PRELIMINARY STUDIES ON ACTIVATED CARBON'S ROLE IN CONVERTING NITROUS OXIDE TO NUTRIENTS

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Abstract

Nitrous oxide is a potent greenhouse gas, produced by intensive agriculture and fossil fuel combustion. In our study, activated carbon had its surface properties modified through 5 secondary treatment processes to explore the potential for enhanced nitrous oxide adsorption. Liquid oxidant treatment (H_2O_2, HNO_3), standard heat treatment (800 ^{0}C, 600 ^{0}C), and microwave heat treatment, were used to change the chemical and textural properties of carbon, followed by study of surface N_2O transformation using XPS. Heat treatment caused the most drastic changes to surface morphology of the carbon, with graphitisation of carbon observed for the 800 ^{0}C treatment and an abnormal surface structure after microwave treatment. The XPS characterization of the carbon surface before and after the adsorption experiment showed definite increases in the nitrogen content on all activated carbon samples. Semi-quantification of the XPS results allowed the binding energy of the N 1s peaks to be determined, showing the presence of nitrates and nitrites on the carbon surface with greatest proportion of surface nitrates and nitrites on the samples treated with liquid oxidants. The mechanisms behind nitrous oxide adsorption are complex and related to both the surface texture and area, and the chemical nature of the surface functional groups on activated carbon. Based on our previous published work, we hypothesize that adsorbed nitrous oxide is converted to nitrite and nitrate and liquid oxidant treatment supports this process. Further work to prove this hypothesis is underway in our laboratory.

Introduction

Studies have shown that the textural and chemical properties of activated carbon (AC) can be tailored and controlled by secondary treatment processes (Bhatnagar, Hogland, Marques, & Sillanpää, 2013; Chingombe, Saha, & Wakeman, 2005). In order to provide an in-depth investigation of the suitability of AC, several secondary treatments were trialled to observe their effect on N_2O adsorption. The activated carbon was exposed to a continuous flow of N_2O gas at room temperature over 8 minutes. XPS was used to detect the quantity of adsorbed nitrous oxide on activated carbon surface. Based on the XPS results we could determine whether AC does have potential for low temperature adsorption of N_2O, and whether certain treatment methods increase or decrease the adsorption capacity.

Methodology

The AC used in this study was coconut shell-based, High Activity Microporous Granular Activated Carbon GC1200 (4*8 mesh) provided by Activated Carbon Technologies (Wellington, NZ).

Secondary treatment

Table 1: The secondary treatments applied to activated carbon

Group	Treatment method
AC-O	No treatment
AC-N	Nitric acid treatment (5M HNO_3, applied for 1 hr at 100 ^{0}C)
AC-H	Hydrogen peroxide treatment (9.7M H_2O, applied for 1hr at ambient temp.)
AC-800	Heat treatment (800 ^{0}C for 1.5 hr)
AC-600	Heat treatment (600 ^{0}C for 6 hr)
AC-M	Microwave heat treatment (1000 W, 2450 Hz, 2 minutes)

XPS analysis

Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer (Kratos Analytical, Manchester, UK) equipped with a hemispherical electron energy analyser was used in this study. Spectra were excited using monochromatic Al Kα X-rays (1486.69 eV) with the X-ray source operating at 150 W. Data analysis was performed using CasaXPS and Shirley backgrounds were used in the peak fitting. Quantification of survey scans utilised relative sensitivity factors supplied with the instrument. Core level data were fitted using Gaussian-Lorentzian peaks (30% Lorentzian).

Nitrous oxide adsorption experiments

The adsorption experiment was carried out using a Secador Mini Dessicator cabinet with gas ports. The experiment involved a static exposure of AC to N_2O over a time period of 36 hours. The carbon was placed in the cabinet, and the air inside was purged by a flow of N_2O. The gas ports were then sealed and the system left to equilibrate. Measurement of the extent of adsorption occurred through comparison of XPS results prior to and after the adsorption experiment. While XPS is only a semi-quantitative measure, the results allow us to spot trends and relative differences between the samples.

Results and discussions

Before and after the N_2O adsorption experiment, we submitted our samples to semi-quantitative XPS characterization and obtained the wide spectra, N1s, O1s and C1s spectra. We calibrated the spectra against the saturated hydrocarbon binding energy (285 eV) and analysed the N1s peaks. The post-adsorption XPS tests were performed in triplicate and a representative N1s spectra from each sample is displayed in Figure 1. The wide spectra of the XPS results were quantified to get an impression of the proportions of elements on the surface of the AC. One discovery from our triplicate data was the potential for variability. While in general there was good repeatability between XPS data sets, there were some large variation in the triplicate data for AC-0 and AC-N. The variation was attributed to our use of granular activated carbon, with a wide variation in granule size it is likely that the treatments were not evenly applied to all surfaces of the granules. The limited lateral range of XPS means the information received is only about a small section of carbon, not an average of the surface. This creates difficulty in comparing nitrogen content information from before and after the adsorption experiment, due to the potential for uneven oxidation of the carbon granules. Where possible we have tried to compare datasets with a similar C:O ratio. For AC-H and AC-800 this was not possible as the initial and final dataset had significant differences.
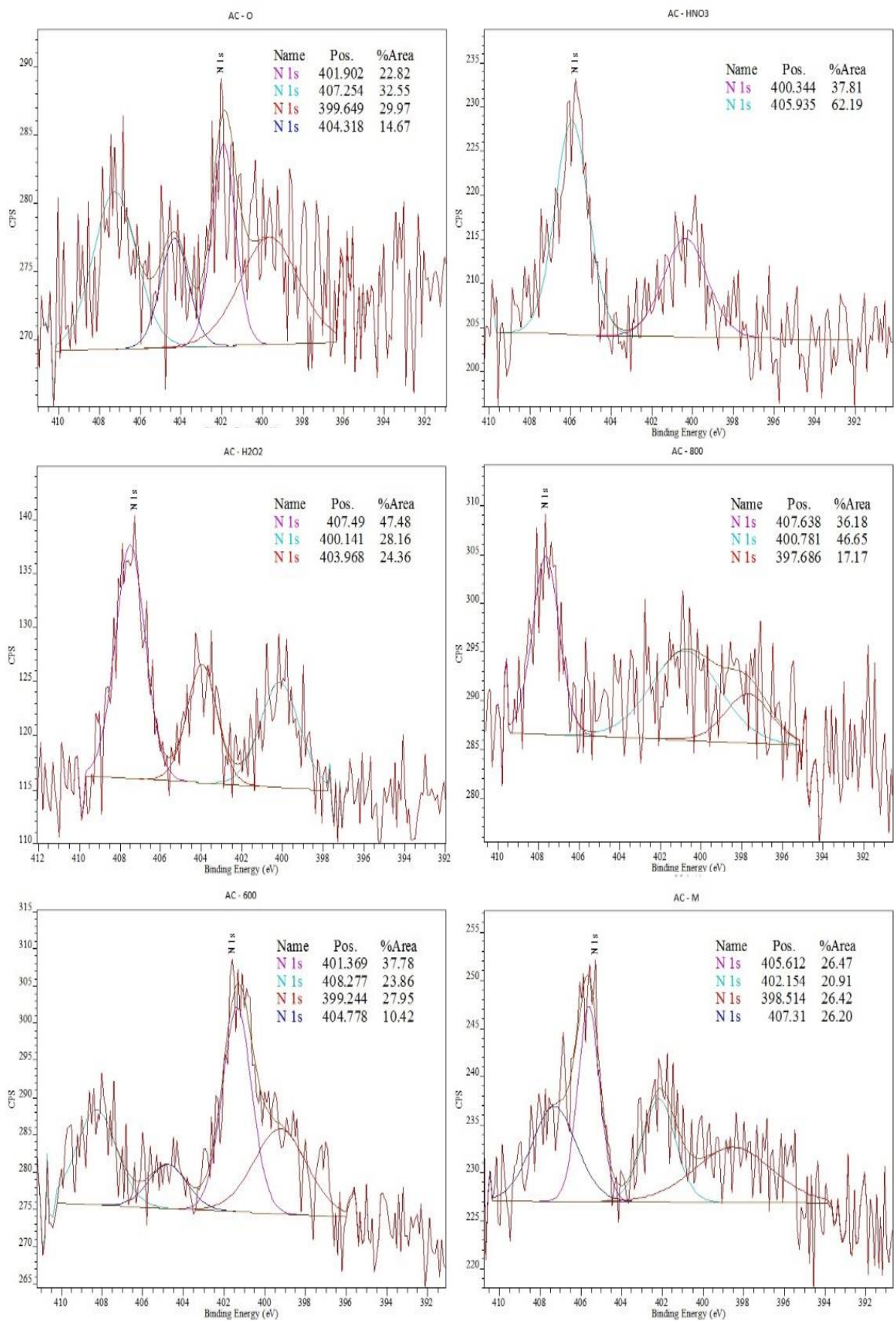
Figure 1: N 1s peaks for the final XPS results.

The N 1s peaks in Figure 1 provide more information about the types of nitrogen species present on the carbon surface, and what proportions they are present in. Manual quantification of N 1s peaks was performed in CasaXPS to determine the binding energies of the nitrogen species present. The range of peak binding energies across the 6 datasets is wide, from 397 to 408 eV. The different binding energies correlate closely with different oxidation states of the nitrogen present – a higher binding energy referencing a higher oxidation state (Baltrusaitis, Jayaweera, & Grassian, 2009).

Liquid oxidant treatment produced narrower ranges of N 1s peaks (400-407 eV) with a greater proportion of total nitrogen present at higher binding energies (407 eV for AC-H, 405 eV for AC-N). Heat treatment typically resulted in a greater spread of nitrogen across different peaks and binding energies with a greater proportion of nitrogen stored in peaks at lower binding energies.

The prevalence of peaks at high binding energies in all samples points to the presence of mineral nitrogen in the form of nitrates (NO_3^-) and nitrites (NO_2^-) on the carbon surface. NO_3^- and NO_2^- have oxidation states of +5 and +3 with typical binding energies 407-408.5 eV and 404-405.5 eV respectively. Lower binding energies could represent nitrogen attached to carbonyl groups (~400 eV), in the form of ammonium (400-402 eV), cyanides (397-400 eV), nitrides (396-398 eV), ammonia (399-400 eV) or other inorganic forms of nitrogen. These binding energy ranges are approximate and no recognised standard exists, but there appears to be consensus that the upper range of N 1s binding energies (>405 eV) are indicative of NO_3^- and NO_2^- (Beard, 1990; Zheng et al., 1997).

The resulting conclusion is that liquid oxidant treatment produces a higher proportion of nitrogen in the form of NO_3^- and NO_2^-, while other treatments are more likely to contain reduced forms of nitrogen. This supports the hypothesis that liquid oxidant treatment promotes the production of NO_3^- and NO_2^- on the surface of activated carbon. Further research is needed to elucidate the pathway from nitrous oxide to NO_3^- and NO_2^-.

Conclusions
This study's overarching goal was to explore the use of activated carbon as a sorbent for nitrous oxide at ambient temperatures and to widen the understanding of the pathway and the species involved in nitrous oxide adsorption. In informing the body of literature that currently exists on nitrous oxide adsorption, to eventually learn how activated carbon might be used in a practical application in agriculture to reduce nitrous oxide emissions.

Our characterization results show a definite increase in nitrogen content on the surface of activated carbon after the adsorption experiment. The adsorbed nitrogen formed several different species on the surface of activated carbon, including nutrient forms, nitrate and nitrite. The XPS results show correlation between the types of secondary treatment applied to activated carbon and the forms of nitrogen species created, enforcing the importance of surface chemistry on the behaviour of activated carbon. Preferential formation of nitrate and nitrite was seen on liquid oxidant treated carbons, while more analysis is required to determine the other nitrogen species being detected on the N1s spectra.

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