International Conference on Oil and Gas Engineering, OGE-2015

Influence of environmental conditions on carbon black oxidation by reactive oxygen intermediates

Razdyakonova G.I.\textsuperscript{a,b}\textsuperscript{*}, Kokhanovskaya O.A.\textsuperscript{a}, Likholobov V.A.\textsuperscript{a,b}

\textsuperscript{a} Institute of Hydrocarbons Processing SB RAS, 54, Neftezavodskaya St., Omsk 644040, Russian Federation
\textsuperscript{b} Omsk State Technical University, 11, Mira Pr., Omsk 644050, Russian Federation

Abstract

The paper examined the influence of hydrogen peroxide and ozone and singlet oxygen co-agents on the functional groups of the carbon black surface. The influence of the ambient temperature and the concentration of the reactants on protogenic functional groups (carboxylic and phenolic) generating has been studied. To assess the functional composition methods of titration with alkali of different strength, differential potentiometer, pyrolysis gas chromatography have been used. It was found that the carbon oxidation depends on the sample structure. It is shown that carbon oxidation with hydrogen peroxide depends on the co-agent nature. With singlet oxygen used as a co-agent, carboxyl groups with the lowest pKa of about 2 are generated on the carbon surface. When using ozone pKa of the group is higher than 2.

1. Introduction

Carbon black (CB) has functional properties which are used for different purposes: as a polymers filler, pigments, conductive material in chemical current sources and condenser, as adsorbents and catalysts [1, 2]. High temperature (above 1500°C) modes of its synthesis lead to thermal destruction of the thermodynamically unstable oxygenated functional groups. Thus, for obtaining a surface with a given set of the oxygenated functional groups (OFG) and new functional properties the technology of postreactor oxidation are developed [3]. The complexity of the process is in multiplicity of CB oxidation directions. It is obvious that the chemisorption of oxygen precedes the carbon oxidation reaction. Chemisorbed oxygen can be on the CB surface as part of the carboxyl (CG), carbonyl, lactone (LG), phenol

\textsuperscript{*} Corresponding author. Tel.: +7 381 256 0207; fax: +7 381 256 0211.
\textit{E-mail address:} rgi@ihcp.ru
(PG), quinones (QG), ethereous, anhydride, pyrone functional groups [4,5]. For CD oxidation acids (H₂SO₄, HNO₃, H₂O₂), sols (Na₂S₂O₈, NaOCl), simple substance (O₃, O₂), oxygenated gases (NO₂, N₂O etc.) are used. It should be noted that high concentration of carboxyl and lactone groups are found only on the surface of the carbon sample, oxidized by HNO₃ and NaOCl [3,6]. However, in practice the use of some of these oxidants is unacceptable because of the CB pollution and waste gases of its side reactions products. On the other hand oxidation conditions can lead to different results (Table 1).

Table 1. Characteristics of carbon materials interaction with oxygen.

<table>
<thead>
<tr>
<th>Process</th>
<th>Process results</th>
<th>Type of chemical reaction</th>
<th>Environment</th>
<th>T, °C</th>
<th>Observed phenomena</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemosorption</td>
<td>Stable oxygroup formation</td>
<td>Addition</td>
<td>Oxygenous</td>
<td>up to 100</td>
<td>OFG formation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a) liquid-phase</td>
<td>160-800</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b) gas-phase</td>
<td>100-400</td>
<td>Dehydration of all OFG</td>
</tr>
<tr>
<td>Thermal desorption</td>
<td>Surface group cleavage</td>
<td>Decomposing</td>
<td>Nonreactive</td>
<td>400-550</td>
<td>Cleavage of PG, LG, QG</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>500-900</td>
<td></td>
</tr>
<tr>
<td>Gasifying</td>
<td>Not-reversible desorption of oxygenate</td>
<td></td>
<td>Oxygenous</td>
<td>up to 150</td>
<td>&quot;Soft&quot; low-temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a) liquid-phase</td>
<td>350-450</td>
<td>&quot;corruption&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b) gas-phase</td>
<td>700 - 1200</td>
<td>High temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&quot;corruption&quot; or burning</td>
</tr>
</tbody>
</table>

Table 1 shows that by conditions (environment and temperature) selecting we can get a variety of carbon black, with the functionalized surface and containing no functional groups. The most complicated mechanism and kinetic effects are chemisorption process in a liquid phase environment, because of the variety of the resulting functional surface of the cover and the influence of groups belonging to the same carbon scaffold on the localization of the subsequent break-down decomposition of oxygen.

The aim of the paper is to develop methods for the liquid phase oxidation of carbon black using environmentally friendly oxidants (hydrogen peroxide, ozone and singlet oxygen) and their mixtures at different conditions of the oxidation (pH and temperature). Using these oxidants in the carbon black preparation can be applied in the manufacturing process at the granulation and product drying stages without emissions and operating costs increasing.

2. Subject of research

In this paper we used such CB types asB N326, N121 and P366-E partially gasified (6-8%) at 1700 °C in water gas environment directly in the reactor in its synthesis [7]. Their basic physical and chemical properties are shown in Table 2.

Table 2. Physical and chemical properties of the carbon samples.

<table>
<thead>
<tr>
<th>Indices</th>
<th>N121</th>
<th>N326</th>
<th>P 366-E</th>
</tr>
</thead>
<tbody>
<tr>
<td>STSA, m²/g</td>
<td>114</td>
<td>75</td>
<td>110</td>
</tr>
<tr>
<td>NSA, m²/g</td>
<td>118</td>
<td>77</td>
<td>173</td>
</tr>
<tr>
<td>pH w.s.</td>
<td>8.0</td>
<td>7.4</td>
<td>7.5</td>
</tr>
<tr>
<td>Weight content of oxygen, %</td>
<td>0.6</td>
<td>1.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Ratio I₀/Iₐ</td>
<td>2.7</td>
<td>2.4</td>
<td>1.3</td>
</tr>
</tbody>
</table>
The degree of a carbon material graphitizing in globules extent was characterized by integrated intensity ratio D- and G-bands (ID/IG) in the Raman scattering (RS). The less it is, the more graphitize carbon material will be, as in the ideal graphite D-band is absent. In the Raman spectra of the initial samples the absorption band G (graphite component) and D (amorphous component) are present, and the ratio of their integrated intensities in the CB sample 121 N has a maximum value than in the other samples, i.e. samples N 326, P366-E are more graphitized. In spectra decomposition the main component of D-band is defined in the frequency range of 1285 - 1300 sm⁻¹, G-band components is in the frequency range of 1591-1594 sm⁻¹ (Fig. 1).

![Fig.1. The smoothed spectra and Lorentzian components of CB Raman spectra N326 (a), N121 (b) and P 366-E (c)](image)

An additional component in the frequency range of 1450-1500 sm⁻¹ is clearly defined in the CB Raman spectrum P366-E due to the presence of micro-crystallites, which is the result of carbon layers thermal treatment in the gasifying process in its synthesis.

CB oxidized samples were obtained in the laboratory conditions at three temperatures (25, 60 and 100°C). Distilled water was added to CB sample weight, the suspension was subjected to ultrasonic cavitation at frequency of 35 kHz for 12 minutes, then a certain amount of concentrated hydrogen peroxide solution was added to achieve the desired (2, 4, 6, 8 or 10 wt.%) concentration, and the air enriched with ozone or singlet oxygen was bubbled into the reaction mixture. The CB reaction mixture contained: H₂O₂ solution in a weight ratio of 1:20. After CB washing from the reaction environment and its drying, its pH was determined by its water suspension (pH w.s.) and the functional group.

3. Methods

Protogenic groups functional analysis on the CB surface was performed by selective neutralization [8-10], differential potentiometric analysis according to the procedure described in [11]. Analysis of carbon oxides released at the temperature range from 200 to 1000 °C in the carbon black pyrolysis in the helium atmosphere, conducted on a chromatograph "Kristallyuks-4000M" "Meta-chrome" SPC (Yoshkar-Ola, Russia) with the detection in the flame-
ionization detector and using a column KH-3 filled with Porapak Q 80/100 sorbent. The chromatographic data processing was conducted using the program "NetChrom v 2.1".

The pH value were measured using pH-meter pH-150MI ("Measuring equipment" LLC), and combined electrode ESK-10603/7. A suspension for CB pH. W.s.p. determining was prepared by the National State Standard method of 25699.6-90. Dispersing of the water suspension prior to oxidation was carried out using an ultrasonic bath USB-9.5 ("Sapphire" LLC) with a frequency of 35 kHz. The specific surface area was determined by nitrogen adsorption at low temperature with equipment Gemini 2380 according to standard procedures [11]. For ozone generating the ozonizer O3ONER («Health Formula») was used with the ozone productivity of 400 mg/hr (~ 0.5 wt.%). The ratio of the integrated intensities of G and D bands, characterising a crystal (G-band) and an amorphous (D-band) phases in a dispersed carbon were investigated by Raman spectrometer RFS-100/s (Bruker) at the laser excitation Nd:Y:Ag with 1.064 mm detection and a 3 см⁻¹-definition. Deviations in parameters of individual components – intensity, peak position, half-width, the area under the component did not exceed 0.5%.

4. Results and discussion

Spontaneous decomposition of hydrogen peroxide in dependence on the environment acidity occurs in different ionic mechanisms [12]:

1) in an acidic environment
\[ \text{H}_2\text{O}_2 + 2\text{H}^+ \leftrightarrow 2\text{H}_2\text{O} \] (1)

2) in alkaline environment hydrogen peroxide molecules dissociate in two stages or decompose
\[ \text{H}_2\text{O}_2 + \text{OH}^- \leftrightarrow \text{H}_2\text{O}^- + \text{H}_2\text{O} \leftrightarrow 3\text{OH}^- \] (2)
\[ \text{HO}_2^- + \text{OH}^- \leftrightarrow \text{O}_2^- + \text{H}_2\text{O} \leftrightarrow 4\text{OH}^- \] (3)
\[ \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e} \] (4)

A hydrogen peroxide decomposition activator is ozone and oxidation activity of organic compounds with mixtures of hydrogen peroxide with ozone is several times more effective than each reagent separately [13]. The activation mechanism of hydrogen peroxide by ozone may be ionic or radical. The process of reagents interaction can result in forming of hydroxyl ions or ion-radicals according to the first of consecutive scheme [14]
\[ \text{HO}_2^- + \text{O}_3 \leftrightarrow \text{HO}_2^\cdot\text{O}_3^- \] (5)
\[ \text{HO}_2^- \leftrightarrow 2\text{O}_2^- + \text{OH}^- \] (6)

or a second scheme
\[ \text{HO}_2^- \leftrightarrow \text{HO}_2^\cdot + \text{O}_3^- \leftrightarrow \text{O}_2 + \text{OH}^- + \text{OH} \] (7)

As follows from the scheme 5, O3 c HO2- reaction can result in an adduct ((HO5-) forming, which in one direction decomposes into reactive oxygen of ion-radical O3^- and radical HO2•, as well as into molecular oxygen, hydroxyl ion OH- and highly reactive hydroxyl radical ON. In the scheme 7 there is only to molecular oxygen and hydroxyl ion OH-. It is also known [15] that in the pH range from 1 to 8 ozone chain destruction process is catalyzed by hydroxyl ions OH-, but with increasing OH-concentration the activation energy values increase slightly up to 84.8 ± 6.8 kJ/mol at pH 6.0 w.s. from 76.0 ± 8.3 kJ/mol at pH 4.7. Therefore, the use of hydrogen peroxide as co-agent at the CB singlet oxygen or ozone oxidation can give a greater effect than the oxidizing agents separate influence. To select an effective hydrogen peroxide concentration with coagents the CB oxidation was carried out during 5 minutes (typical CB time in mixer-granulator during the production). Figure 2 shows an all samples overview of the water suspension pH variation of the carbon black depending on the hydrogen peroxide concentration.
Figure 2 shows that the CB pH of w.s. varies from ≈8 to ≈4, which is favorable for changing the CB oxidation mechanism from radical to ion. Hydrogen peroxide concentration increasing in the oxidation systems with a co-agent O₃ and O₂ has a significant impact on the monotonic decrease in CB pH w.s. at temperatures below 100 °C. At a temperature of about 100 °C changes in CB pH w.s.are faster and have a constant value when the hydrogen peroxide concentration of about 2% (≈0.6M). Based on these results the hydrogen peroxide concentration in the subsequent experiments was 2%.

In the CB oxidation process its functional structure was determined. The changes in the content of carboxylic and phenolic groups are shown in Fig. 3. Figure 3 shows that the CB N326 oxidation with 2% hydrogen peroxide in the presence of singlet oxygen leads to more CG and PG, than in the presence of ozone. However, according to data from Table 2 in the CB P366-E oxidation the singlet oxygen acts more aggressively.

Table 2. PKa and concentration values of CB samples functional groups, oxidized by 2% hydrogen peroxide water solution with different coagents at 25°C during 5 min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxidizer</th>
<th>pKa</th>
<th>Q, ng-eg/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>P366-E/N121</td>
<td>(H₂O₂ 2% +O₃)</td>
<td>3.7/2.1</td>
<td>121/85</td>
</tr>
<tr>
<td>P366-E/N121</td>
<td>(H₂O₂ 2% +O₂)</td>
<td>1.3/1.9</td>
<td>162/68</td>
</tr>
</tbody>
</table>

Fig.3. Content change in the of carboxyl (1) and phenolic groups (2) of CB N326 oxidized at 25 °C H₂O₂ +O₃ (a) and H₂O₂ +O₂ (b).
The contradiction is that the oxidants effects on CB N121 and 366 R-E go through different mechanisms. According to the data in Table 2 oxidation of the most graphitized CB P366-E is higher than the CB N121 particle oxidation. The latter is more strongly oxidized by hydrogen peroxide with ozone coagent, whereas the CB P366-E is mostly oxidized with singlet oxygen coagent. Application of the titration method revealed that the results of various CB oxidation in an absolutely identical conditions are various protogenic groups concentrations depending on the initial CB properties. In general, it can be noted that a more amorphous N CB 121 is effectively oxidized with ozone coagent. It proved the authors observation [15], that the decomposition products of ozone primarily reacts with CB less organized areas particles.

To test the effect of oxidizing agents on other functional groups the CB pyrolysis method combined with chromatographic analysis was used. CB pyrolysis gases were composed of N, H, CH, CO and CO2. Fig. 4 shows typical thermograms of mono- and carbon dioxide release formed by the decomposition of CB oxygenated groups. CB N121 thermograms show that the carbon dioxide CO2 release in the pyrolysis gases prevails at samples heating in the range of 300⁰-350⁰C and 400⁰-650⁰C. According to the method of temperature-programmed desorption of carbon materials [16] (Table 3), these temperature ranges correspond to the decomposition of the weak carboxyl groups and carboxylic CB anhydride.

![Thermograms of surface decomposition of CB N121 functional groups, the initial (1) and oxidized at 25 25⁰C H2O2 + O3 (2) and H2O2 + O2 (3).](image)

**Table 3. The decomposition temperature of the functional groups of carbon surface [16].**

<table>
<thead>
<tr>
<th>Group</th>
<th>T, °C</th>
<th>Pyrolysis gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>245</td>
<td>CO2</td>
</tr>
<tr>
<td>WA</td>
<td>325</td>
<td>CO2</td>
</tr>
<tr>
<td>CA</td>
<td>480/500</td>
<td>CO2/CO</td>
</tr>
<tr>
<td>LD,LC</td>
<td>616-755</td>
<td>CO2</td>
</tr>
<tr>
<td>PH</td>
<td>635</td>
<td>CO</td>
</tr>
<tr>
<td>CQ</td>
<td>700-950</td>
<td>CO</td>
</tr>
</tbody>
</table>

Carbon monoxide CO release during CB heating up to 600⁰C corresponds carboxylic anhydride decomposition, and at higher temperature corresponds phenolic and carbonyl groups decomposition, including quinone decomposition.

A distinctive feature of thermograms of CB oxidized is the increase in the CO proportion of in the pyrolysis gas oxidized samples and the shift of the CO2 release curve into a higher temperature region by using singlet oxygen as an oxidation coagent. According to Table 3 the observed shift corresponds to weak carboxyl groups WA generating, the precursors of the carboxylic anhydrides CA. When using ozone coagent the proportion of functional groups containing two oxygen atoms increases whose decomposition occurs in the form of carbon dioxide decomposition at a temperature of about 600⁰C, corresponding lactones decomposition temperature. Lactone formation on the carbon surface occurs by successive reactions involving atomic oxygen both as singlet and produced by ozone.
decomposition. The oxidation of the carbon surface can be represented by the formation mechanism of the activated complex of carbon black with atomic oxygen O (CB (O)) and further along the scheme shown in Fig. 5.

![Scheme of carbon black oxidation.](image)

In the first CB oxidation stage the atomic oxygen breaks --C-C- bonds in the aromatic ring to form protonogenic groups at point of fracture (1, 2), then the second stage as the result of dehydration reaction of adjoint carboxyl groups the carboxylic anhydrides CA may be formed. In the case of phenol and carboxyl groups formation at the point of bonds fracture in the aromatic ring at their dehydration lactone is formed (3, 4). Lactone group reacts with ozone molecule to form a carboxylic acid anhydride CA. Thus, the observed CO₂ release curve shift into a higher temperature region due to the formation of weak carboxyl groups localized at point of fracture of the carbon layer aromatic ring, and carboxylic acid anhydrides CA. These findings correspond to the authors’ conclusions [15] on the different simultaneous ozone decomposition product reactions with CB that reacts with CB less organized particles areas.

5. Conclusion

Influence of hydrogen peroxide, ozone coagent and singlet oxygen on functional groups on the carbon black surface depends on several factors. It was found that the oxidation of various CB in completely identical conditions are different in strength and concentration of protonogenic groups depending on the graphene layers organization in the CB initial globules. It is found that the decomposition products of hydrogen peroxide and ozone primarily reacts with less CB organized particles areas. It is shown that the most active oxidant of the gasified carbon black is hydrogen peroxide with singlet oxygen coagent. When singlet oxygen is used as a co-agent, carboxyl groups with the lowest pKa of about 2 are formed on the carbon surface, or higher pKa when using ozone coagent.

Acknowledgements

The work carried out with according to the Program of fundamental scientific research of the state academies of sciences in of 2013-2020 direction V.49. project № V.49.1.7. with the involvement of the instrument base of the Omsk regional center for collective use of the Siberian Branch of the Russian Academy of Sciences. We are grateful to Kahn V.E., Candidate of Physical and Mathematical Sciences, research professor of the Omsk regional center for collective use of the Siberian Branch of the Russian Academy of Sciences for the CD study, Vishnevskaya A.Y. and

References

[7] Razdyakonova G.I., Likholobov V.A. Zakonomernosti obrazovanija i fiziko-himicheskie svojstva jelektroprovodnogo technicheskogo ugleroda, sintezirovannogo metodom termoookislitel'nogo piroliza uglevodorodov v turbulentnyh potokah Kauchuk i rezina 3 (2013) 16-
[15] Li N., Ma X., Zha Q., Kim K., Chen Y., Song Ch. Maximizing the number of oxygen-containing functional groups on activated carbon by using ammonium persulfate and improving the temperature-programmed desorption characterization of carbon surface chemistry Carbon 49 .15 (2011) 5002-5013