Preparation of graphene / carbon **hybrid** nanofibers and their performance for

NO oxidation

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Abstract

A series of novel microdomain-graphitized polyacrylonitrile (PAN)-based nanofibers were prepared by adding varied amounts (2, 5, 10, 15, and 20wt %) of graphene oxide (GO) into the precursor via the electrospinning method. The electrospun nanofibers with GO (the **hybrid** carbon nanofibers were referred to as PGCNFs) sheets were stabilized in ambient atmosphere, carbonized in nitrogen atmosphere and treated in NH₃ atmosphere for NO oxidation with low concentration (50 ppm) at room temperature. The samples were characterized by scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectroscopy, and nitrogen adsorption at 77 K. Oxidation of NO into NO₂ at room temperature (303 K) was investigated with a PGCNF fixed-bed. The results demonstrated that the reduced

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graphene oxide sheets behave as catalytic active sites embedded in the PAN-based nanofibers. In addition it was determined that nitrogen-containing functional groups played important roles in the enhancement of the catalytic oxidation of NO to NO₂. The samples with 5wt % GO exhibit the most catalytic oxidation of NO into NO₂.

1. Introduction

Carbon nanofibers (CNFs) are regarded as promising materials because of their porous structure and excellent properties, and are expected to be useful in a variety of applications such as catalysts or catalyst supports, adsorbents and energy storage devices [1-4]. Their high specific surface area and well-developed pore structures of porous carbon materials such as activated carbon fibers and activated carbon nanofibers make them attractive candidates for removing nitrous oxides. Nitrogen oxides (NO_x: NO, NO₂, and N₂O) originating from stationary sources and automobiles are major air pollutants that can result in the depletion of stratospheric ozone and the generation of tropospheric ozone. In addition, nitrogen oxides can cause the formation of acid rain, photochemical smog, greenhouse effects, and many other environmental hazards, thereby endangering both people and ecosystems [5-8]. Therefore, eliminating NO_x is an urgent task that increasingly arouses global concern. It is known that the differing properties exhibited by NO and NO₂ are ascribed to their intrinsic molecular structures. While NO is nearly insoluble in water, NO₂ is readily dissolved. In addition, at lower temperatures in the presence of a high concentration of O₂, most of the NO_x is present in the form of NO₂. However, at low concentration of O₂, most of the

NO_x is present in the form of NO [9]. Recently, many methods have been applied to remove NO. Selective catalytic reduction has been regarded as an efficient process to treat NO from a stationary emission source such as vehicle gas, but this method requires a high temperature, approximately 300°C above ambient [10], and reducing agents such as ammonia and hydrocarbons. Therefore, it is not a suitable way to remove NO_x present in the atmosphere at room temperature.

The graphitic CNFs (pyrolytically stripped) were found to be the most active in the catalytic process followed by heat treatment from 1500°C to 3000°C [11]. In our previous study [5], we studied activated polyacrylonitrile carbon nanofibers (PCNFs) to determine effect of high temperature treatment on their catalytic activity during the oxidation of NO to NO₂. The oxidation conversion was dramatically improved by employing heat-treated (graphitized) PCNFs. However, this method requires higher temperatures, in excess of 2000°C [12, 13] that consumes considerable energy and is not economical; therefore it is necessary to prepare CNFs with similar structure that can be formed at low temperatures. Graphene is a commercially attractive material that possesses a large theoretical specific surface area[14-18], a high Young's modulus, good thermal conductivity and good electrical conductivity that could be used for a variety of potential applications including in transparent conductive electrodes [19, 20]. In previous studies [21] GO has been added to the precursor of a nanoporous carbon and the resulting materials exhibited notable electrochemical behavior because of the spatial constraints on the development of porosity imposed by the addition of the

GO layers.

In this study, PAN is mixed with GO sheets in N, N-dimethylformamide (DMF) and prepared for the electrospinning solution. After carbonization and activation, polyacrylonitrile graphene oxide nanofibers (PGCNFs) can be obtained. It is expected that the electrospun PGCNFs would be effective in removing NO at room temperature without loading any other catalysts because of the increased number of catalytic activity sites and a developed microporous structure.

2. Experimental

2.1 Materials and reagents

PAN ($M_w = 150,000$) was purchased from the Aldrich Chemical Company Inc. (USA) and used without further purification. N, N-dimethylformamide (DMF) dissolves PAN. Microcrystal graphite (MG) was provided by Chen-Zhou Graphite Co., Ltd. sulfuric acid (H_2SO_4 A.R. 95.0% – 98.0%), phosphoric acid (H_3PO_4 A.R. above 85.0%), Potassium permanganate ($KMnO_4$ A.R. above 99.5%), and hydrogen peroxide (H_2O_2 A.R. above 30.0%) were used for preparation of GO. Deionized water was used throughout this work to prepare the solutions.

2.2 Preparation of GO and PGCNFs

The GO was prepared by an improved synthesis method [22]. The main process is as follows: a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (270 mL/30 mL) was added to a mixture of MG (2.0 g) and $KMnO_4$ (13.5 g), and this new mixture was then heated to 50°C and stirred for 12 h. The reaction temperature was cooled to room temperature and poured onto ice (~300 mL) with 30% H_2O_2 (2 mL). The yellow

solution was centrifuged (5000 rpm for 30 min), and the supernatant was decanted away. The remaining solid material was then washed in succession with 200 mL of water, 200 mL of 30% HCl, and 200 mL of ethanol. The washing process was repeated until the solution became neutral. The solid obtained was vacuum-dried overnight at room temperature.

The as-prepared GO sheets (2, 5, 10, 15, 20wt % of PAN) were added into DMF, ultrasonically treated for 2 h, and then PAN was added and stirred vigorously at 333K for 24 h to obtain a homogeneous solution. Then the viscous polymer solution was electrospun as seen in the schematic diagram of the experimental set-up shown in Figure 1a. The brownish black solution obtained was placed in a 20 mL syringe with a capillary tip (diameter is 0.5 mm). The anode of the high voltage power supply was clamped to a syringe needle tip; the cathode was connected to a metal collector. The electrospun fibers were collected on aluminum foil. The applied voltage was 25 kV, the distance between the tip and the collector was 19 cm, the flow rate of the spinning solution was 1 mL/h, and the relative humidity was approximately 20%. The as-spun nanofibers were stabilized by heating to 553K at a rate of 1°C/min in air, and maintaining them in this environment for 2 h. The stabilized fibers were carbonized for 10 min by heating to 850°C at a rate of 5°C /min in nitrogen and then the carbonized fibers were activated with NH₃ for 10 min at 1123K. The GO content in PAN, treatment condition, and yield are listed in Table 1. The obtained samples were denoted as PGCNF2, PGCNF5, PGCNF10, PGCNF15, and PGCNF20 respectively. For comparison, the PAN-based carbon nanofiber (PCNF) was prepared by the same

procedure.

Table 1 Composition of polyacrylonitrile carbon nanofibers (PGCNFs) and various samples of polyacrylonitrile graphene oxide carbon nanofibers (PGCNFs) and, processing condition, and final yield

Sample	GO/(GO+PAN) (wt. %)	Treatment condition	Post-activation yield (%)
PCNF	0		40.78
PGCNF2	2		41.86
PGCNF5	5	1123K	42.54
PGCNF10	10	N ₂ 10 min	43.53
PGCNF15	15	NH ₃ 10 min	45.58
PGCNF20	20		46.27

Post activation yield values are wt % graphene oxide (GO) incorporated into polyacrylonitrile (PAN)

2.3 Characterization

The morphologies of the carbonized and activated PCNFs and PGCNFs were examined by SEM in a LEO-1530. XRD (Rigaku D/Max 2500PC, Japan) and Raman spectroscopy (Renishaw Invia RM200, England) were used to examine the structural properties of the different samples. The functional groups of the samples were evaluated using Fourier transform infrared spectroscopy (FT-IR). Atomic force microscopy (AFM) was used to obtain the lateral dimension and thickness of as-prepared GO. The specific surface areas and pore size distributions of the samples were analyzed by physical adsorption of gases (N₂ at 77 K) in volumetric adsorption systems (BELSORP-max, BEL, Japan). All samples were degassed at 468K for 18 h prior to the adsorption measurements. The total micropore volume (pores smaller than

2 nm) was calculated by applying the Horvath–Kawazoe (HK) equation. The specific surface areas of all samples were measured in a relative pressure interval of 0.05–0.30 by using the BET method. The micropore size distributions were calculated by applying the non-local density functional theory (NLDFT) to the N₂ isotherms using the Bel analysis software.

Figure 1 Schematic of the experimental equipment (a) for electrospinning and (b) for testing NO catalytic oxidation

2.4 NO oxidation testing

Figure 1b displays the schematic diagram of the experimental setup to measure NO oxidation. In the mixed gas section, three electronic mass flow controllers (MFCs) were used to control and measure the flow rates of O₂, N₂, and NO. Gas mixtures were prepared from the pure gas streams by mixing in a stainless steel chamber. Gas mixtures could be fed to analytical instrumentation for calibration and measurement of inlet concentrations. A quartz tubular reactor (L = 100 mm, i.d. = 5 mm) was filled with samples. The temperature was controlled via a water bath with a thermostat. A humidity sensor was used to measure the relative humidity. The NO_x analyzer (42i model, Thermo electron Co., USA) was used to detect the concentrations of NO and NO₂. The desired sample quantities (0.05 – 0.10 g) were packed in the tubular reactor

and dipped in a water bath. The reactor was maintained at the desired reaction temperature to stabilize the system and provide a uniform bed temperature. The required gas flow rates were adjusted using MFCs to obtain the desired concentrations of NO and O₂ in N₂. The O₂ content was adjusted to 21 vol %. The inlet and outlet concentrations of the gases were measured by the NOx analyzer wherein the data obtained remains available for further analysis. In this study the inlet concentration was set at 50 ppm.

3. Results

3.1 Morphology of as-prepared GO

The morphology of as-prepared GO sheets (after ultrasound) was presented in Figure 2. It is apparent that the GO sheets include both smaller and larger fragments that range in size from approximately 200 nm to 1.5 μ m. Four different areas were tested to ascertain the mean thickness of the GO sheets, and the resulting thickness values are 0.48 nm, 0.35 nm, 0.73 nm and 0.86 nm respectively. The thicknesses of selected area fragments are under 1 nm, indicating that the as-prepared GO sheets can be considered to be monolayers [23-25]. The bright strips visible on the surface of the GO sheets are the boundary of wrinkles induced during ultrasonication.

Figure 2 Atomic force microscopy (AFM) and transmission electron microscopy (TEM) images of graphene oxide (GO) sheets: (a) AFM image of as-prepared GO after ultrasonication and lateral dimension and thickness of different GO fragments, (b) TEM image of GO sheets, and (c) Edge magnification image of GO sheet.

3.2 Characterizations of as-spun, carbonized, and activated PCNFs and PGCNFs

The optical images of the as-spun and stabilized samples were shown in Figure 3a. The pristine PAN sample appears white and monochromatic, and the colors gradually grow darker as the GO content increases, revealing the homogenous dispersion of GO. Figure 3b displays the colors of nanofibers that have been stabilized in air. After stabilization, some of the samples become brown while others become black as the GO content increases. To convert electrospun polymer nanofibers to carbon nanofibers, the carbonization process has to be performed. Following stabilization and carbonization, the samples experience significant weight loss and shrinkage, resulting

in a decrease in the fiber diameter [1].

Figure 3 Morphology of (a) as-spun and (b) stabilized in air carbon nanofibers. Graphene oxide (GO); %GO: the % of the sample consisting of GO; Polyacrylonitrile (PAN).

The SEM images of the PCNF, PGCNF2, PGCNF5, PGCNF10, PGCNF15, and PGCNF20 samples are displayed in Figure 4. The samples experienced instantaneous cyclization, dehydrogenation and cross-linking reactions in the presence of oxygen at a certain temperature, thereby creating nanofibers that are infusible at higher temperatures [26, 27]. The PCNFs are homogeneous, and smooth with average diameters of approximately 200 nm. With the addition of GO, the surface of the PGCNFs becomes coarser. Further, large amounts of tiny reduced graphene oxide (rGO) fragments are embedded inside the PCNFs and are not externally visible. However, the large-scale GO sheets with lateral dimensions of approximately 0.5 μm to 1.0 μm cannot be enclosed completely by the PCNFs resulting in the presence of some “rose-like” nodes on the surfaces of the materials.

Figure 4 Scanning electron microscopy images of Polyacrylonitrile carbon nanofiber (PCNF) and Polyacrylonitrile graphene oxide carbon nanofiber (PGCNF) samples as follow: (a) PCNF, (b) PGCNF2, (c) PGCNF5, (d) PGCNF10, (e) PGCNF15, and (f) PGCNF20. Note that the numerals following PGCNF reflect the wt% of graphene oxide incorporation.

X-ray diffraction patterns were measured to investigate the structure of the PCNF and PGCNF samples, as shown in Figure 5a. All the patterns exhibit a strong peak at approximately 22.5° and a weak peak at approximately 42.5° , corresponding to the (002) and (10) reflections of the turbostratic carbon. As the addition of GO content increases, the (002) peak gets sharper, suggesting a corresponding enhancement of crystallinity, specifically the GO content reaches 15% relative to the bulk composition of the PCNF samples. This indicates that the addition of GO sheets can play an important role in the promotion of crystallinity. However, increased in crystallinity was not found in sample PGCNF20 because at that concentration, the GO sheets aggregate, hindering the crystalline effect of the PGCNFs [20, 28-31]. Figure 5b displays the Raman spectra of the PCNFs and PGCNFs. All the spectra show the D (at approximately 1350 cm^{-1}) and G (at approximately 1580 cm^{-1}) peaks associated with

disordered and graphitized structures, respectively, and indicate that these CNFs should exhibit the properties of microcrystalline graphitic materials[32, 33]. The peak parameters such as peak position, full width at half maximum (FWHM), and integrated intensity ratio (I_D/I_G) of different samples were obtained by Lorentzian fitting and are listed in Table 2. The FWHM and the I_D/I_G ratio decline and then rise as the GO content increases, suggesting that the addition of GO sheets is capable of enhancing the degree of graphitization.

Figure 5. Characterization of polyacrylonitrile carbon nanofiber (PCNF) and various polyacrylonitrile graphene oxide carbon nanofiber (PGCNF) samples using (a) X-ray diffraction patterns and (b) Raman spectra. Polyacrylonitrile (PAN); Graphene oxide (GO); %GO: the % of the sample **consisting** of GO.

Table 2 Fitting results of the Raman peaks for the Polyacrylonitrile graphene oxide carbon nanofiber (PGCNF) samples with differing GO content

Sample	D peak		G peak		I_D/I_G^b
	Position	FWHM ^a	Position	FWHM ^a	
	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	
PCNF ^c	1371	306	1586	112	1.2
PGCNF2	1368	300	1584	110	1.1
PGCNF5	1370	288	1586	101	0.9
PGCNF10	1368	300	1584	111	1.1
PGCNF15	1368	303	1586	112	1.2
PGCNF20	1369	305	1586	115	1.4

^aFull width at half maximum (FWHM); ^bIntegrated intensity *ratio* (I_D/I_G); ^cPolyacrylonitrile carbon nanofiber (PCNF). Note that numerals following PGCNF reflect the wt% of the graphene oxide incorporation.

Figure 6a presents the isotherms of the PCNF and PGCNF samples. All of the isotherms are type I isotherms according to the International Union of Pure and Applied Chemistry classification system and are therefore representative of the adsorption characteristics of the micropores. The size distributions of the samples pores were calculated by NLDFT and are presented in Figure 6b. This distribution reveals that the PCNF and PGCNF2 samples possess multimodal microporous structures while the other four samples have negligible mesopores that can be attributed to the increasing GO content. The pore structural parameters such as specific surface area and pore volume of various carbonized and activated nanofibers are listed in Table 3. It is apparent that the specific surface and pore volume of the

samples declines as the GO content increases.

Figure 6. N₂ adsorption-desorption isotherms (a) at -196°C and (b) pore size distributions of samples. Polyacrylonitrile (PAN); Graphene oxide (GO); %GO; % of the sample consisting of GO.

Table 3 Pore structural parameters of the polyacrylonitrile carbon nanofiber (PCNF) and polyacrylonitrile graphene oxide carbon nanofiber (PGCNF) samples.

Sample	S^a (m ² g ⁻¹)	S_m^b (m ² g ⁻¹)	V_T^c (cm ³ g ⁻¹)	V_m^d (cm ³ g ⁻¹)
PCNF	480	429	0.226	0.166
PGCNF2	498	460	0.228	0.167
PGCNF5	472	428	0.244	0.181
PGCNF10	435	393	0.217	0.158
PGCNF15	425	403	0.216	0.156
PGCNF20	402	353	0.214	0.137

^a S : specific surface area by the multi-point BET method (P/P_0 from 0.004 to 0.04). ^b S_m : micropore surface area by the t-plot method. ^c V_T : total pore volume according to the capacity of the N₂ adsorption isotherm at P/P_0 of 0.99. ^d V_m : micropore volume by the t-plot method. Note that numerals following PGCNF reflect the wt% of the graphene oxide incorporation.

Fourier transform infrared spectra have been used as a tool to identify the

presence of certain functional groups on a solid surface because it enables detection of the unique energy adsorption band formed by each specific chemical bond [34]. Figure 7 depicts the characteristic vibrations of the PCNFs with and without NH_3 activation and exhibits the following functional groups [22, 34-37]. O-H stretching (associated with the peak at 3435 cm^{-1}), C=O stretching (associated with the peak at 1628 cm^{-1} and 1235 cm^{-1}), C-O stretching and O-H bending (partially associated with the peak at 1162 cm^{-1}), The presence of a mixture of C=N, C=C and N-H groups (associated with the peak at 1580 cm^{-1}) [38]. After activation by NH_3 , the peaks at 1162 cm^{-1} and 1628 cm^{-1} disappeared, but new absorption bands emerge at 1235 cm^{-1} and 1585 cm^{-1} . This result indicates that nitrogen-containing functional groups such as -N-H, have been introduced into the PCNFs.

Figure 7 Fourier transform infrared spectra of the Polyacrylonitrile carbon nanofibers (PCNFs) (black line) obtained in N_2 at 1123K and (red line) in NH_3 at 1123K.

4.3 Measurement of NO removal at room temperature

Figure 8 displays the typical NO_x breakthrough curves of the various CNFs examined in this study. It is apparent that no NO_x (NO and NO_2) was detected in the

outlet gas during the initial stage, while the molecules of NO and NO₂ were adsorbed into the micropores. When NO₂ adsorption saturation is reached, a sharp increase in the NO₂ concentration is observed. After reaching peak maximum, the decrease in NO concentration that occurs for the achievement of the steady state is attributed to the rapid increase in NO₂ desorption and NO oxidation that ensues when the amount of NO₂ adsorbed nears saturation. However, the final total concentration (~48 ppm) of NO and generated NO₂ was not in accordance with the initial given concentration (~50 ppm) of NO, because the equipment of NO-NO₂-NO_x analyzer is unable to detect other nitric oxide except NO and NO₂. Thus, it is highly possible that NO partly transformed into other gases during the process of adsorption-desorption. Figure 9 exhibits the change in breakthrough time of NO and NO₂ for six samples, and the changes in the NO conversion rate (R_c). This rate is determined by the equation, $R_c = \frac{C_{NO_2, out}}{C_{NO, in}} \times 100\%$, where C_{NO₂} is the concentration of nitrogen dioxide and C_{NO} is the concentration of nitrogen oxide. Collectively, as the GO content of the PGCNFs was increased, the six samples evaluated for NO breakthrough time experienced an initial increase followed by a decrease prior to reaching a maximum value. Figure 9c shows that the NO₂ yield curve increases gradually and then declines with increasing of the GO, and gets the maximum value (47.5%) on sample PGCNF5, which indicates that the addition of GO is not the more the better. The maximum yield for the catalytic oxidation of NO occurs when the GO content is 5%.

Figure 8 Adsorption and catalytic oxidation of NO into NO₂ on polyacrylonitrile carbon nanofibers (PCNFs) and various polyacrylonitrile graphene oxide carbon nanofibers (PGCNFs). Note that numerals following PGCNF reflect the wt% of the graphene oxide incorporation. Sample weight: 70 mg, NO: 50 ppm (N₂ as balance gas); O₂: 21 vol. %; Flow rate = 100 SCCM; Temperature = 303 K; RH: 0%; Breakthrough curves of NO and NO₂ on different samples as following: (a) PCNF, (b) PGCNF2, (c) PGCNF5, (d) PGCNF10, (e) PGCNF15, and (f) PGCNF20.

Figure 9 Variations in (a) NO breakthrough time, (b) NO₂ breakthrough time and (c) NO to NO₂ conversion rate of the polyacrylonitrile carbon nanofiber (PCNF) and polyacrylonitrile graphene oxide carbon nanofiber (PGCNF) samples. Note that numerals following PGCNF reflect the wt% of the graphene oxide incorporation.

4 Discussion

The GO nanosheets can be embedded in the electrospun fibers and converted to rGO by heat treatment, thus, the PGCNFs were fabricated and are depicted in a schematic diagram shown in Figure 10. A series of rGO content was embedded into the PCNFs forming a carbon-carbon **hybrid** material that exhibited a microdomain-graphitized and porous structure.

Figure 10 Schematic diagram of a microdomain-graphitized polyacrylonitrile carbon nanofiber

4.1 Effects of rGO on the structure and morphology of PGCNFs

The lateral dimensions of the as-prepared GO sheets are not uniform, ranging from approximately 300 nm to 1.5 μm . The latter is larger than the size of the PCNFs; therefore, some smaller GO sheets can be embedded in the PCNFs that cannot be seen on the surface of PCNFs. In contrast, some of the larger rGO fragments (>500 nm) are exposed at the surface and display floriated features that clearly visible. It also can be observed from Figure 4 that the rGO sheets do not exhibit the morphological characteristics of a single monolayer. Rather, randomly corrugated and crumpled sheets result as compared to the as-prepared GO sheets. This discrepancy arises because of the overlap that occurs between the GO sheets during mixing and

electrospinning. It has been previously reported that GO sheets become more singular and isolated compared to as-spun samples when exposed to high temperatures[39], but in this work, the GO sheets remain strongly bond to one another because of the low processing temperatures.

Figure 6 displays the N₂ adsorption-desorption isotherms at 77K and pore size distributions of the PCNFs and PGCNFs, indicating that some mesopores were introduced as the GO content increased. Samples without or with only trace amounts of GO cannot produce mesopores, so it can be inferred that the observed mesopores from once the GO content reaches a particular threshold [21]. Based on non-local density function theory (NLDFT) [40, 41], the sample has a more narrow micropore size distribution with a predominance of pores below approximately 1 nm. This phenomenon may be related to the NO adsorption caused by the dimerization of NO in the micropores [42]. Although the specific surface and pore volume **decrease** because of the addition of GO, the presence of the GO sheets provides more active sites [43] for the rapid catalysis of NO into NO₂. X-ray diffraction and Raman spectroscopy results indicate that rGO can effectively enhance the degree of crystallinity; however the addition of an excess amount such as 15% GO content can hinder rather than aid crystallization. This result occurs because the wrinkling and adhesive bonding of the GO sheets leads to a non-uniform of dispersion.

4.2 Analysis of the NO catalytic oxidation on hybrid PGCNFs

According to the results of NO catalytic oxidation, the NO was first adsorbed in micropores of hybrid PGCNFs, and then NO was oxidized into NO₂ at atmospheric

pressure at room temperature. However, the inlet concentration of NO (~50 ppm) was not equal to the total outlet concentration of NO and NO₂ (~48 ppm), thus it is likely that the N₂O was generated during the disproportionation reaction of NO. NO can be filled in the micropores in the form of the dimer since NO is a supercritical gas, and the dissociation equilibrium for the NO dimer below 380 K is: $(NO)_2 = 2NO$ [42]. The disproportionation reaction of NO dimers in the micropores of active carbon fiber leads to formation of N₂O and NO₂ [44, 45], according the reactions: $4NO = N_2 + NO_2$, $\Delta G^0 = -121.8 \text{ kJ/mol}$ and $3NO = NO_2 + N_2O$, $\Delta G^0 = -104.2 \text{ kJ/mol}$, although these reactions are very slow at room temperature [46, 47]. N₂ produced is accompanied by the formation of NO₃-type adsorbed species in the decomposition of NO, and the N₂O produced is accompanied by the formation of both NO₂-type adsorbed species and adsorbed O species. It is reported that NO₃-type and NO₂-type adsorbed species formed on Cu-ZSM-5, together with adsorbed O species at 523 K, the decomposition of NO is accompanied by the evolution of N₂, N₂O, and NO₂ [48]. Besides, since oxygen reacts most strongly with carbon active sites, and the facile production of oxygen surface complexes hinder activated diffusion, it may be expected that the composition of the species in micropores may differ significantly from that of the original synthesized gas mixture. So, the nature of micropore penetration mechanisms may result in a somewhat more oxygen-deficient mixture in the micropores in comparison to that in the larger porosity. Thus, the undetected gases are assumed to N₂O and N₂ (~2 ppm), however, the N₂ is unable to be detected because it was used as the carrier gas. Efforts of attempting to identify or detect N₂O

formation should be made more clearly in future work.

4.3 Dual influences of GO addition and NH₃ treatment on the catalytic oxidation of NO into NO₂

For this study, it was desirable for the breakthrough time of NO and NO₂ to have an extended duration, and for the Rc value to be as high as possible. Figure 9 demonstrates that sample PGCNF5 possesses the longest NO breakthrough time, the shortest time for NO₂ breakthrough time and the highest Rc value. These results correlate well with those obtained for the I_D/I_G from the Raman spectra. Sample PGCNF5 has the lowest I_D/I_G indicating that it had the highest degree of graphitization and is the specimen wherein the most chemical active sites were introduced, thereby enabling more NO to be oxidized into NO₂ during a shorter period, and resulting in the highest Rc. GO sheets play an important role in the removal of NO by facilitating the catalytic oxidation of NO to NO₂. Nitrogen-containing functional groups such as -NH has been introduced on the surface of PCNFs and PGCNFs from Figure.7. The Rc value 32.83% of NO to NO₂ conversion for PCNFs activated by NH₃ is considerably higher than the 11% Rc value obtained when activation is induced by exposure to 30 vol% steam in nitrogen for 30 min [5]. The improvement of the catalytic activity of the NO oxidation was ascribed to the dual effects of the addition of the GO sheets and the activation with NH₃. The mechanism for this can be explained in that the addition of rGO sheets to form microdomain-graphitized PGCNFs can introduce more active sites for the oxidation of NO at room temperature. Further, the introduction of nitrogen groups can enhance

the oxidation of NO to NO₂ because the extra electrons resulting from the substitution of N for C are delocalized, and can be transferred to adsorbing species to form reactive surface intermediates [49].

5. Conclusions

A range of various percentages of GO content was added to the PCNFs and activated in NH₃ at 1123K for ten minutes to form microdomain-graphitized PGCNF samples. The GO sheets and NH₃ treatments have an important role in the observed improvement of the catalytic oxidation of NO to NO₂ because of the active sites and nitrogen-containing functional groups respectively, which their inclusion introduces into the CNFs. The efficiency of Rc for the transition of NO to NO₂ becomes more notable with increasing amounts of GO under the same environmental conditions. Further, the PGCNF5 sample possessed a more developed pore structure, greater specific surface area, and the most desirable catalytic oxidation for converting NO to NO₂.

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