; Verma, N. Catalytic oxidation of NO by activated carbon fiber (ACF). Chem. Eng. J. 2006, 116, 25−37.
(9) Atkinson, J. D.; Zhang, Z.; Yan, Z.; Rood, M. J. Evolution and impact of acidic oxygen functional groups on activated carbon fiber cloth during NO oxidation. Carbon 2013, 54, 444−453.
(10) Sousa, J. P. S.; Pereira, M. F. R.; Figueiredo, J. L. Catalytic oxidation of NO to NO₂ on N-doped activated carbons. Catal. Today 2011, 176, 383−387.
(11) Loidl, J. A.; Lobo, R. F. Low temperature catalytic NO oxidation over microporous materials. J. Catal. 2014, 311, 412−423.
(12) Sousa, J. P. S.; Pereira, M. F. R.; Figueiredo, J. L. NO oxidation over nitrogen doped carbon xerogels. Appl. Catal., B 2012, 125, 398−408.
(13) Zhang, Z.; Atkinson, J. D.; Jiang, B.; Rood, M. J.; Yan, Z. Nitric oxide oxidation catalyzed by microporous activated carbon fiber cloth: An updated reaction mechanism. Appl. Catal., B 2014, 148−149, 573−581.
(14) Mochida, I.; Kisamori, S.; Motohiro, H.; Kawano, S.; Matsumura, Y.; Yoshikawa, M. Oxidation of NO into NO₂ over active carbon fibers. Energy Fuels 1994, 8, 1341−1344.

### AUTHOR INFORMATION

#### Corresponding Author

Seyed A. Dastgheib — Illinois State Geological Survey, Prairie Research Institute, University of Illinois, Champaign, Illinois 61820, United States; orcid.org/0000-0001-7997-9730; Phone: +1 217-265-6274; Email: seyed@illinois.edu; Fax: +1 217-333-8566

#### Authors

Hafiz Salih — Illinois State Geological Survey, Prairie Research Institute, University of Illinois, Champaign, Illinois 61820, United States

Tina Ilangovan — Illinois State Geological Survey, Prairie Research Institute, University of Illinois, Champaign, Illinois 61820, United States

Justin Mock — Illinois State Geological Survey, Prairie Research Institute, University of Illinois, Champaign, Illinois 61820, United States

Complete contact information is available at:

https://pubs.acs.org/10.1021/acsomega.0c02891

### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work was partially supported by the U.S. Department of Energy, National Energy Technology Laboratory (Cooperative Agreement DE-FE0029161). This document does not necessarily reflect agency views. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use. Neither the United States Government, nor any agency thereof, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.
(15) Mochida, I.; Kawabuchi, Y.; Kawano, S.; Matsumura, Y.; Yoshikawa, M. High catalytic activity of pitch-based activated carbon fibers of moderate surface area for oxidation of NO to NO₂ at room temperature. *Fuel* 1997, *76*, 543−548.

(16) Guo, Z.; Xie, Y.; Hong, L.; Kim, J. Catalytic oxidation of NO to NO₂ on activated carbon. *Energy Convers. Manage.* 2001, *42*, 2005−2018.

(17) Ghafari, M.; Atkinson, J. D. Catalytic NO oxidation in the presence of moisture using porous polymers and activated carbon. *Environ. Sci. Technol.* 2016, *50*, 5189−5196.

(18) Law, K-Y. Definitions for hydrophilicity, hydrophobicity, and superhydrophobicity: Getting the basics right. *J. Phys. Chem. Lett.* 2014, *5*, 686−688.

(19) Ting, T.; Stanger, R.; Wall, T. Laboratory investigation of high pressure NO oxidation to NO₂ and capture with liquid and gaseous water under oxy-fuel CO₂ compression conditions. *Int. J. Greenhouse Gas Control* 2013, *18*, 15−22.

(20) Bagreev, A.; Menendez, J. A.; Dukhno, I.; Tarasenko, Y.; Bandosz, T. J. Bituminous coal-based activated carbons modified with nitrogen as adsorbents of hydrogen sulfide. *Carbon* 2004, *42*, 469−476.

(21) Karlsson, H. T. Exact solution to NO₂ absorption. *J. Chem. Eng. Jpn.* 1984, *17*, 214−215.

(22) Schwartz, S. E.; White, W. H. Solubility Equilibria of the Nitrogen Oxides and Oxyacids in Dilute Aqueous Solution. In *Advances in Environmental Science and Engineering*; Pfafflin, J. R.; Ziegler, E. N., Eds.; Gordon and Breach Science Publishers: New York, NY, 1981; Vol. 4, pp 1−45.

(23) Granite, E. J.; Pennline, H. W. In *Mercury Control for Coal-Derived Gas Streams*; Senior, C., Ed.; Wiley-VCH, 2015.

(24) Granite, E. J.; Pennline, H. W. Photochemical removal of mercury from flue gas. *Ind. Eng. Chem. Res.* 2002, *41*, 5470−5476.