Adsorption of acetaldehyde onto carbide-derived carbon modified by oxidation

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HIGHLIGHTS

- The influence of oxidation modification on the properties of CDC was studied.
- The relationship between the properties and adsorption performance was studied.
- The acidic oxygen-containing groups in CDC increase the adsorption capacities.
- DFT predicts the role of acidic oxygen-containing groups for adsorption.

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ABSTRACT

The adsorption of acetaldehyde over carbide-derived carbon (CDC) modified with nitric acid, hydrogen peroxide, or air was investigated. The physicochemical properties of the original and modified CDCs were characterized by N₂ adsorption, Fourier transform infrared spectrometer, temperature programmed desorption and X-ray photoelectron spectroscopy. It was observed that the oxidation modification, especially the nitric acid treatment, could significantly enhance the adsorption performance of CDC for acetaldehyde. The increase of acidic oxygen-containing groups like carboxylic acids and anhydrides in the modified CDCs results in the increase of adsorption performance. The density functional theory calculations and in situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy show that these acidic oxygen-containing groups display strong hydrogen bonding interactions with acetaldehyde molecule, leading to the enhanced adsorption performance.

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1. Introduction

The air quality of cabins such as manned spacecraft and submarine has been a great concern since the cabins are in airtight states. A healthy and safe atmosphere is a fundamental requirement for the crew members' health, the quality of their work, and even the safety of airtight cabins. To meet this requirement, the development of highly reliable and efficient life-support system is required. A key function of the system is the removal of trace volatile organic compounds (VOCs), which are introduced through the offgassing of spacesuit materials, or through the metabolic production (e.g. breathing, sweating, etc.) of crew members. These VOCs can be hazardous to crew members' health with side effects ranging from headaches to heart damage, based on the exposure level and duration [1–4]. Therefore, the removal of VOCs is essential for improving cabin air quality.

Adsorption by activated carbon (AC) is a common approach for VOC removal in cabins and works well for macromolecule organic

compounds like aromatics [2,3]. However, those highly volatile, low molecular weight organic compounds such as acetaldehyde are typically poorly adsorbed onto the traditional AC. In our previous study, we found out that a new type of porous carbon material, carbide-derived carbon (CDC), could adsorb much more acetaldehyde than commercial activated carbons and appears as a promising adsorbent in cabins due to its unique pore properties [5]. However, it is well known that the adsorption performance of an adsorbent such as carbon material depends not only on its pore properties but also on its surface chemistry [6]. The surface chemistry of carbon is related to the presence of heteroatoms (e.g. hydrogen, oxygen, nitrogen, sulfur and phosphorus), which are bonded at the edges of the graphite-like layers and form organic functional groups such as carboxylic acids, anhydride, lactones, phenols, amines, nitro compounds, and phosphates [7]. These functional groups, especially oxygen functional groups, have significant influence on the performance of AC as adsorbent, because they can promote the polarity and wettability of carbon and consequently benefit the adsorption performance, especially for the polar organic compounds [8]. Considering the huge

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influence of oxygen functional groups on the performance of carbon materials, methods allowing the control of both the nature and concentration of oxygen functional groups for specific applications have been studied and the oxidation treatment is the most commonly used method. The oxidation process of carbon materials can be carried out in the gas phase (dry method) using oxygen, air, or ozone [9,10], or in the liquid phase (wet method) by means of H_2O_2 , HNO_3 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, etc. [9,11] to introduce surface oxygen complexes on the carbon surface. There are many factors that are responsible for the nature of surface groups created during oxidation treatment, such as the type of the oxidant, the oxidation temperature and time. Besides, the characteristics of carbon materials including origin and history of preparation also play an important part [12,13]. However, to the best of our knowledge, the influence of oxidation modification on the pore properties and surface chemistry of CDC, and the relationship between these properties and adsorption performance, have not been systematically studied. The unique structure of CDC may yield surface properties that are different from those of most other carbon materials, which may affect its adsorption performance significantly.

For these reasons, the main objective of this study was to investigate the effect of oxidation modification, by means of liquid phase oxidation (HNO_3 and H_2O_2) and gas phase oxidation (air), on the properties and adsorption performance of CDC for acetaldehyde. The pore structure and surface chemistry of CDCs were characterized by N_2 adsorption, fourier transform Infrared Spectrometer (FT-IR), temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). Meanwhile, the adsorption phenomena were simulated by the density functional theory (DFT) and compared with the experimental results.

2. Experimental

2.1. Preparation of original and modified CDCs

The original CDC was prepared by selective etching Ti from commercial TiC precursor (99.5% purity, 30–40 mesh, Zhuzhou GuangYuan Cemented Material Co., Ltd, PR China) by freshly prepared chlorine. The chlorination equipment and methodology is well described elsewhere [5]. The TiC precursor was placed in a horizontal quartz tube furnace. The tube was purged with argon (Ar) at room temperature for 30 min to remove air, and then heated to 700 °C at the heating rate of 10 °C min⁻¹. Once the desired temperature was reached, the Ar flow was stopped and chlorine gas was passed through the tube furnace at a flow rate of about 30 ml min⁻¹ for 2 h, and then the furnace was cooled down to room temperature under Ar purge.

Subsequently, the CDC was oxidized in the liquid phase (HNO_3 , H_2O_2) and gas phase (air). In the first two cases, 1 g of CDC was mixed with 10 ml of HNO_3 (5 mol ml L⁻¹) or H_2O_2 (30%) solutions for 12 h at room temperature. The oxidized CDCs were washed with deionized water until neutral pH, and dried at 105 °C for 3 h. The samples were designated as CDC-N and CDC-H, respectively. For the gas phase oxidation, the CDC was heated in the tube furnace from room temperature to 300 °C under the constant flow of N_2 , and then, the reactor was kept at this temperature under a flow of air for 1 h. After that, the furnace was cooled down to room temperature in N_2 and the sample obtained was denoted as CDC-A. All samples prepared were kept in glove box under N_2 atmosphere, before subsequent experiments.

2.2. Evaluation of adsorption performance

The details of the adsorption test were well described in previous work [5] and only brief description was given here. The

acetaldehyde was prepared by bubbling air into liquid acetaldehyde that was kept at 10 °C with a thermostat water bath. Then, the acetaldehyde was mixed with diluent gas at a gas-mixing chamber to obtain the desired concentration ($23 \pm 0.5 \text{ mg m}^{-3}$), which was monitored by an online gas chromatograph (GC-17A, Shimadzu) with a flame ionization detector. The adsorption measurement of acetaldehyde was performed in a continuous flow fixed-bed quartz reactor (i.d. = 10 mm) containing 0.26 g adsorbent, operating under atmospheric pressure at 25 °C. Relative humidity of the reaction gas was $35 \pm 5\%$. It was noteworthy that prior to all measurements, samples were degassed at 120 °C in flow of N_2 for 1 h to clear the possible adsorbates.

2.3. Characterizations of adsorbents

The porosity of CDCs was characterized by N_2 adsorption at -196 °C using a QuadraSorb Station 1 instrument. Prior to the N_2 adsorption, the samples were first outgassed at 200 °C for more than 12 h. The specific surface area (SSA) was calculated by using the Langmuir method. The micropore volumes (V_{mic}) were determined by the t-method. The pore size distributions (PSDs) were determined by using the nonlocal density functional theory method for slit shaped pores provided by Quantachrome data reduction software.

The FT-IR measurements were performed on a FT-IR spectrometer (E55Xfra106, BRUKER, Germany) in the frequency range of 400–4000 cm⁻¹, using KBr disk method.

The TPD was performed with a custom built setup equipped with a mass spectrometer (Omnistar™ Baltazar). In a typical experiment, the sample (100 mg) was placed in an U-shaped quartz tube inside an electrical furnace and heated up to 900 °C at 10 °C min⁻¹ in a constant Ar flow of 50 ml min⁻¹. The desorbed CO_2 ($m/z = 44$) and CO ($m/z = 28$) were monitored with the mass spectrometer during the heating process. Prior to desorption experiments, the samples were degassed for 1 h in Ar stream (50 ml min⁻¹) at 120 °C.

XPS were acquired on an ESCALAB 250 electron spectrometer equipped with a 150 W Al K α radiation as a primary excitation source. The binding energy scale was calibrated to 284.6 eV for the main C1s peak.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) spectra were recorded in a Nicolet 6700 FTIR spectrometer equipped with a smart collector and a liquid N_2 cooled MCT detector. The DRIFTS cell (Harrick) with ZnSe windows is fitted a heating cartridge that allows sample to be heated under atmospheric pressure. Before each experiment, 0.05 g finely ground sample was pretreated at 120 °C for 1 h in a flow of N_2 and then cooled down to room temperature. The background was collected before switching N_2 with the reaction gas and the spectra were recorded with a resolution of 4 cm⁻¹ and accumulating 32 scans after subtraction of the background.

2.4. DFT calculation

The molecular geometries of all compounds (acetaldehyde, CDC models and their adsorption complexes) were fully optimized using the DFT at the B3LYP/6-31G(d) computational level. All DFT calculations were performed with the Gaussian 09 program [14]. The original CDC model, graphene was composed of 4 benzene rings and hydrogen atoms that were used to saturate the carbon atoms with dangling bonds at the edge of graphene sheet, which is nearly the same size of model reported in previous work [15]. The oxygen functional groups considered in this work are carboxylic acid, anhydride and phenol groups. These functional groups were selected based on the characterization results that confirmed their presence and effects on adsorption. The acetaldehyde

and different molecular models of simulated CDCs with various functional groups are depicted in Fig. 1.

To evaluate the interaction between acetaldehyde molecule and adsorbent surface, the adsorption energy (ΔE_{ads}) of the acetaldehyde molecule adsorption on CDCs (original or functionalized graphene) was calculated, which is defined as

$$\Delta E_{\text{ads}} = E_{\text{adsorbent/acetaldehyde}} - E_{\text{adsorbent}} - E_{\text{acetaldehyde}}$$

where $E_{\text{adsorbent/acetaldehyde}}$ denotes the total energies of acetaldehyde adsorbed on original or functionalized graphene. $E_{\text{adsorbent}}$ and $E_{\text{acetaldehyde}}$ are the total energies of original or functionalized graphene and an isolated acetaldehyde molecule, respectively.

3. Results and discussion

3.1. Evaluation of dynamic adsorption performance

The dynamic adsorption performance of acetaldehyde over original and modified CDCs was evaluated, as shown in Fig. 2.

It is apparent that the adsorption of acetaldehyde for samples is different and associates with the modified process using different oxidants which changes the physicochemical properties of CDCs. The adsorption performance of oxidized CDCs is much better than that of the original CDC, suggesting that the oxidation modification is effective for improving the acetaldehyde adsorption. On the basis of the breakthrough curve, the breakthrough capacity of

CDC-N is 3.5 times as high as that of original CDC, and the treatment with H_2O_2 or air enhances the capacity from 1.5 to 2.5 folds.

3.2. Characterizations of the adsorbents

3.2.1. Porous structure characterization

Fig. 3 shows the N_2 adsorption–desorption isotherms and PSDs of the original and modified CDCs.

As shown in Fig. 3(a), the N_2 adsorption is nearly completed at a low relative pressure ($P/P_0 < 0.05$), and it shows a plateau over a wide range of relative pressure. Thus, all isotherms belong to Type I by IUPAC classification, indicating that these CDCs are typically microporous. As a result, the oxidation modification does not significantly change the pore structure of CDC. But the adsorption platform is different, which is attributed to the change of surface area. Treatment with HNO_3 results in a slight decrease in the volume of adsorbed–desorbed N_2 . The decreases could be associated with the collapse of some pore walls to diminish the micropore volumes [16], or partial blockage of the micropore entrances by oxygen functional groups introduced by the HNO_3 treatment [6]. Nevertheless, the loss of surface area is not as significant as that reported in literatures, in which the severe HNO_3 oxidation conditions might even lead to complete destruction of the carbon texture [17]. Concerning the CDC-H, the amount of adsorbed N_2 is quite close to the original CDC, suggesting that the loss of surface area on CDC-H is negligible. On the other hand, air oxidation results in more adsorbed N_2 , which is attributed to the partial

Fig. 1. Optimized geometries of acetaldehyde, original and functionalized CDCs obtained at the B3LYP/6-31G(d) level (red circles represent O atoms; Gray circles represent C atoms; White circles represent H atoms). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Adsorption performance of acetaldehyde over different CDCs (a) breakthrough curves; (b) breakthrough adsorption capacity.

Fig. 3. (a) The N_2 adsorption–desorption isotherms, and (b) PSDs of different CDCs.

Table 1
Pore characteristics of different CDCs.

Sample	SSA ($m^2 g^{-1}$)	V_t^a ($cm^3 g^{-1}$)	V_{mic} ($cm^3 g^{-1}$)	V_{meso}^b ($cm^3 g^{-1}$)	D_A^c (nm)
CDC	1473	0.644	0.477	0.167	1.85
CDC-N	1329	0.618	0.424	0.194	1.97
CDC-H	1440	0.654	0.473	0.181	1.92
CDC-A	1593	0.643	0.551	0.092	1.70

^a Total pore volume.

^b Mesopore volume.

^c Average pore width.

activation of carbon during the air oxidation process at high temperature [18,19]. This activation takes place by partial gasification of carbon to produce CO and CO_2 . As a result, more micropores are generated, which is shown in Fig. 3(b) and Table 1.

From Fig. 3(b), it can be seen that the oxidation does not change the PSDs significantly. All CDCs exhibit bimodal pore size distributions in the range of 0.7–1.5 nm fitting for acetaldehyde adsorption [5]. While it also can be seen that there is a slight decrease in differential pore volume for liquid phase oxidation CDCs and an increase for air oxidation CDC. Besides, there is a widening of pores after liquid phase oxidation, which is mainly due to the transition of micropores into mesopores after oxidation process.

As shown in Table 1, the pore structure does not change considerably, although it is clear that the HNO_3 and air oxidation produce some slight variations in porosity, especially in the SSA and the V_{mic} values which are important parameters for gas adsorption [20]. For liquid phase oxidation, the adsorption performance is enhanced even though the parameters are slightly decreased, especially for CDC-N. However, with the most developed porosity, CDC-A exhibits the lowest adsorption performance among the oxidized CDCs. The results imply that the differences among CDCs in surface chemistry may cause much more variations in the adsorption performance than the pore properties by oxidation modification.

3.2.2. Surface chemistry characterization

The surface chemistry of CDCs before and after oxidation was further investigated. The FT-IR spectra of the original and oxidized CDCs were presented in Fig. 4. The spectra of these CDCs are rather similar in shape but vary in intensity. The broad band observed at the range of 3700–3000 with a maximum at about $3440 cm^{-1}$ is assigned to the stretching vibration of O–H functional groups because of the intermolecular and intramolecular hydrogen

bonding of polymeric compounds such as alcohols, phenols, and carboxylic acids [21–23]. Small peaks at around $3000–2800 cm^{-1}$ denote the presence of the stretching C–H in aliphatic hydrocarbons [24,25]. In addition, there is a band at $1625 cm^{-1}$ indicating the overlapping of the $\nu(C=C)$ stretching vibration mode of the aromatic ring of the carbon with the $\nu(C=O)$ absorption bands of carboxylic, ester, lactone, and carbonyl groups [26,27]. As for the band at $1455 cm^{-1}$, it can be attributed to either an O–H deformation vibration in carboxyl groups or C–H bending vibrations in CH_2 or CH_3 groups [28,29]. The band at $1384 cm^{-1}$ indicates the C=O belonged to the carbonate groups [25,30,31]. Moreover, some small weak peaks in the region of $1300–1000 cm^{-1}$ consist of a series of overlapping absorptions that can be ascribed to C–O bands in various chemical surroundings, where out of plane bending of O–H in ring ethers and primary C–OH occur [10,32]. The band at around $1270 cm^{-1}$ is the C–O stretching in carboxylic groups, anhydrides, phenols, ethers and lactones [33] or C–O–C stretching vibration in lactones and ethers [34,35]. And the bands at 1120 and $1050 cm^{-1}$ are assigned to phenolic O–H bending [36–38]. Bands below $1000 cm^{-1}$ are characteristic of out-of-plane deformation vibrations of C–H groups in aromatic structures [35,39–41].

It can be noted from Fig. 4 that the surfaces of the modified CDCs contain the same oxygen functional groups mainly including carboxylic acids, carboxylic anhydrides, phenols and lactones as the original CDC does, while we could not determine the amount of a specific group because the bands are overlapped. However,

Fig. 4. FT-IR spectra of CDCs.

the intensity of the bands is elevated with the oxidation treatments with the order of CDC-N > CDC-H > CDC-A > CDC, which indicates that more oxygen functional groups have been introduced on the CDC surface after oxidation. Besides, this trend is consistent with that of adsorption performance, implying that the increased adsorption capacity of oxidized CDCs can be attributed to the increase of oxygen functional groups. These results are in agreement with previous researches [42,43] which pointed out the oxygen functional groups appeared to play an important role on adsorption of acetaldehyde even it remained unclear what the active sites of adsorption are. Similar chemical behavior of the adsorbent surface and the adsorbate can enhance the interaction between them [44]. Thus, the oxidized CDCs with more polar surface related to higher oxygen functional groups can allow the enhancement of adsorption tendency for polar acetaldehyde compared with original CDC.

To find out which type of oxygen functional group is responsible for this enhancement, the TPD of original and oxidized CDCs was carried out, as shown in Fig. 5. As expected, oxidation treatments increase the amount of oxygen functional groups, which is evidenced by the increase of the CO₂ and CO peaks. The CO₂ spectra are quite distinct: the liquid phase treatments increase the CO₂ evolution at low temperatures (below 400 °C), which is due to the decomposition of carboxylic acid functional groups with different acid strengths or located on energetically different carbon sites [9,10,45,46]. However, the oxidation in gas phase induces high CO₂ evolution at higher temperatures, which results from the decomposition of carboxylic anhydrides and lactones [47]. The tails in CDC-N and CDC-H after 400 up to 800 °C also suggest the presence of anhydrides and lactones in them. Besides, the gas phase treatment gives much more CO than the liquid phase treatments, but in all cases the CO-TPD profiles show one wide peak at around 700 °C which may originate from phenols. The appearance of small CO desorption peaks at low temperatures may be due to the thermal decomposition of carbonyl groups in α -substituted ketones and aldehydes [45,48]. In addition, compared with the original CDC, the peaks of oxidized CDC are located at higher temperature, which indicates that these groups are more stable on oxidized CDC.

In addition, the amounts of released CO₂ and CO were calculated by integration of the areas under the TPD peaks and their ratios were given in Table 2. The listed values were normalized by the area of original CDC arbitrarily set to 1.0. This ratio increases significantly after liquid phase treatments, and increases slightly after gas phase treatment. The results are consistent with a significant increase in CO₂-evolving groups like carboxylic acid after liquid phase treatments, whereas gas phase oxidation increases more phenol surface groups, which release mostly in CO. Moreover, considering the acidic

Table 2Amounts of CO₂ and CO evolved after heating up to 900 °C in Ar flow.

Sample	CO ₂	CO	CO ₂ /CO	O _T
CDC	1.0	1.0	1.00	3.0
CDC-N	4.0	2.1	1.90	10.1
CDC-H	3.2	1.7	1.88	8.1
CDC-A	2.7	2.4	1.12	7.7

nature of the CO₂ releasing groups and the relatively neutral and/or basic character of CO releasing groups, CDC-N exhibits the highest acidity, followed by CDC-H, CDC-A and CDC, which is also consistent with the trend of adsorption performance. These acidic oxygen functional groups improve the hydrophilic of carbon surfaces [49,50] and the polar compound of acetaldehyde is apt to be adsorbed by a hydrophilic surface, which leads to the enhancement of adsorption performance.

From the amounts of CO₂ and CO evolved, the total oxygen content, O_T, was also obtained. It can be seen that the HNO₃ treatment results in a significant increase of oxygen functional groups and the O_T is about 3.5 times higher as that of original CDC. H₂O₂ treatment also leads to an increase of O_T which is around 2.7 higher as that of CDC. Treatment with air results in relatively mild modification, with an increase of only about 2.5 times. Thus, the promotion effect of various oxidation treatments on the introduction of oxygen functional groups to CDC surface follows the order of HNO₃ > H₂O₂ > air, which is consistent with FT-IR results and adsorption performance. Therefore, it confirms that the oxygen functional groups play a key role in affecting the acetaldehyde adsorption after oxidation.

Moreover, the TPD profiles of CDC-N and CDC-H are similar, especially there is almost no difference in the shape and intensity of CO evolving profiles. HNO₃ treatment produces CDC with large amounts of surface acidic groups, mainly carboxylic acids and anhydrides. Whereas H₂O₂ treatment produces less these groups, which results in the main difference of the CO₂ evolving profiles between them. However, the significant variations in adsorption performance between the two samples are observed, which suggests that the effect of phenol groups on the adsorption is limited while the carboxylic acids and anhydrides play an important role. This is also the reason why the more the acidic functional groups on the CDC surfaces are, the higher the amount of acetaldehyde adsorbed on the corresponding CDC is.

Furthermore, XPS analysis was used for evaluating the changes in the chemical bonding states and concentrations of surface functional groups formed by oxidation modification. The XPS spectra of CDCs usually show two distinct peaks from carbon (C1s) and oxygen (O1s). The ratio C1s/O1s represents a measure of describing the

Fig. 5. TPD profiles of different CDCs: (a) CO₂ evolution; (b) CO evolution.

Table 3

Relative contents of functional groups in C1s from XPS spectra and distribution of oxygen groups on CDCs.

Sample	C 1s (%)					O _x ^a (at.%)	C/O _x	O _x /O _T	N.O. ^b
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5				
CDC	58.34	24.23	8.66	4.68	4.09	10.85	6.82	3.62	1
CDC-N	56.76	25.06	9.35	5.24	3.59	13.67	5.37	1.34	0.37
CDC-H	57.02	25.68	8.85	4.95	4.95	13.24	5.47	1.63	0.45
CDC-A	54.50	26.54	10.09	4.78	4.78	11.16	6.56	1.45	0.40

^a The oxygen content from XPS measurement.^b Normalized oxygen group distribution as N.O. = $\frac{[O_x/O_T]_{CDC-N} - [O_x/O_T]_{CDC-H} - [O_x/O_T]_{CDC-A}}{[O_x/O_T]_{CDC}}$.

degree of oxidation. It is noticed that the ratio (Table 3) decreases when the CDC is oxidized, which indicates that more oxygen functional groups have been introduced on CDC surface after oxidation. This agrees well with the FT-IR and TPD results that much more CO₂ and CO are desorbed after oxidation. Another difference among the CDCs is that the atomic percent of oxygen on the surface increases in the order of CDC < CDC-A < CDC-H < CDC-N. This order is consistent with that of adsorption performance, which corroborates the view that the oxygen functional groups on the CDC surface improve the adsorption performance for acetaldehyde.

For the sake of a better understanding of the surface chemistry change by the oxidation, the C1s signals were deconvoluted. Although modern XPS instruments provide a good resolution even for O1s spectra, it is generally known that the measurement of the C1s signals is more convenient [51]. The C1s spectra are resolved into five individual component peaks, as illustrated in Fig. 6, namely the following [52,53]: peak 1 (284.6 eV), graphitized carbon (C–C); peak 2 (285.6 eV), carbon in phenol, alcohol, or ether groups (C–O–); peak 3 (287 eV), carbon in carbonyl or quinone groups (C=O); peak 4 (288.5 eV), carbon in carboxyl or ester (anhydrides) groups (O–C=O); and peak 5 (290.2 eV), carbon in carbonate groups and/or adsorbed CO and CO₂. Through the same fitting method, the relative amounts of carbon atoms in different functional groups calculated by the area of bonding energy peaks are summarized in Table 3.

After oxidation modification, the relative amount of the graphitized carbon (peak 1) decreases and that of the carbon bonded to oxygen functional groups (peaks 2–5) increases. For the CDC modified with air, this increase results primarily from an increase in peak 2 (phenolic, alcohol, or ether group) and 3 (carbonyl or quinone groups). However, for the CDC modified with HNO₃ and H₂O₂, the increase mostly originates from an increase in peak 4 assigned to carboxyl or anhydrides groups. Interestingly, the HNO₃

oxidation reduces the content of CO₃ (peaks 5) from 4.09 % for CDC to 3.59 % for CDC-N, probably due to the removal of carbonate existing in CDC in the HNO₃ oxidation treatment [54]. Overall, the XPS results are in line with the TPD results.

In addition, given that the XPS method only measures the groups on the uppermost layers of CDC whereas TPD can be considered as a bulk analysis method, the comparison of the two results can give an idea about the distribution of oxygen groups on samples [12,55]. In Table 3, the ratio of the total oxygen content of XPS to TPD is taken as a measure of the distribution of oxygen (i.e., the lower ratio means formation of more oxygen groups in interior surface). The last column, normalized oxygen group distribution (N.O.) is obtained after normalizing the O_x/O_T ratio of all samples by that of original CDC. The data given in Table 3 indicates that the oxygen groups of original CDC are essentially concentrated on external surface, while the oxidized CDCs have similar distribution of oxygen groups mainly in internal surface. However, compared with the other two treatments, the formation of oxygen groups in internal surfaces of CDC-N is pronounced. This could be linked to a higher erosion of the surface that facilitates the access of HNO₃ [23], which also results in its slight loss of porosity. In addition, the adsorption performance depends on the accessibility of adsorbate molecules to the interior surface of the adsorbent [56]. As a result, the massive incorporation of oxygen functional groups in the internal surface of CDC-N compensates the loss of porosity, increasing the adsorption capacity of acetaldehyde.

3.3. Calculation results

The optimized molecular geometries of acetaldehyde adsorption over original and functionalized graphene surfaces and the adsorption energies are shown in Table 4. From Table 4, the calculated adsorption energies of acetaldehyde on the original and functionalized graphene are negative, which indicates that these adsorbed states are energetically favorable. The lowest adsorption energy is obtained between acetaldehyde molecule and the original graphene, which is the reason of the worst adsorption performance on original CDC. In the case of acetaldehyde adsorption on functionalized graphenes, calculations show that the adsorption energies are much higher than those of original graphene, which confirms that the acetaldehyde adsorption of CDC is significantly increased by oxidation treatment. In addition, surfaces functionalized with carboxylic acid or anhydride groups exhibit high adsorption energies, suggesting that the acetaldehyde molecule tends to approach much more conveniently towards these acidic groups and the interactions between them are strong. The CDC-N has the highest concentration of carboxylic acid and anhydrides, resulting in the highest adsorption capacity of acetaldehyde. Also, the phenols functionalized graphene displays stronger interaction with acetaldehyde molecule than original graphene even though the improvement is very limited. Therefore, the CDC-A with the high concentration of phenol groups and a certain amount of anhydride groups also exhibits better adsorption performance than original CDC.

Fig. 6. Curve-fitted C1s of XPS spectra for different CDCs.

Table 4

DFT optimized geometries of the acetaldehyde interaction with the functional groups on CDC surface and the corresponding adsorption energies.

Functional group	Adsorption complex	ΔE_{ads} (kJ mol ⁻¹)
Bare		-10.79
-COOH		-39.95
-COOCO		-30.95
-OH		-12.47

forces were involved for the adsorption of acetaldehyde except coordination and chemical bond forces. Also, if hydrogen bonding is present, it is the main force as compared with van der Waals, hydrophobic bond, and dipole bond forces [59]. Thus, we deduced that hydrogen bonding interaction dominated the process of acetaldehyde adsorption onto oxidized CDCs. The results are in agreement with previous researches [42,43] which pointed out the oxygen functional groups enhance adsorption via hydrogen bonding and dipole interactions.

To obtain the surface species formed during adsorption of acetaldehyde on the surface of modified CDC, in situ DRFIT spectra of the CDC-N interaction with acetaldehyde were recorded, and the representative time resolution spectra are presented in Fig. 7. It can be seen that four distinct bands at 3730, 3680, 1720 and 1535 cm⁻¹ appear and the intensity increases as the reaction proceeding. The 1720 cm⁻¹ can be ascribed to $\nu(\text{C}=\text{O})$ of acetaldehyde in the gas phase [60]. While the very strong band observed at 1550 cm⁻¹ is assigned to C=O stretching vibrations of adsorbed acetaldehyde because of hydrogen bonding which shifts the absorption to lower wavenumber [61]. The observation indicates that the adsorbed acetaldehyde is molecular. In addition, the bands at 3730 and 3680 cm⁻¹ also show that acetaldehyde may be adsorb through hydrogen bonding with oxygen functional groups of the adsorbent [60]. Therefore, hydrogen bonding interaction dominates the process of acetaldehyde adsorption onto oxidized CDCs as predicted by the DFT calculation.

4. Conclusions

A combined fixed-bed adsorption and DFT calculation study was carried out to clarify the effect of oxidation modification on the properties and adsorption performance of CDC for acetaldehyde. It was observed that the oxidation modification could significantly enhance the adsorption performance of CDC. After oxidation, the effects of oxygen functional group on acetaldehyde adsorption are much stronger than that of pore properties. The CDC oxidized by HNO₃ exhibits the highest adsorption performance due to its largest number of acidic oxygen-containing groups like carboxylic acids and anhydrides. These groups are mainly in the internal surface and create favorable interactions with the acetaldehyde molecule. In agreement with the experimental results, the DFT calculations show that the acidic oxygen-containing groups display strong hydrogen bonding interactions with acetaldehyde molecule, leading to the enhanced adsorption performance.

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Fig. 7. In situ DRIFTS of acetaldehyde adsorption on CDC-N.

Generally, the attraction between adsorbate and adsorbent arises from some of forces listed below: van der Waals forces (4–10 kJ/mol), hydrophobic bond forces (5 kJ/mol), hydrogen bond forces (2–40 kJ/mol), coordination exchange (40 kJ/mol), dipole bond forces (2–29 kJ/mol), and chemical bond forces (>60 kJ/mol) [57,58]. In this study, the adsorption energies ranged from -10.79 to -39.95 kJ/mol. This suggested that the above-mentioned

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