Enhanced Catalytic Hydrogen Peroxide Production from Hydroxylamine Oxidation on Modified Activated Carbon Fibers: The Role of Surface Chemistry

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Abstract: Herein, direct production of hydrogen peroxide (H$_2$O$_2$) through hydroxylamine (NH$_2$OH) oxidation by molecular oxygen was greatly enhanced over modified activated carbon fiber (ACF) catalysts. We revealed that the higher content of pyrrolic/pyridone nitrogen (N5) and carboxyl-anhydride oxygen could effectively promote the higher selectivity and yield of H$_2$O$_2$. By changing the volume ratio of the concentrated H$_2$SO$_4$ and HNO$_3$, the content of N5 and surface oxygen containing groups on ACF were selectively tuned. The ACF catalyst with the highest N5 content and abundant carboxyl-anhydride oxygen containing groups was demonstrated to have the highest activity toward catalytic H$_2$O$_2$ production, enabling the selectivity of H$_2$O$_2$ over 99.3% and the concentration of H$_2$O$_2$ reaching 123 mmol/L. The crucial effects of nitrogen species were expounded by the correlation of the selectivity of H$_2$O$_2$ with the content of N5 from X-ray photoelectron spectroscopy (XPS). The possible reaction pathway over ACF catalysts promoted by N5 was also shown.

Keywords: activated carbon fiber; surface modification; hydrogen peroxide; hydroxylamine; pyrrolic/pyridone nitrogen

1. Introduction

Hydrogen peroxide (H$_2$O$_2$), as a green chemical, attracts research attention in both energy and environmental related fields because it has the highest content of reactive oxygen among the common oxidants and the green by-product [1]. It has been widely used as a bleach in the paper and textile industry, an energy carrier in fuel cells, an oxidant in chemical production, wastewater treatment, hydrometallurgy and electronics industry [2]. Notwithstanding, the current industrial production of H$_2$O$_2$ is mainly through the anthraquinone oxidation process [3], which involves multistep reactions, massive energy consumption and waste generation. Furthermore, the cost and safety problems are also raised ineluctably by the handle, transport and storage of high concentration H$_2$O$_2$. Nevertheless, in many practical applications, H$_2$O$_2$ with only a low concentration could satisfy the demand in the reactions, such as selective oxidation, on-site degradation of dye, sewage treatment and disinfection (<30 mM) [4–6]. In this context, research on alternative production methods of H$_2$O$_2$ and it’s in situ use has been the research focus [5,7–15]. The direct generation of H$_2$O$_2$ by the reaction of molecular hydrogen (H$_2$) and oxygen (O$_2$) is considered the most promising method [16–19], but the industrial application is obscured by the dangers of the explosive reaction mixture and the insufficiency of catalysts with high selectivity without considering the reaction systems of O$_2$ and H$_2$ at high pressure [20–25]. In recent years, both photo- and electro-catalytic H$_2$O$_2$ production techniques are in the process of research, but the former is still suffered from a low selectivity and yield of H$_2$O$_2$.
with affordable raw materials while the latter faces the problems of low efficiency and complicated devices accompanied with high cost [2,26,27].

Therefore, in order to avoid the risk of explosion, it would be an effective way to choose an appropriate hydrogen source replacing H\textsubscript{2} in the direct synthesis process of H\textsubscript{2}O\textsubscript{2}. Thus, hydroxylamine (NH\textsubscript{2}OH) was viewed as an available alternative to H\textsubscript{2} since it could be transformed into H\textsubscript{2}O\textsubscript{2} by O\textsubscript{2} in the conditions of room temperature and normal pressure in an aqueous solution (2NH\textsubscript{2}OH + O\textsubscript{2} = N\textsubscript{2} + 2H\textsubscript{2}O + H\textsubscript{2}O\textsubscript{2}) [28]. This reaction is a simple step and easy to handle procedure with two major kinds of catalytic systems. Homogeneous manganese complexes catalysts with high TOF values were firstly studied in this reaction [29–31], but they suffered from separating and recycling problems. Afterward, noble metal particles (Au and Pd) dispersed on different supports were reported to catalyze this system effectively [32–34], but the low concentration of H\textsubscript{2}O\textsubscript{2} (0.05–0.1 wt.%) generation and the high cost of noble metal remain as the major impediment for the industrial applications.

Based on the research above, activated carbon (AC) was found to be an effective catalyst used in the direct H\textsubscript{2}O\textsubscript{2} production process through NH\textsubscript{2}OH oxidation by O\textsubscript{2} in our earlier research [35,36]. We found that the catalytic properties of AC were closely related to the surface oxygen-containing groups. In order to fulfill wider and higher demands in practical application, the selectivity and activity towards H\textsubscript{2}O\textsubscript{2} formation still need to be further improved. Moreover, the reactivity usually originated from the structure of carbon materials. Considering this, nitrogen doping on carbon materials has been found to be one of the most effective ways to improve the selectivity of H\textsubscript{2}O\textsubscript{2} in metal-free catalytic systems, although the selectivity usually depends on both oxygen- and nitrogen-doped atoms [13]. It is noteworthy that N-doping played a beneficial role for H\textsubscript{2}O\textsubscript{2} selectivity only at a low active surface site density while becoming detrimental at higher contents in some reactions [37,38]. Meanwhile, the microporous volume content on carbon materials was also found to have proportionality with selectivity in many catalytic systems [37,39].

Considering the above factors, the easily available polyacrylonitrile-based (PAN-based) activated carbon fiber (ACF) would be an ideal candidate catalyst material. On the one hand, compared to the AC material with a large number of mesopores, PAN-based ACF has only microporous structures and the pore channels are directly open on the surface. More importantly, PAN-based ACF has an intrinsic nitrogen content without any further nitrogen-doped steps and the relatively simple surface modification process would be cost-effective [40]. In the present work, for the sake of comparative study of the generation and modification on the surface doped species, the improvements on the content and type of surface functional groups were intended by treating the PAN-based ACF with concentrated mixed acid in different volume ratios. The selectivity and yield of H\textsubscript{2}O\textsubscript{2} in the reaction on modified ACF catalysts were well interconnected with the amounts of pyrrolic/pyridone nitrogen (N5) and desorbed carboxyl-anhydride groups from the ACF surface. The possible reaction pathway over ACF catalysts promoted by N5 was also shown.

2. Results and Discussion

2.1. Material Structure

Figure 1 shows the scanning electron microscopy (SEM) images of ACF-0 sample and the corresponding elemental mapping images, along with the SEM images of ACF samples before and after surface modification by different volume ratios of concentrated H\textsubscript{2}SO\textsubscript{4} and HNO\textsubscript{3} (H\textsubscript{2}SO\textsubscript{4}/HNO\textsubscript{3} (v/v)). From Figure 1a–d, three main elements (C, N, O) were found on the ACF-0 sample which exhibited a long fiber feature with a diameter of about 15 µm. The surface roughness of the ACF samples gradually increased with the increase of H\textsubscript{2}SO\textsubscript{4}/HNO\textsubscript{3} (v/v) from 0.5 to 4, as shown from Figure 1e–h. For the ACF-Rw sample, the surface still kept smooth similar to the ACF-0 sample, while slight surface roughness was observed on the surface of ACF-R1. By increasing the value of
H$_2$SO$_4$/HNO$_3$ (v/v) to 2 and 4, some auricular-like sheet protrusions were both found on the surface of ACF-R2 and ACF-R4 samples. Consequently, the surface modification caused differently morphological changes on the ACF samples through the erosion of carbon surface by different H$_2$SO$_4$/HNO$_3$ (v/v), and some microporous structures on the ACF samples might be destroyed through mixed acid treatment with higher content of concentrated H$_2$SO$_4$.

Figure 1. SEM images of the ACF-0 sample and the corresponding elemental mapping images for (a) overlap, (b) C, (c) N, (d) O. The SEM images of ACF samples after surface modification (e) ACF-Rw, (f) ACF-R1, (g) ACF-R2, (h) ACF-R4.

The pore size distribution of ACF-0 and ACF-R4 samples, and nitrogen adsorption-desorption isotherms of the ACF-0 sample without surface modification is shown in Figure 2. The detailed texture parameters for the ACF samples were shown in Table 1. Moreover, the ACF-0 sample displayed the features of type I isotherm, indicating the existence of micropores. There were two types of pores on the ACF-0 sample: micropore (1.41 nm and 1.13 nm) and supermicropore (0.78 nm and 0.57 nm) [41]. As for the ACF-R4 sample, the micropore content (1.14 nm) was greatly enhanced and some micropores enlarged to 1.69 nm while the supermicropore content was decreased compared with the ACF-0 sample. As displayed in Table 1, minor changes in the pore size and surface area were found between the ACF-0 and ACF-Rw samples but obviously decrease in micropore volume and surface area were observed on the ACF-R2 and ACF-R4 samples. As for the ACF-Rw sample, the surface area of micropores ($S_{\text{mic.}}$), the total surface area ($S_{\text{BET}}$) and the surface area of mesoporous ($S_{\text{mes.}}$) was 895, 934 and 39 m$^2$/g, respectively. Correspondingly, the micropore volume ($V_{\text{mic.}}$), the total pore volume ($V_{\text{total}}$) and the micropore width ($d_{\text{pore}}$) of ACF-Rw were calculated to be 0.361, 0.395 cm$^3$/g and 0.85 nm. These results were similar to those of the ACF-0 sample. With the increase of H$_2$SO$_4$/HNO$_3$ (v/v), the values of $V_{\text{total}}$ and $S_{\text{BET}}$ initially reduced to 0.323 cm$^3$/g and 686 m$^2$/g on the ACF-R1 sample, then declined to 0.229 cm$^3$/g and 481 m$^2$/g on the ACF-R2 sample. Moreover, the $d_{\text{pore}}$ for ACF samples by mixed acid oxidation increased slightly from 0.87 to 0.95 nm, with increasing H$_2$SO$_4$/HNO$_3$ (v/v) from 0.5 to 4. Notably, the mesopores of the ACF samples were not altered much through the modification by mixed acid, whereas the micropores decreased remarkably by higher values of H$_2$SO$_4$/HNO$_3$ (v/v), especially in the ACF-R2 and ACF-R4 samples. This suggests that the higher content of H$_2$SO$_4$ caused severe destruction of the microporous structures while the higher content of HNO$_3$ preserved the textual characteristics of the ACF sample.
The intensities of the peaks at 910 cm$^{-1}$ were wholly enhanced to different extents, suggesting the formation of large quantities of oxygen-containing species on ACF surface. For ACF-R1, ACF-R2 and ACF-R4 samples, the intensities of the above peaks at 910 cm$^{-1}$, 1225 cm$^{-1}$, 1405 cm$^{-1}$, and 1580 cm$^{-1}$ were all greatly enhanced, which confirms the further enrichment of anhydride and carboxylic groups by a higher content of H$_2$SO$_4$ in mixed acid.

The peak at 1405 cm$^{-1}$ is respectively related to the nitrogen groups and the double bond of C=C in quinoid structure. Meanwhile, the peak at 1730 cm$^{-1}$ is related to the stretching vibration of the C=O band in carboxyl and lactones groups attached to the aromatic rings, and the peak at 910 cm$^{-1}$ was all greatly increased, indicating the enlargement in phenols, quinones, lactones, carboxyls and anhydrides. The highest peak intensity was found on ACF-R2 and ACF-R4 samples, especially at the position of 1730 cm$^{-1}$, which confirms the further enrichment of anhydride and carboxylic groups by a higher content of H$_2$SO$_4$ in mixed acid.

The Fourier transformation infrared (FTIR) spectra of ACF samples is shown in Figure 3a. According to the references, the peak at 1225 cm$^{-1}$ is originated from the stretching mold of C–N and C–O in carboxylic anhydrides, ethers, lactones and phenols [42,43]. The peak at 1405 cm$^{-1}$ and 1580 cm$^{-1}$, which confirms the further enrichment of anhydride and carboxylic groups by a higher content of H$_2$SO$_4$ in mixed acid.

![Figure 2](image-url)  
Figure 2. The pore size distribution (PSD) of ACF-0 and ACF-R4 samples obtained from the density functional theory method and N$_2$ adsorption-desorption isotherms of ACF-0 sample.

Table 1. Textural parameters of the ACF samples before and after surface modification.

| Catalyst | S$_{BET}$ [a] (m$^2$/g) | S$_{mic}$ [b] (m$^2$/g) | S$_{mes}$ [b] (m$^2$/g) | V$_{mic}$ [b] (cm$^3$/g) | V$_{Total}$ [c] (cm$^3$/g) | d$_{pore}$ [d] (nm) |
|----------|------------------------|-----------------------|------------------------|------------------------|------------------------|-------------------|
| ACF-0    | 944                    | 909                   | 35                     | 0.374                  | 0.411                  | 0.87              |
| ACF-Rw   | 934                    | 895                   | 39                     | 0.361                  | 0.395                  | 0.85              |
| ACF-R1   | 686                    | 601                   | 85                     | 0.261                  | 0.323                  | 0.94              |
| ACF-R2   | 481                    | 356                   | 124                    | 0.146                  | 0.229                  | 0.95              |
| ACF-R4   | 368                    | 322                   | 46                     | 0.132                  | 0.160                  | 0.95              |

[a] Multipoint Brunauer-Emmett-Teller (BET). [b] Calculated by the t-plot method. [c] Estimated from the amounts of gas adsorbed at a relative pressure of 0.994. [d] Average pore diameter calculated from 2V$_{Total}$/S$_{BET}$ for slit pore.

2.2. Surface Properties

The Fourier transformation infrared (FTIR) spectra of ACF samples is shown in Figure 3a. According to the references, the peak at 1225 cm$^{-1}$ is originated from the stretching mold of C–N and C–O in carboxylic anhydrides, ethers, lactones and phenols [42,43]. The peak at 1405 cm$^{-1}$ and 1580 cm$^{-1}$ is respectively related to the nitrogen groups and the double bond of C=C in quinoid structure. Meanwhile, the peak at 1730 cm$^{-1}$ is owing to the stretching vibration of the C=O band in carboxyl and lactones groups attached to the aromatic rings, and the peak at 910 cm$^{-1}$ is related to the anhydride groups [41,43,44]. After modification by different values of H$_2$SO$_4$/HNO$_3$ (v/v), the intensities of the above peaks were wholly enhanced to different extents, suggesting the formation of large quantities of oxygen-containing species on ACF surface. For ACF-R1, ACF-R2 and ACF-R4 samples, the intensities of the peaks at 910 cm$^{-1}$, 1225 cm$^{-1}$, 1580 cm$^{-1}$ and 1730 cm$^{-1}$ were all greatly increased, indicating the enlargement in phenols, quinones, lactones, carboxyls and anhydrides. The highest peak intensity was found on ACF-R2 and ACF-R4 samples, especially at the position of 1730 cm$^{-1}$, which confirms the further enrichment of anhydride and carboxylic groups by a higher content of H$_2$SO$_4$ in mixed acid.
As shown in Figure 3b, Raman spectroscopy detection was conducted to investigate the defects on carbon structure of ACF samples with surface modification. Usually, carbon fiber mainly has two characteristic peaks, one of which is the D peak at the position of 1350–1375 cm\(^{-1}\), and the other is the G peak at the position of 1580–1603 cm\(^{-1}\) [45]. The D peak is related to amorphous and defects of carbon structure while the G peak is related to graphite crystal structure. Generally, the calculation of \(I_D/I_G\) ratio from integral areas values of D and G peak was used to measure the structural defects of carbon materials [46]. It is widely known that \(I_D/I_G\) value increases with more structural defects generated on the carbon material. Obviously, the intensity of Raman spectra on ACF samples gradually increased, meanwhile the \(I_D/I_G\) values of all the ACF samples increased from 0.95 to 1.07 with increasing H\(_2\)SO\(_4\)/HNO\(_3\) (\(v/v\)) from 0.5 to 2. Whereas the \(I_D/I_G\) values of ACF-R4 decreased to 1.06 with increasing H\(_2\)SO\(_4\)/HNO\(_3\) (\(v/v\)) from 2 to 4. Therefore, it is believed that there were more surface defects and structural changes on the ACF carbon framework according to the surface modification with more H\(_2\)SO\(_4\) contents in mixed acid. These results were well matched with the textural characteristics in ACF samples shown in Table 1.

The narrow scan of C 1s regions in X-ray photoelectron spectroscopy (XPS) of ACF samples is exhibited in Figure 4a. Moreover, the deconvolution results of the C 1s spectrum are given in Table 2. For modified carbon materials, the C 1s spectra usually involved graphitic carbon (C–graphite, Peak I), ether, alcohol or phenolic groups (C–O, Peak II), carbonyl or quinone groups (C=O, Peak III), carboxylic groups (–COO–, Peak IV) and Peak V for the satellite peak from the \(\pi-\pi^*\) electron shake-up [47–49]. The intensities of peak I was decreased by the oxidation of mixed acid, whereas the intensities for the peaks attributed by C–O groups were increased [49]. However, the areas of peak II of all ACF samples by acid oxidation increased not so obviously compared to that of peak III or peak IV, which indicated phenolic groups may not be tailored much by adjusting different values of H\(_2\)SO\(_4\)/HNO\(_3\) (\(v/v\)). Similarly, the integral area of peak IV for both ACF-Rw (4.5%) and ACF-R1 sample (5.4%) was more than two times larger than that of the ACF-0 (2.0%). Notably, the area of peak IV increased to 7.9% and 8.7% on the ACF-R2 and ACF-R4 samples respectively, clearly confirming the generation of a large amount of surface carboxylic groups by the higher content of H\(_2\)SO\(_4\).
Table 2. Deconvolution results of the C 1s XPS spectra for the ACF samples, values given in % of total intensity.

| Catalyst | Peak I C–graphite (eV) | Peak II C–O (eV) | Peak III C=O (eV) | Peak IV –COO– (eV) | Peak V π–π* (eV) |
|----------|------------------------|-----------------|------------------|-------------------|-----------------|
| ACF-0    | 284.7–284.8            | 286.0–286.3     | 287.7–288.1      | 289.2–289.6       | 291.2           |
| ACF-Rw   | 67.9                   | 19.9            | 6.4              | 4.5               |                 |
| ACF-R1   | 63.4                   | 23.4            | 7.8              | 5.4               |                 |
| ACF-R2   | 57.4                   | 24.8            | 9.5              | 7.9               | 1.9             |
| ACF-R4   | 56.5                   | 23.7            | 10.3             | 8.7               | 0.8             |

Figure 4a exhibits the narrow scan of XPS spectra in O 1s regions of the ACF samples. Moreover, the deconvolution results of the O 1s spectrum are displayed in Table 3. As shown in Figure 4b, the O 1s XPS spectra can be deconvoluted into three main peaks, namely Peak I, Peak II and Peak III, which are associated with the C=O group, C–O group and adsorbed H₂O or O₂, respectively [42]. The adsorbed CO or CO₂ in the ACF surface can be attributed to the minor Peak IV, the binding energy of which was at 536.9–537.0 eV. Obviously, the intensities of both Peak III and Peak IV decreased by surface modification, whereas the peaks corresponding to C=O groups increased evidently. As for Peak I, the intensities increased from 25.5 to 30.5% by surface modification with increasing the content of H₂SO₄, and similar results were obtained on ACF-R2 and ACF-R4 samples.
Additionally, the atomic ratio of surface O/C in the ACF samples by acid oxidation was enhanced significantly from 21.3 to 32.9% with increasing the H$_2$SO$_4$/HNO$_3$ (v/v) from 0.5 to 4. The above results suggested that more carboxylic species were generated by mixed acid oxidation with higher content of H$_2$SO$_4$, being consistent with the results of FTIR measurement.

Table 3. Deconvolution results of the O 1s XPS spectra for the ACF samples, values given in % of total intensity.

| Catalyst  | Peak I C=O (eV) | Peak II C–O (eV) | Peak III H$_2$O$_{ads}$ (eV) | Peak IV CO$_{2ads}$ (eV) | O/C (%) |
|-----------|----------------|-----------------|----------------------------|--------------------------|---------|
| ACF-0     | 531.6–531.8    |                | 532.9–533.0                |                          | 12.0    |
| ACF-Rw    |                | 51.0           |                            | 23.3                     | 21.3    |
| ACF-R1    |                | 54.2           |                            | 20.1                     | 24.9    |
| ACF-R2    | 27.6           | 56.3           |                            | 15.3                     | 32.2    |
| ACF-R4    | 30.7           | 56.0           |                            | 12.9                     | 32.2    |

For the sake of examining the crucial role of the intrinsic nitrogen doped in ACF samples, the deconvolution results of N 1s XPS profiles of ACF samples are exhibited in Figure 5. Moreover, the corresponding results of the deconvolution are displayed in detail in Table 4. According to the curve fitting results and references, five distinct types of nitrogen contained species were deconvoled from the N 1s spectra: NX (-NO$_2$), N4 (pyridine-N oxide), NQ (quaternary N), N5 (pyrrolic/pyridone) and N6 (pyridine) [50–53]. It was evident that the content of N6 in ACF-0 was highest among all ACFs. Moreover, the content of N5 significantly increased to 33.2%, 43.4%, 50.5% and 46.3% for the ACF-Rw, ACF-R1, ACF-R2 and ACF-R4, respectively. As shown in Table 4, the content of N6 on the ACF-0 decreased from 15.6 to 5.2% corresponding to the ACF-R2. Moreover, the content of both NQ and N4 on the ACF sample decreased nearly one half by surface modification. It was reported that –NO$_2$ and pyridine were the main forms of the nitrogen introduced from HNO$_3$ oxidation and different forms of nitrogen can be transformed to each other [42,54]. The content of NX initially reached the maximum (32.3%) on ACF-Rw, then decreased to 22.3%, 15.3% and 19.0% on ACF-R1, ACF-R2 and ACF-R4, respectively. No content of NX can be observed on the ACF-0 sample without surface modification. Accordingly, when the nitrogen form predominated in the ACF sample was quaternary N, the mixed acid modification transformed them to –NO$_2$ with the higher content of HNO$_3$. Meanwhile, more pyrrolic nitrogen species were generated by a higher content of H$_2$SO$_4$. In addition, the atomic ratios of surface N/C on ACF samples were gradually enhanced from 1.5 to 2.4 with the increase of H$_2$SO$_4$/HNO$_3$ (v/v) from 0.5 to 2, whereas that on ACF-R4 sample decreased to 2.0 by increasing the value of H$_2$SO$_4$/HNO$_3$ (v/v) to 4. These results suggest that the surface N-containing groups could be effectively tuned by mixed acid oxidation with different volume ratios of concentrated H$_2$SO$_4$ and HNO$_3$. 
The temperature-programmed desorption (TPD) results of the ACF samples were shown in Figure 6. After being heated, carbon oxides were the main decomposition products of surface oxygen-containing functional groups [55–58]. As shown in Figure 7, the anhydrides and carboxylic acids usually decomposed into CO$_2$ at relatively lower temperatures while the lactones decomposed into CO$_2$ at higher temperatures. Meanwhile, the carboxylic anhydrides, ethers, phenols, carbonyl-quinones generally decomposed into CO [58]. Only little quantities of CO$_x$ were obtained on the ACF-0 sample while significant quantities of CO$_x$ were obtained on the other three ACF samples. For the ACF samples modified by mixed acid, the data of CO$_x$ gradually rose with increasing the H$_2$SO$_4$/HNO$_3$ ($\nu/\nu$) from 0.5 to 4. Especially, the desorption quantity of CO from the ACF-R1 sample was almost five-fold larger than that of the ACF-0 sample, illustrating the formation of large quantities of phenol and carbonyl-quinone groups. On the flip side, the desorption amount of CO$_2$ from the ACF-R2 sample was almost more than 15 times greater than the

Figure 5. High resolution of XPS spectra in N 1s regions of ACF samples.

Table 4. Deconvolution results of the N 1s XPS spectra for the ACF samples, values given in % of total intensity.

| Catalyst | N6 Pyridine 398.7 | N5 Pyrrolic/Pyridone 400.1–400.2 | NQ Quaternary N 401.2–401.3 | N4 Pyridine-N-oxide 402.6 | NX –NO$_2$ 406.0 | N/C (%) |
|----------|------------------|-------------------------------|-----------------------------|-----------------------------|-------------------|---------|
| ACF-0    | 15.6             | 20.2                          | 46.8                        | 17.5                        | —                 | 1.4     |
| ACF-Rw   | 3.2              | 33.2                          | 26.0                        | 5.4                         | 32.3              | 1.5     |
| ACF-R1   | 2.8              | 43.4                          | 24.3                        | 7.3                         | 22.3              | 1.7     |
| ACF-R2   | 5.2              | 50.5                          | 22.8                        | 6.2                         | 15.3              | 2.4     |
| ACF-R4   | 4.7              | 46.3                          | 22.9                        | 7.1                         | 19.0              | 2.0     |
ACF-0 sample, primarily owing to the remarkable generation of lactones, anhydrides and carboxylic acids. The quantities of CO obtained from ACF-R4 were very similar to the ACF-R2 sample.

Figure 6. TPD profiles of ACF samples before and after surface modification.

Figure 7. Deconvolution of the TPD profiles for ACF samples, in which peak a, peak b, peak c from the CO\textsubscript{2} desorption of the carboxyl, anhydride, lactone groups while peak d, peak e, peak f from the CO desorption of the anhydride, phenol, carbonyl groups on ACF samples.
Tables 5 and 6 show the detailed data of CO and CO\(_2\) desorbed from specific surface groups on ACF samples. The desorption quantities of CO and CO\(_2\) on ACF-0 sample were 244 \(\mu\)mol/g and 65 \(\mu\)mol/g, severally, and they were raised to 1008 \(\mu\)mol/g and 400 \(\mu\)mol/g on ACF-Rw sample. Upon increasing the H\(_2\)SO\(_4\)/HNO\(_3\) (v/v) from 0.5 to 1, the desorption quantities of CO and CO\(_2\) on the ACF-R1 sample remarkably raised to 1207 \(\mu\)mol/g and 678 \(\mu\)mol/g, respectively. Nevertheless, the amounts of CO desorbed from carbonyl-quinone groups on the ACF-R2 sample decreased to 125 \(\mu\)mol/g. While compared with ACF-Rw, more than two times larger amounts of CO\(_2\) desorbed from carboxyl and anhydride groups were also found on the ACF-R2 sample. The desorption quantities of CO\(_2\) and CO on the ACF-R4 sample were very similar to the ACF-R2 sample. Considering all these examinations, it could be deduced that the largest amounts of carboxyl (407 \(\mu\)mol/g) and anhydride (425 \(\mu\)mol/g) were obtained on the ACF-R2 and ACF-R4 samples while the most enrichment of phenol groups was detected on the ACF-R1 sample. This means that the moderate content of H\(_2\)SO\(_4\) produced more phenol groups while the higher content of H\(_2\)SO\(_4\) in the mixed acid created more carboxylic and anhydride groups. These results were consistent with the FTIR and XPS results of ACF samples.

Table 5. The desorption quantities of CO\(_2\) from the ACF samples by the deconvolution of the TPD profiles.

| Catalyst | Carboxyl [a] | CO\(_2\) Desorption (\(\mu\)mol/g) | Anhydride [b] | Lactone [c] | Total |
|----------|--------------|-----------------------------------|---------------|-------------|-------|
| ACF-0    | 32           |                                   | 15            | 17          | 65    |
| ACF-Rw   | 195          |                                   | 132           | 73          | 400   |
| ACF-R1   | 317          |                                   | 245           | 116         | 678   |
| ACF-R2   | 407          |                                   | 420           | 136         | 963   |
| ACF-R4   | 406          |                                   | 425           | 122         | 953   |

Desorption temperatures: [a] 255–275 °C, [b] 430–451 °C, [c] 611–623 °C.

Table 6. The desorption quantities of CO from the ACF samples by the deconvolution of the TPD profiles.

| Catalyst | Anhydride [d] | CO Desorption (\(\mu\)mol/g) | Phenol [e] | Carbonyl [f] | Total |
|----------|--------------|--------------------------------|------------|--------------|-------|
| ACF-0    | 15           |                                 | 83         | 146          | 244   |
| ACF-Rw   | 132          |                                 | 739        | 137          | 1008  |
| ACF-R1   | 245          |                                 | 823        | 139          | 1207  |
| ACF-R2   | 420          |                                 | 627        | 125          | 1172  |
| ACF-R4   | 425          |                                 | 551        | 67           | 1043  |

Desorption temperatures: [d] 458–491 °C, [e] 630–660 °C, [f] 785–812 °C.

2.3. \(H_2O_2\) Production

Figure 8a shows the concentration of \(H_2O_2\) production from NH\(_2\)OH oxidation by O\(_2\) on the ACF catalysts. For the ACF-0 catalyst without surface oxidation, the cumulative concentration of \(H_2O_2\) was very low and cannot be detected after reacting for 300 min. For the ACF-Rw catalyst, the concentration of \(H_2O_2\) increased to 55.9 mmol/L at 420 min and then increased slightly. Similar trends plots were observed on the ACF-R1, ACF-R2 and ACF-R4 catalysts, on which the \(H_2O_2\) concentration increased gradually with the increase of reaction time. When the reaction was conducted for 660 min, the concentration of \(H_2O_2\) approached 88.6 mmol/L and 112 mmol/L on the ACF-R1 and ACF-R4 catalyst, respectively. With increasing the H\(_2\)SO\(_4\)/HNO\(_3\) (v/v) from 1 to 2, the maximum concentration of \(H_2O_2\) reached 123 mmol/L on the ACF-R2 catalyst, which clearly demonstrates more reactive species were generated on the ACF-R2 surface by an appropriately higher content of H\(_2\)SO\(_4\) in mixed acid. In order to explore the stability of ACF catalysts, the recycling tests of ACF-R2 were performed as shown in Figure 8b. After three cycles, there was almost
no decrease in the activity of the reused ACF-R2 catalyst with the yield of H$_2$O$_2$ about 49% (123 mmol/L) after reacting for 660 min.

The selectivity of H$_2$O$_2$ along with the NH$_2$OH conversion on the ACF catalysts at the reaction time of 180 min was shown in Figure 9a. The selectivity of H$_2$O$_2$ was only 46.0% on the ACF-Rw catalyst although the higher conversion of NH$_2$OH (30%) was observed on it, which was possibly induced by the higher surface area and more carbonyl-quinone groups generating through the surface modification. In view of similar conversion toward NH$_2$OH (~22%) consumption, the selectivity of H$_2$O$_2$ was 73.6% on the ACF-R1 catalyst prepared by an equal volume of H$_2$SO$_4$ and HNO$_3$. Whereas the selectivity of H$_2$O$_2$ was greatly enhanced to 99.3% on the ACF-R2 catalyst obtained by further increasing the content of H$_2$SO$_4$. However, the selectivity of H$_2$O$_2$ decreased to 87.6% on the ACF-R4 catalyst by the increase of the H$_2$SO$_4$/HNO$_3$ (v/v) from 2 to 4. Thus, the formation of more reactive nitrogen and oxygen containing groups on the ACF catalysts greatly enhanced the selectivity toward H$_2$O$_2$ formation.
The activity of H$_2$O$_2$ decomposition over ACF catalysts was shown in Figure 9b. According to the reference [59], the activity toward H$_2$O$_2$ decomposition was directly related to the basic sites (chromene groups) on the AC materials surface, while the formation of surface carboxylic groups (–COOH) will accordingly retard the catalytic decomposition of H$_2$O$_2$. It was also found that the acidic function groups of AC materials treated by HNO$_3$ would suppress the H$_2$O$_2$ decomposition rate. As shown in Figure 9b, almost no decomposition of H$_2$O$_2$ was detected on the ACF-R2 and ACF-R4 catalyst during the first 60 min. After reacting for 420 min, the concentration of H$_2$O$_2$ in the ACF-R1, ACF-R2 and ACF-R4 catalyst system only decreased to 246 mmol/L, 247 mmol/L and 248 mmol/L, respectively. As for the ACF-Rw catalyst, with the smallest amounts of carboxylic groups, the concentration of H$_2$O$_2$ quickly decreased to 245 mmol/L only within 180 min. Therefore, the modified ACF catalysts with large amounts of carboxylic groups by mixed acids retarded the catalytic decomposition of H$_2$O$_2$ and exhibited a higher activity of H$_2$O$_2$ generation.

The catalytic performance in the reaction of H$_2$O$_2$ production from NH$_2$OH oxidation over modified ACF catalysts was listed and compared to those of previously reported catalysts in Table 7. The modified ACF catalysts showed a higher formation concentration of H$_2$O$_2$ than the Au/MgO and Pd/Al$_2$O$_3$ system with a longer reaction time. The ACF-R2 and ACF-R4 catalysts exhibited similarly catalytic performance with the ACH system but with higher selectivity toward H$_2$O$_2$. As for the homogeneous Mn (II/III)-complex system, both the concentration and the yield of H$_2$O$_2$ were higher than all heterogeneous catalysts systems without considering their separating and recycling problems. Meanwhile, the concentration of H$_2$O$_2$ over ACF-R2 and ACF-R4 catalysts was higher than the most reactive carbon supported Au and Pd catalysts, which were used in the direct H$_2$O$_2$ production process from H$_2$ and O$_2$ at high pressure. Thus, compared with the Au-Pd/C catalyst, the ACF catalysts system had a longer reaction time (>9 h) while the supported Au and Pd catalysts system only took 0.5 h to obtain a similar concentration of H$_2$O$_2$. Considering the practical application, the reaction of the ACF catalysts system was easy to handle at atmospheric pressure whereas the high pressure was necessary for the supported Au and Pd catalysts system.

Table 7. Comparative performance in the production of H$_2$O$_2$ over ACF catalysts with reference catalysts (pH = 7.0–8.6, temp. = 2–27°C).

| Catalyst | [H$_2$O$_2$] (mmol/L) | Reaction Time (h) | Hydrogen Source | Conversion (%) | Selectivity (%) | Yield (%) | Reference |
|----------|----------------------|-------------------|----------------|---------------|----------------|-----------|-----------|
| ACF-Rw   | 60.8                 | 11.0              | NH$_2$OH       | 72.9          | 33.3           | 24.3      | This work |
| ACF-R1   | 88.5                 | 11.0              | NH$_2$OH       | 50.5          | 70.1           | 35.4      | This work |
| ACF-R4   | 112                  | 11.0              | NH$_2$OH       | 47.4          | 94.5           | 44.8      | This work |
| ACF-R2   | 123                  | 11.0              | NH$_2$OH       | 49.2          | 100            | 49.2      | This work |
| ACF-R2*  | 117                  | 11.0              | NH$_2$OH       | 56.0          | 83.6           | 46.8      | This work |
| ACF-R2   | 53                   | 3.0               | NH$_2$OH       | 21.3          | 99.3           | 21.2      | This work |
| ACH      | 114                  | 7.0               | NH$_2$OH       | -             | -              | 46.7      | [35]      |
| ACP      | ~50                  | 3.0               | NH$_2$OH       | ~23           | ~87            | 20.0      | [36]      |
| Mn$^{2+}$-Tiron | ~225             | 6.0               | NH$_2$OH       | -             | -              | ~90       | [29]      |
| Mn$^{3+}$-Complex* | ~185               | 0.75              | NH$_2$OH       | -             | -              | ~74       | [30]      |
| Au/MgO   | 32.6                 | 1.0               | NH$_2$OH       | -             | -              | 81.5      | [32]      |
| Pd/Al$_2$O$_3$ | 37.6             | 1.0               | NH$_2$OH       | -             | -              | 94.0      | [33]      |
| Au-Pd/C* | 69                   | 0.5               | H$_2$          | -             | -              | -         | [21]      |
| Au-Pd/C | 62                   | 0.5               | H$_2$          | -             | -              | -         | [22]      |
| Au-Pd   | 94                   | 0.5               | H$_2$          | -             | -              | -         | [23]      |
| Au + Pd/C | 79                 | 0.5               | H$_2$          | -             | -              | -         | [24]      |
| Pd[Au]/C  | 77.5                | 0.5               | H$_2$          | -             | -              | -         | [25]      |

* The third cycle of the ACF-R2 catalyst. * The [Na$_2$[Mn(3,5-(SO$_3$)$_2$-Cat)$_2$]·10H$_2$O complex with addition of Tiron as catalyst. * Reaction conditions: 10 mg catalyst in 5.6 g methanol and 2.9 g water solvent, 420 psi 5% H$_2$/CO$_2$ + 160 psi 25% O$_2$/CO$_2$, with stirring 1200 rpm at 2°C.
2.4. Effect of Surface Nitrogen- and Oxygen-Containing Groups

Obviously, there was no direct correlation between the selectivity of H₂O₂ with the surface area or the microporous volume of ACF catalysts. That is, the H₂O₂ formation was affected little by the microporous structure. With the aim of exploring the reactivity and the surface chemistry of ACF catalysts, we correlated the selectivity of H₂O₂ with the percentage of N5 (pyrrolic/pyridone) from XPS spectra, and the concentration of H₂O₂ on the specific surface area of ACFs with the amounts of desorbed carboxyl-anhydride groups over the ACF catalysts from TPD results, as shown in Figure 10. Clearly, there was a perfectly positive correlation between the selectivity and the percentage of N5 on the ACF catalysts shown in Figure 10a. It has been considered that, for nitrogen doping, the wholeness of the π-conjugate system was broken by the higher electronegativity on the N atom doped in the carbon basal framework of ACF. Moreover, this could induce charge redistribution, which changes the adsorption performance of the reactive intermediates over the carbon materials [57,58]. Thus, compared with pyridine, pyrrolic/pyridone structure in the carbon skeleton possessing more electronegativity was beneficial for the effective adsorption of reactants, which greatly enhanced the selectivity of H₂O₂ on ACF-R2 with higher content of N5.

![Figure 10](image-url)

Figure 10. The relationship between (a) the selectivity of H₂O₂ and percentage of N5, (b) the concentration of H₂O₂ and the amounts of carboxyl-anhydride groups on the ACF catalysts (pH = 8.6, temp. = 25 °C, time = 180 min.).

On the other hand, the correlation between the concentration of H₂O₂ on a specific surface area of ACFs with the amounts of CO₂ desorbed from carboxyl-anhydride groups demonstrated that the yield of H₂O₂ increased in a positive correlation way with the increment of carboxyl-anhydride groups on ACF catalysts, as shown in Figure 10b. This could be ascribed to the more hydrophilic surface on ACFs induced by the formation of large quantities of carboxyl-anhydride species, which are in favor of both effective contact with the hydrophilic reactant and maintaining the existence of H₂O₂. Therefore, the highest selectivity of the ACF-R2 catalyst can be sensibly and directly ascribed to the great quantity of surface oxygen-containing groups and nitrogen-containing groups, particularly the pyrrolic/pyridone nitrogen groups.

For the sake of further clarifying the crucial function of the surface nitrogen, a possible promotion mechanism is proposed. Scheme 1 shows the possible reaction pathway of H₂O₂ production from NH₂OH and O₂ on ACF catalysts promoted by N5. Similar to the reaction mechanism proposed in our previous work [60], NH₂OH loses protons and electrons when contacted with the quinone species on the ACF surface, forming the HNO intermediate. Then the HNO reacts with NH₂OH, producing N₂ and H₂O. The quinoid groups subsequently transfer the protons and electrons to O₂ through the redox cycles of quinone and hydroquinone, completing a typical process of H₂O₂ formation. The role of N5 can be explained from two aspects, namely pyrrolic nitrogen and pyridone structure.
The pyrrolic nitrogen doped on a carbon structure with more electronegativity formed in the edges of the carbon basal plane on ACF, which promotes the electrons transfer between O₂ and NH₂OH. Thus, the adsorbed O₂ species on the ACF surface received the electrons transferred easily from the nitrogen species with extra electrons, and then formed HO₂•* intermediates [53]. For the pyridone structure, the NH group is considered a portion of the six-membered ring on the brink of an extended carbon basal plane. The electronic surrounding of the NH species is thought similar to that of pyrrole because the excess electrons of the N atom could be delocalized among the condensed aromatic system and entrapped at defects on the carbon basal layer [40]. Meanwhile, the pyridone structure is usually in presence of two tautomeric structures including 2-hydroxypyrididine and α-pyridone. Usually, these two tautomeric forms are transformed to each other by the intramolecular proton transfer, which may facilitate the protons transfer to the HO₂•* intermediates, forming H₂O₂. Therefore, the higher selectivity of H₂O₂ can be attributed to the higher content of N₅ on the ACF catalyst.

Scheme 1. The possible reaction pathway of H₂O₂ production from NH₂OH and O₂ on ACF catalysts promoted by N₅.

3. Materials and Methods

3.1. Surface Modification of ACF

Ten grams of PAN-based ACF (Jilin, Jiyan high-tech Fibers) were put into 100 mL of concentrated hydrochloric acid (HCl, 37%) and mixed for removing the possible impurities including ashes or inorganic substances. The mixtures were firstly stirred for 3 h at ambient temperature, then Cl⁻ was thoroughly removed from the filtrate by washing with hot water (detected with AgNO₃). The obtained sample was put into a vacuum oven and dried at 80 °C overnight, which was christened ACF-0. Then, the ACF-0 (0.5 g) was mixed and stirred in 50 mL of concentrated sulfuric acid (H₂SO₄, 98%) and concentrated nitric acid (HNO₃, 68%) at 60 °C for one hour with a volume ratio of 0.5, 1, 2 and 4, respectively. The oxidized ACF was washed by hot water in order to obtain nearly neutral pH of the filtrate and put into a vacuum oven, then dried at 80 °C overnight. The samples as prepared thus were noted as ACF-Rw, ACF-R1, ACF-R2 and ACF-R4, respectively.

3.2. Characterization of the ACF Catalysts

Field-emission scanning electron microscopy (FE-SEM) images were recorded on a Philips Fei Quanta 200F instrument operating at 20 kV, while elemental mapping images of ACF-0 were obtained on a Hitachi SU8220 SEM instrument working at 15 kV. Nitrogen adsorption-desorption detection was measured by a Micrometrics ASAP 2460 instrument under −196 °C. Moreover, the ACF catalysts were outgassed at 250 °C overnight before
the start of measurement. The multipoint Braunauer–Emmett–Teller (BET) analysis was used to calculate the specific surface area ($S_{\text{BET}}$). Fourier transformation infrared (FTIR) spectra of the ACF catalysts were conducted on an IR spectrometer (Bruker Vector 22) by making KBr pellets containing 0.5 wt.% of ACF. The Raman spectra of ACF catalysts were obtained on a Horiba LabRAM HR Evolution Raman spectrometer by using a 532 nm laser. The measurements of X-ray photoelectron spectroscopy (XPS) were carried out on an ESCALAB MK-II spectrometer (VG Scientific Ltd., West Sussex, UK) with an Al Kα radiation source under an accelerated voltage of 20 kV. For correcting the charge effect, the binding energy (BE) of C1s was adjusted to 285.0 eV. The sensitivity factors and the peak areas of the elements were used to calculate the surface atomic ratio of O/C [61]. Temperature-programmed desorption (TPD) was accomplished in a quartz tubular reactor, which was linked to a quadrupole mass spectrometer (Omnistar, Balzers). After the ACF catalyst (40 mg) was filled in the reactor, the temperature was increased to 900 °C with a heating rate of 10 °C/min in helium flow of 30 mL/min. The mass spectrometer was used to monitor the outlet gas.

3.3. Catalyst Testing

The general reaction of NH$_2$OH with O$_2$ was performed in a 100 mL of jacketed glass reactor by stirring at room temperature under atmospheric pressure, as reported elsewhere [31]. In a typical reaction process, 0.15 g of ACF catalyst was put into the aqueous solution of reactant, which was made of hydroxylammonium chloride (NH$_2$OH•HCl, 1.74 g) and 50 mL of deionized water. Before adding the ACF catalyst, the pH value of NH$_2$OH•HCl aqueous solution was regulated to 8.6 by the solution of 1 M NaOH. Moreover, O$_2$ was bubbled into the reaction mixtures at a constant flow rate of 25 mL/min, which was tailored by a mass flow controller. Samples of the reactants were taken out periodically in order to analyze the concentration of H$_2$O$_2$ by the colorimetric method, which was based on the titanium (IV) sulfate [62]. Similarly, the colorimetric method with the Fe (III)-1,10-phenanthroline complexes was used to detect the concentration of NH$_2$OH•HCl [63]. The recycling tests of ACF catalysts were performed with the same conditions mentioned above. For each cycle, the used ACF catalyst was washed with hot water and dried at 80 °C in a vacuum oven overnight. The tests of H$_2$O$_2$ decomposition were carried out in similar reaction conditions only without feeding NH$_2$OH•HCl and O$_2$. The initial concentration of H$_2$O$_2$ was 0.25 M without adjusting the pH value. The dosage of ACF catalyst for each decomposition test was 0.15 g. The yield toward H$_2$O$_2$ formation was calculated in accordance with the stoichiometric ratio of the reaction (2NH$_2$OH + O$_2$ = H$_2$O$_2$ + 2H$_2$O + N$_2$), as the following equation:

$$\text{H}_2\text{O}_2 \text{ Yield} \% = 2 \times \frac{n(\text{H}_2\text{O}_2)}{n(\text{NH}_2\text{OH} \cdot \text{HCl})} \times 100\% \quad (1)$$

where $n(\text{H}_2\text{O}_2)$ is the moles of H$_2$O$_2$ generated in the reaction, and $n(\text{NH}_2\text{OH} \cdot \text{HCl})$ is the moles of NH$_2$OH•HCl in feed.

4. Conclusions

Proper tuning of the surface chemistry of ACFs with intrinsic nitrogen content could expeditiously promote the selectivity of H$_2$O$_2$ production through NH$_2$OH oxidation. Mixed acid oxidation of ACF under mild reaction conditions effectively increased the surface oxygen groups and tailored the pyrrolic/pyridone nitrogen doped on a carbon structure, which then accelerated the selectivity for H$_2$O$_2$ over 99.3% on ACF-R2 catalyst. The higher content of H$_2$SO$_4$ in the mixed acid created more pyrrolic/pyridine nitrogen, carboxyl and anhydride groups, enhancing the selectivity and yield toward H$_2$O$_2$ formation. In our present work, both an easy and low-priced synthetic process for H$_2$O$_2$ generation was described, while a new comprehension on the conception and mechanistic examination of metal-free N- and O-doped carbon materials were also provided.
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