Notes

Surface functionalities of nitric acid treated carbon – A density functional theory based vibrational analysis

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The appropriate combination of surface functionalities and their relative contribution to the total surface functionalities of oxidized carbon by nitric acid are evaluated by density functional theory calculations. Though the computed and experimental spectra do not exactly match in all respects, the methodology adopted has a definite role in understanding the complex surface functionalities of treated carbon.

The chemical functionalization of carbon materials has always been a challenge in chemistry and engineering. The term "functionalizing" generally refers to the introduction of functional groups to the carbon materials. Typical functional groups introduced in the course of the method of preparation include, but are not limited to, the acidic groups like -COOH, -CHO, -CO, -OSO₃H, -OSO, -O, -OH and also basic groups like quinone, pyrone etc. For the past few years, intensive research has been carried out both experimentally and theoretically for the identification of surface functional groups of the modified carbon materials[1-3], since these groups significantly facilitate self-organization (aggregation in dyestuffs, laser toners), chemical stability (oxidative attack in structural applications), the reactivity towards stoichiometric (adsorbent) and catalytic processes (synthesis of small molecules, gas mask filters). The surface chemistry of activated carbon is basically determined by the amount and type of oxygen functionalities on the surface. The oxygen functionalities can be introduced by treating the carbon with different oxidizing agents such as HNO_3, $(NH_4)_2S_2O_8$, and H_2O_2[4-6]. Even though many spectroscopic techniques have been used to characterize the oxygen functionalities on carbon

surface, information on these materials on molecular level is difficult to obtain. However, IR spectroscopy has been widely used to characterize these materials, even though there are technical difficulties in recording the spectra and in interpreting the spectra obtained. In order to overcome the difficulty in the interpretation of spectra, nowadays theoretically predicted assignments are employed. However, how close the theoretical predictions are with the experimental data is yet to be established. Hence, a real picture of the carbon surface functionalities remains unclear due to the complicated nature of its structure. For the processes like adsorption of inorganic compounds on activated carbon from aqueous solution[7-9], adsorptive desulphurization[10] and for anchoring the active species[11-13], the amount and nature of the surface functionalities have considerably more influence than the surface area and porosity of the carbon surface. Hence identification of surface functional groups on activated carbon prepared under different conditions is important from its application point of view.

The aim of the present work, therefore, is to identify the nature of the functional groups on the HNO_3-treated carbon surface. Since this is difficult to identify experimentally, in this study, we have attempted theoretically to identify the same by carrying out density functional theory (DFT) based vibrational analysis on the models of carbon surface which have been constructed based on experimental FTIR data.

Experimental

Activated Calcon carbon (MRX-M 10×30, sample ID: T06B10S-1) was purchased from Tianjin Co. Ltd., China.

Oxidation of activated calgon carbon was performed by boiling the carbon with conc. HNO_3 (Carbon:acid = 1:5; w:w%) for 2 h at 60°C in a round bottom flask fitted with a reflux condenser. After oxidation, the sample was filtered, washed thoroughly with hot distilled water until free of nitrate ions and then dried at 110°C for 2 h.

The FTIR spectra of solid samples of HNO_3-oxidised and as-received Calgon carbons were

recorded on Nicolet 6700 spectrometer as KBr pellets in the 4000-400 cm^{-1} spectral range.

The molecular geometries of all the model structures studied in this work were fully optimized at DFT using the Gaussian 03 suite of program on a IBM p-series machine server without any geometrical restrictions. Gauss view 3.0 was used as a graphical user interface. The effects of electron correlation on the geometry optimization were taken into account intensively by using Becke's three-parameter exchange functional with the Lee-Yang-Parr gradient-corrected correlation functional[14] (B3LYP) in conjunction with the 6-31G(d) basis set that is double-ς augmented with one set of polarization functions on heavy atoms[15]. The frequency calculations were carried out at the same level as the respective optimization process involving the calculation of infrared frequencies and intensities by analytic evaluation of second derivatives of energy with respect to the nuclear displacement. Calculated frequencies are reported without any additional scaling factors.

Results and discussion

The FTIR transmission spectra of HNO$_3$-oxidized and as-received activated calgon carbon samples are shown in Fig. 1. The FTIR spectrum of as-received activated carbon presents a broad and intense band at about 3500 cm^{-1}, which may be assigned to the O-H stretching mode of carboxylic and phenolic groups[1,9]. An intense and medium broad band centered at 1638 cm^{-1} may be assigned to the C=O stretching vibration of ketone, lactone and carboxyl groups. A broad

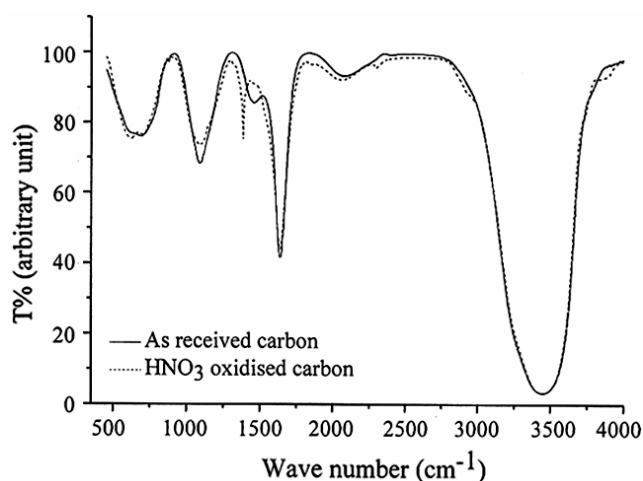Fig. 1—FTIR spectra of HNO$_3$ oxidised and as-received carbon samples.

absorption band centered around 1086 cm^{-1} has been assigned to C-O stretching and O-H bending mode of alcoholic, phenolic and carboxylic groups[16]. Absorption below 800 cm^{-1} can be assigned to the out-of-plane deformation vibration of C-H groups located at the edges of aromatic planes[17-20]. In HNO$_3$ -oxidised carbon sample, along with the original bands present in as-received carbon, a new sharp peak is observed at 1384 cm^{-1} which may be assigned to the formation of or to an increase in the already available oxygen functionalities[5]. Shoulders observed at 2301 and 2914 cm^{-1} are ascribed to the presence of aliphatic compounds. Only a slight decrease in intensity of absorption is observed in the band at 1085 cm^{-1} indicating the reduction in basic oxygen functionalities on carbon surface after treatment with HNO$_3$. However, there is no marked difference in the absorption intensity and location of other bands when compared to the as-received carbon. This is due to the limited oxidation of activated carbon by conc. HNO$_3$.

In order to identify the exact nature of oxygen functionalities on the surface of oxidized carbon material, four different models of carbon surface structures involving only 4 to 6 fused aromatic carbon rings (in order to limit the computational time) are considered herein. The oxygen functionalities like –COOH, -OH, C=O and C-O-C which have been identified in the HNO$_3$ treated activated carbon by FTIR spectroscopy were then introduced at the edges of model carbon surfaces with different combinations. These four models were then subjected to geometry optimization in the gas phase at the B3LYP/6-31G (d) level of theory. Following geometry optimization, harmonic vibrational frequencies and infrared intensities were calculated analytically. The optimized geometries of four model carbon surface structures are shown in Fig. 2.

Generally, the edges of carbon surfaces are decorated with combinations of acid groups when they are treated with oxidizing agents like HNO$_3$. Hence in model structure I, a combination of carboxyl – hydroxyl groups which are coplanar with the poly aromatic system is considered. IR spectrum of this model shows peaks above 3000 cm^{-1} corresponding to O-H stretching frequency of carboxyl and phenolic groups. The C=O stretching frequency appears at 1721 cm^{-1}. This value is approximately 23 cm^{-1} lower than that of carboxyl only models[3] as a consequence of the stronger polarization of the carbonyl bond due to –C$^{\delta+}$=O$^{\delta-\cdots\delta+}$H-O interaction.
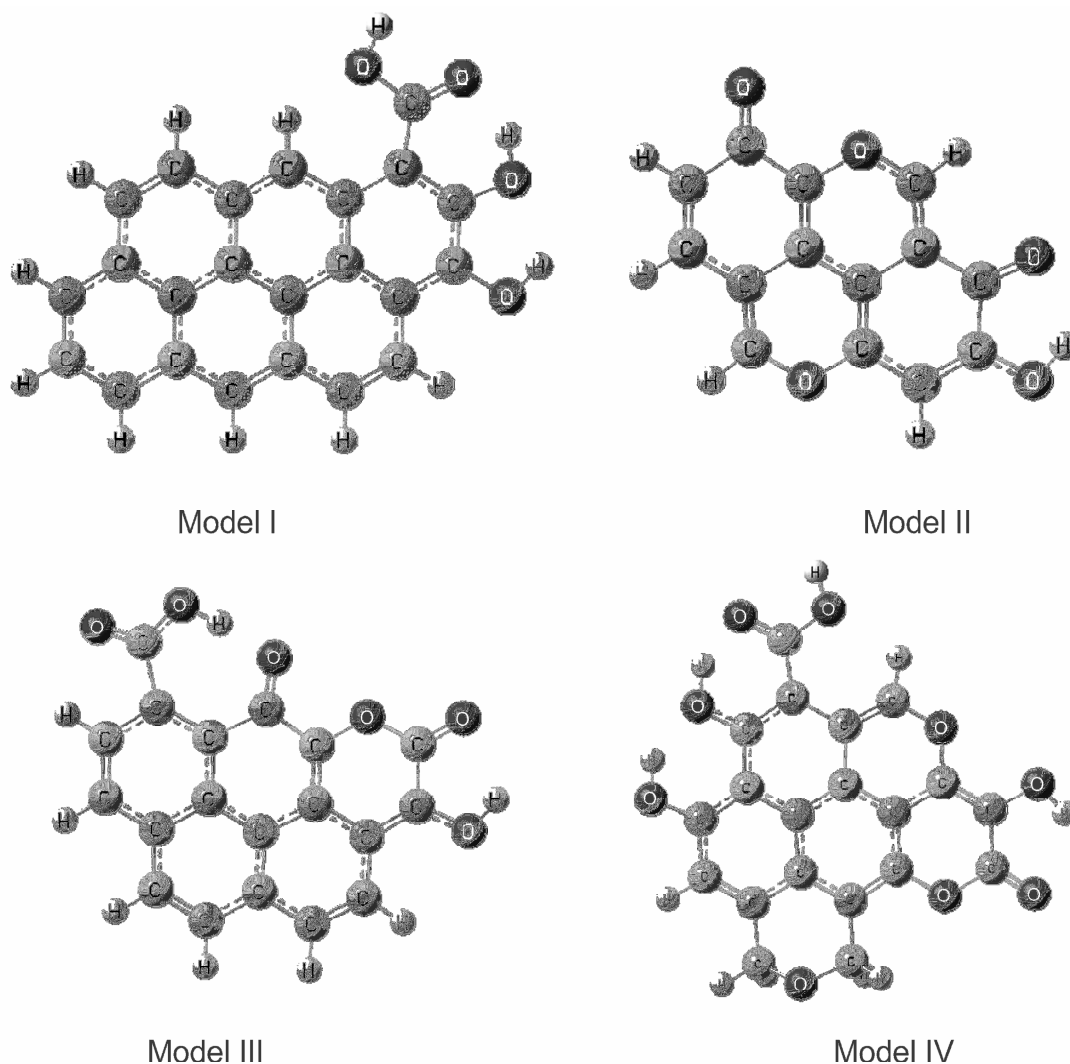
Fig. 2—Geometry optimized structures of carbon surface models I, II, III and IV.

Apart from acidic oxide groups, there may be some oxides with basic character like ether or ketone rings that exist on the surface of carbon materials. In order to identify the presence of these functional groups on the HNO₃ treated carbon, a model structure II is considered with a combination of ketone and ether at adjacent and isolated position along with a single hydroxyl group adjacent to an isolated carbonyl group. The IR spectrum of this model structure shows two peaks at 1680 and 1634 cm^{-1} which may be assigned to the stretching frequency of carbonyl groups. Many peaks due to carbon ring vibrations are distributed across a wide interval, from 1450 to 1600 cm^{-1}, due to the influence of two opposite effects, i.e., the C=C-C=O conjugation and the disruption of –C=C-C=C- conjugation by the sp^3 O atoms.

As oxidation time progresses, the probability of finding some carboxyl groups close to phenol groups increases and it leads to the formation of lactone groups on the carbon surface. Hence in model structure III, along with carboxyl and ketone groups, a combination of lactone-hydroxyl functional group is also considered. The IR spectrum of this model shows two peaks at 3031 and 3051 cm^{-1} corresponding to lactone –OH and carboxyl –OH respectively. Similarly, the C=O stretching frequency of lactone and cyclicketone are observed at 1781 and 1658 cm^{-1} respectively.

By combining all the functional groups present in models I, II and III, a model structure IV is designed. In addition to this, a single aliphatic ether ring is also included. The IR spectrum of this model shows peaks at 2889, 2973, 3580. 3620 and 3684 cm^{-1}

corresponding to four different –OH groups present in it. The carbonyls peaks of lactone and cyclic ketone are observed at 1784 and 1712 cm^{-1} respectively. A peak observed around 1644 cm^{-1} is due to vibrating C=C bonds in aromatic rings. An intense peak at 1219 cm^{-1} is ascribed to the C-O stretching and O-H bending mode of phenolic and carboxylic groups present in the model.

Thus, four different carbon surfaces which are sufficient to describe the nature of oxygen functionalities on the surface of HNO$_3$ oxidized carbon materials are modelled and then subjected to DFT based vibrational analysis. The theoretical IR spectra of all the four models (I to IV) are shown in Fig. 3.

While comparing the IR spectrum of HNO$_3$ oxidized carbon with the theoretical IR spectrum of model IV (since it consists of all the oxygen functionalities as evidenced from experimental IR data), we were unable to reproduce a few bands in the region below 1200 cm^{-1} and another set of bands in the range of 3250-3500 cm^{-1}. The former bands are reproduced in the model II and latter are reproduced in the models I and III. It is, therefore, deduced that a single model is not sufficient to mimic the HNO$_3$ oxidized carbon surface and hence, the relevant model would be one in which a combination of all the oxygen functional groups as present in these four models may exist together. Hence, the IR spectral data of these four model carbon surfaces were mixed in different proportions in order to find out which proportion matches exactly with the experimental one. Among various combinations of the theoretical IR data of models I to IV, the one in which the models I, II, III and IV are in the ratio of 10:70:10:10 matched to some extent with the experimental spectrum. This indicates that the oxidized carbon surface has more number of basic functionalities like ether and cyclic ketone as compared to carboxylic and lactone groups. This may be due to the limited oxidation of activated carbon by HNO$_3$. The comparison of normalized IR spectrum of the mixed carbon surface models to experimental spectrum is shown in Fig. 4.

The reasons for not being able to reproduce the exact locations and the relative intensities of the absorption bands for the sample treated with HNO$_3$ by theoretical method is due to neglecting factors such as environment, anharmonicity, Fermi resonance,
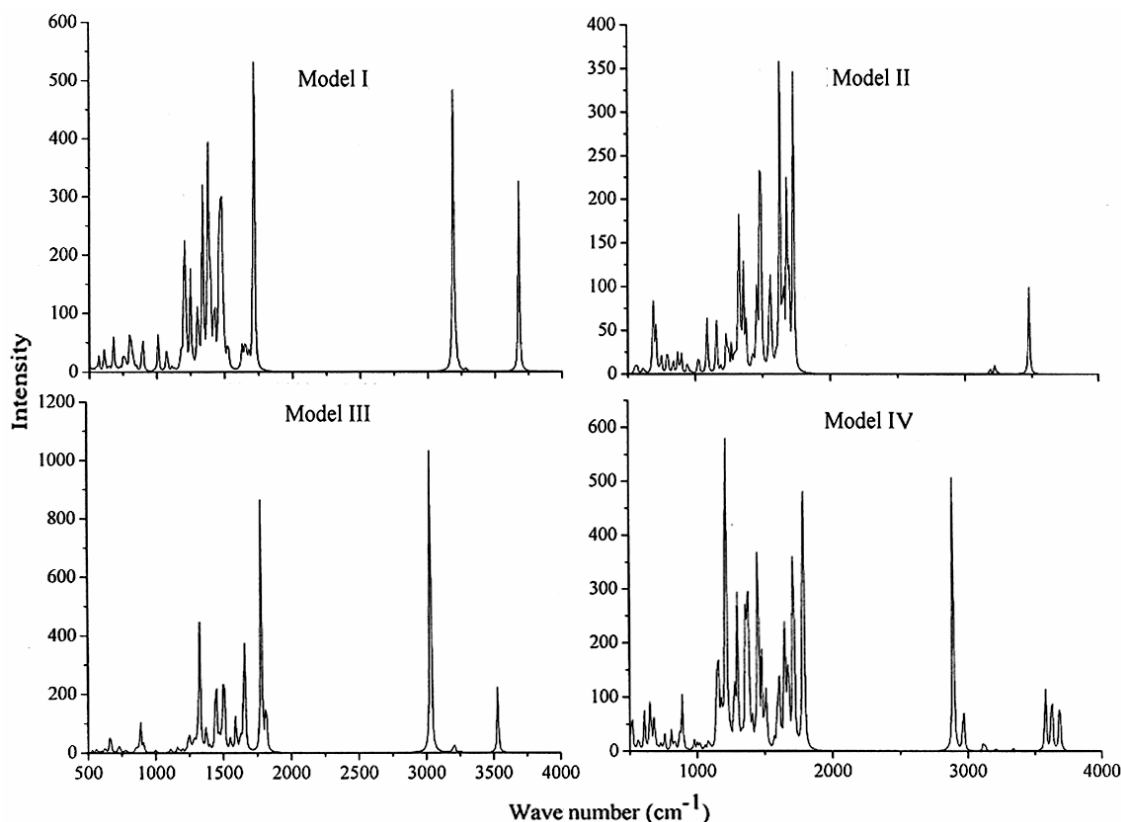

Fig. 3—Theoretical IR spectra of carbon surface models I, II, III and IV, computed based on B3LYP/6-31G (d) level of theory.
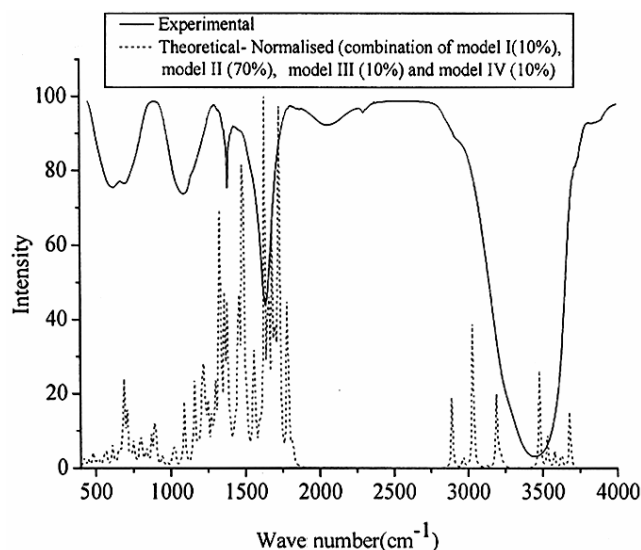
Fig. 4—Comparison of normalized theoretical IR spectrum of the mixed carbon surface models to the IR spectrum of HNO_3 oxidised carbon.

solvent effect and scale factor for each level. Use of a small basis set like B3LYP/6-31G (d) and not large basis set like B3LYP/6-311+G (2d, 2p) for computing vibrational frequencies and consideration of a limited number of functional groups and carbon rings in the theoretical models may also be contributing to the discrepancy observed.

In the present study, in an attempt to identify the oxygen functionalities on the HNO_3 oxidized activated carbon material, a DFT based vibrational analysis has been performed on four different carbon surface structures which are modeled on the basis of FTIR spectral data. Since a single model is not sufficient to describe the oxygen functionality on carbon surface, IR data of these four models have been mixed. It is seen that the fused functional groups and cooperative effects with suitable and appropriate combinations account for the observed IR spectrum, especially in the fingerprint region. A combination spectrum consisting of models I, II, III and IV mixed in the ratio of 10:70:10:10 is approximately similar to the observed spectrum and is probably the relevant model to mimic the oxygen functionalities on oxidized carbon material. Even though this result appears to be limited to the work discussed herein, the application and the general procedure adopted would be a contribution to processes like adsorptive desulphurization on modified carbon materials, where the exact information of the carbon surface functionalities is essential.

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