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The effect of surface chemical functional groups on the adsorption and desorption of a polar molecule, acetone, from a model carbonaceous surface, graphite

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Abstract

The role of surface chemical heterogeneity in adsorption on a model carbonaceous surface (highly oriented pyrolitic graphite, HOPG) was investigated by temperature programmed desorption of acetone, a representative polar volatile organic compound. It was observed that oxygen-containing functional groups exist on air cleaved HOPG. The presence of surface functional groups reduces the binding energy, while increasing the uptake kinetics at low coverage. At high coverage, i.e., beyond a monolayer, the amount of acetone adsorbed is independent of surface heat treatment and depends only on total exposure. Thermal treatment (>1000 K) appears essential for the removal of functional groups from a carbonaceous surface. Removal of these groups allows acetone molecules to adsorb directly on the HOPG surface. The binding energy of the monolayer adsorption was determined by a combination of desorption line shape simulation and variation of desorption heating rates. The monolayer is characterized by a zero coverage binding energy of 55.5 ± 3 kJ/mol and a pre-exponential factor of $10^{20\pm1.5}$ s^{-1}. Coverage dependent, attractive intermolecular interactions at about 5% of the binding energy were determined in the monolayer.
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1. Introduction

In spite of the importance of carbonaceous materials, our understanding of the role that the chemical and morphological characteristics of the surface play in interfacial properties is less developed compared to our understanding of other substances. Unequivocal characterization of the chemical properties of carbon surfaces lags behind that of metals, for example, due to the complexity of carbonaceous surfaces compared to metals. Carbonaceous materials and their surface properties are important for a number of applications [1–3]. Activated carbon is employed as a support for metal catalysts [4], or used as a catalyst in its own right [3,5,6]. Activated carbon is used for environmental control of hazardous pollutants [7].

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Carbon is also used to protect the surface of magnetic data storage media [8,9]. Carbonaceous surfaces, typically in the form of soot particles, play an important role in the chemistry of our atmosphere [10]. These carbons are characterized by a high degree of chemical and morphological heterogeneity that affects their function. These characteristics affect their interactions with molecular adsorbates and, hence, the adsorption capacity (or efficiency) and catalytic activity [3,11, 12]. Therefore, understanding the chemistry of carbonaceous surfaces is essential to optimize the function and usefulness of carbon materials [13].

It is known that oxygen can chemisorb onto various carbon surfaces, well-ordered or amorphous, forming oxygen-containing functional groups [14]. Low coverages of adsorbed oxygen species have recently been reported on highly oriented pyrolitic graphite (HOPG) [15,16]. The surfaces of carbonaceous materials under atmospheric conditions probably contain functionalities that affect their behavior. This has important potential implications for the behavior of a range of carbons from atmospheric soot particles to activated carbon. These oxygen-containing functional groups can be removed from carbon surfaces by heat treatment over 500 K resulting in CO and CO_2 evolution [17,18]. It was also suggested that thermal treatment of carbon surfaces at 1000 °C in hydrogen conditions is an effective method to remove carbon–oxygen complexes [19,20]. Depending on the adsorbate, these oxygen-containing functional groups can either enhance or reduce the adsorption capacity of activated carbons [21]. For example, the oxidation of activated carbon with nitric acid hinders the adsorption of alkanes on energetically favorable sites of activated carbon surfaces and decreases the enthalpies and free energies of alkane adsorption [22].

Our experiments were designed to probe the role of surface chemical heterogeneity on the adsorption of a representative polar organic compound (acetone) on a model carbonaceous surface (HOPG). Graphite is an ideal substrate to study the adsorption and the structure of simple polar molecules [23]. However, there is still a need for fundamental understanding of the role of carbonaceous surface chemistry and how it affects the adsorption and desorption of simple molecules. Our experiments show that polar surface functionality does not prevent acetone adsorption. However, it does modify the energetics. This is contrary to the case of simple non-polar species, where our previous studies showed that polar functionality almost completely suppresses adsorption of propane on HOPG at 90 K [24].

2. Experimental setup

A stainless steel ultra high vacuum (UHV) chamber, pumped by a turbo molecular pump backed by a mechanical pump, provides a base pressure of 5×10^{-10} Torr after bakeout. The main residual gas is H_2 (70%), while CO_2 (20%), H_2O (5%), and CO (5%) are detected as minor background species. The adsorbent sample is highly oriented pyrolitic graphite (HOPG, grade SPI-1, SPI Supplies). A schematic view of the sample-mount is provided in Fig. 1. A Cu block, mounted on a stainless steel liquid nitrogen reservoir, holds two electrically isolated Cu rods as sample-support. The HOPG sample is attached to a $10 \times 10 \times 0.05$ mm Ta plate by two stainless steel screws and Ta fixable plates. The Ta plate is connected to the copper sample holder by 0.5 mm thick Ta wires
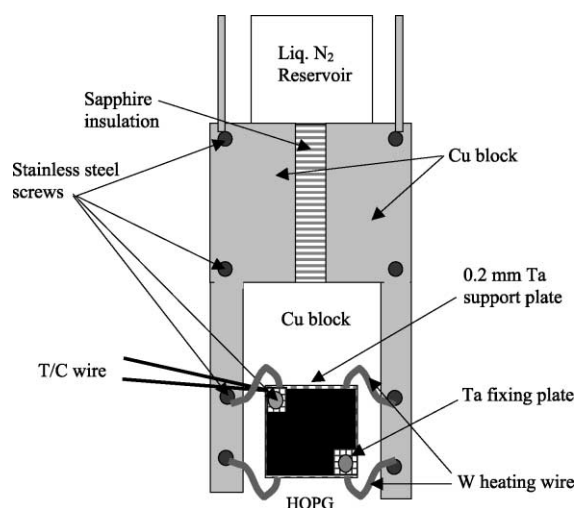

Fig. 1. Schematic view of the sample mount.

spot-welded to the Ta plate. The Ta wires are connected to the Cu rods with washers and stainless steel screws. A similar design has been employed for the study of molecular adsorption and desorption on HOPG [25]. The sample temperature is measured with a K-type thermocouple (chromel–alumel) spot-welded to one of the Ta sample fixing plates and wedged against the sample. With the present design, the sample can be heated resistively up to 1320 K, and cooled to 110 K by liquid nitrogen. The sample temperature was measured at three different spots during testing of heating and cooling performance, resulting in uniform temperature distribution through the sample. Uniform glowing of the sample was observed when heated to high temperature, which also suggests even heat distribution through the sample. The narrowness of the TPD peaks is also consistent with uniform heating.

The chamber was equipped with an ion gauge and a quadrupole mass spectrometer (QMS, Stanford Research, AccuQuad300) to measure total and partial pressures in the chamber. The QMS was fitted with a stainless steel shield to ensure collection of molecules from the sample alone during thermal desorption experiments [26]. The shield aperture could be repeatedly positioned to within <1 mm of the sample for TPD experiments and retracted about 20 mm to allow for adsorbate exposure. The sample was typically held at 110 K during dosing. The constant temperature ramping rate, typically 2.5 K/s, is accomplished by a computer interfaced (LabView, National Instruments) power supply. Partial and total pressure, as well as sample temperature, were monitored via a personal computer equipped with an A/D board controlled by a customized LabView program.

Gas exposure was performed by backfilling the chamber. Acetone pressure and exposures are reported in Langmuir units (1 L = 10^{-6} Torr s), determined by uncorrected ion gauge readings. Acetone desorbed from the sample during heating for TPD experiments was monitored via the QMS partial pressure reading at 43 atomic mass unit (amu). The resulting QMS signal ($m/e = 43$), integrated over the desorption temperature range, gives the relative amount of acetone desorbed.

The HOPG sample was cleaved in air, using Scotch™ tape to remove the topmost layers and kept for 24 h in air to allow air-formed functional groups to form on the surface prior to installation in the UHV chamber [24]. In order to study the effects of air-formed surface chemical functional groups on acetone adsorption and desorption, the sample was heated to predetermined temperature, followed by a series of acetone TPD experiments with successively higher acetone doses. Adsorption and desorption of acetone was probed on HOPG surfaces treated at 473, 673, 873, 1073 and 1273 K. A 24 h lapse was allowed between each heat treatment.

3. Results and discussion

Heating the HOPG leads to desorption of 16, 18, 28 and 44 amu containing species, probably H_2O, CO and CO_2 related compounds, at temperatures above 500 K [24]. There is no reappearance of these features over the ~24 h that elapse between each successive heat treatment. CO and CO_2 evolution from heterogeneous carbon surfaces has been reported to occur at temperatures above 500 K [18,27]. The complete thermal decomposition of these surface oxides requires treatment over 1273 K [18,27]. These functional groups are most likely polar species, e.g., quinone, carbonyl or carboxylic acid [28,29].

In order to verify that gas desorption during heat treatment originated from the HOPG samples, control experiments were performed where the air cleaved HOPG sample was replaced by a gold-coated Ta sample (10 × 10 × 0.05 mm). No gas desorption was observed upon heating to 873 K, indicating that the origin of the gas desorption is the HOPG sample itself.

TPD spectra for surfaces dosed at 110 K with increasing acetone exposures after the desired heat treatment are shown in Fig. 2, where the partial pressure of acetone (QMS signal at 43 m/e) is plotted as a function of the sample temperature. For all exposures after 473 K heat treatment, a single desorption peak with a common leading edge appears at around 130 K (Fig. 2(a)).
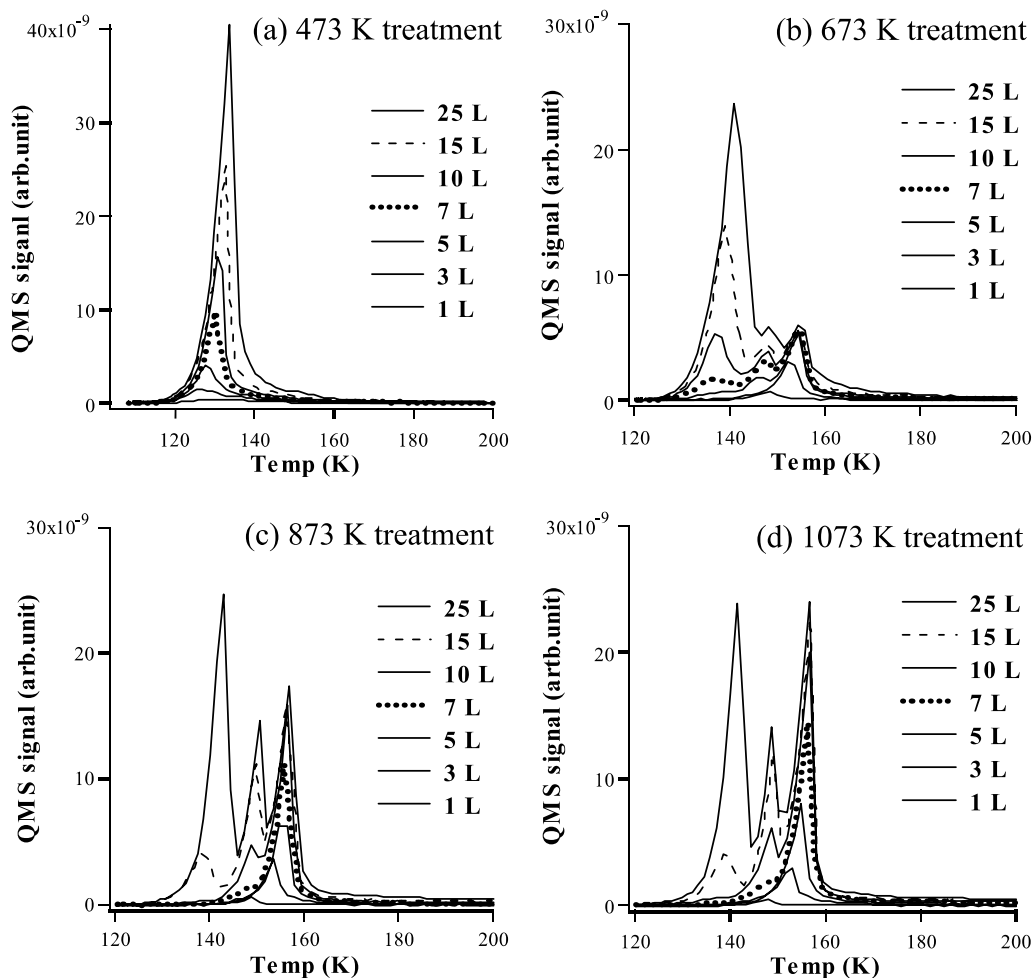
Fig. 2. TPD spectra of acetone on HOPG after heat treatment at various temperatures. Note that identical vertical scales are used for all figures except for 473 K. The 7 and 15 L are distinguished by the dashed and dotted lines, respectively.

For 673 K heat treatment (Fig. 2(b)), the TPD spectra at the lower exposures (below 5 L) consist of only one peak at around 155 K. For exposures above 5 L, two peaks are seen at about 147 and 155 K. For 7 L exposure, three peaks can clearly be seen at around 137, 147, and 155 K. Each TPD peak is associated with molecules desorbing from different surface layers similar to acetone desorption from a graphitic monolayer on Pt(1 1 1) [30]. The highest temperature peak for the TPD spectra after 673 K heat treatment (150–155 K) represents desorption from the monolayer, i.e., acetone bound directly to the HOPG surface [30,31]. The

second TPD peak (around 147 K) is associated with desorption from the bilayer [30]. The lowest temperature TPD peak (at about 137 K) represents desorption from the multilayer [30,31]. These three characteristic peaks are also present at higher exposures. The two high temperature peaks saturate while the lowest temperature peak grows with increasing exposure.

TPD spectra after 873 K heat treatment (Fig. 2(c)) shows the same three peaks at temperatures identical to those in TPD spectra after 673 K heat treatment. The acetone exposure required for monolayer peak saturation, as well as the magni-

tude of this peak, increases as the heat treatment temperature increases. It can be seen in Fig. 2 that the monolayer saturates at 5 L for 673 K, between 7 and 10 L for 873 K and around 10 L for 1073 and 1273 K (not shown) heat treatments, respectively. The saturation exposure for the bilayer also increases as the temperature of the heat treatment increases. This three-layer feature in TPD spectra was observed in our previous study, which describes acetone adsorption and desorption from a bare HOPG surface, i.e., thermally treated to 1273 K to remove functional groups [32].

Essentially identical results to those reported herein were obtained using an HOPG sample manufactured by a different company (Grade ZYA, Advanced Ceramics Co). Heat treatment leads to similar gas evolution profiles from HOPG. The acetone TPD spectra were essentially identical to those shown in Fig. 2. Exposure of HOPG samples, thermally treated to 1273 K, to ambient laboratory air at room temperature results in re-generation of the surface functionalities and a TPD behavior similar to that depicted in Fig. 2. The similarity of the behavior of samples from different sources, and the reappearance of the functionality upon exposure to air, suggests that the experimental observations reflect intrinsic properties of HOPG exposed to air, as opposed to HOPG cleaved in vacuum.

The results shown in Fig. 2 suggest that the removal of the surface functional groups from HOPG by heat treatment creates a surface that is representative of a clean HOPG surface for ace-tone adsorption because TPD spectra are almost identical to those for acetone desorbing from a single graphitic layer [30]. The higher temperature associated with the monolayer peak suggests that acetone molecules bind more tightly on the clean HOPG surface than on the functional groups that are initially present on the air cleaved surface.

Each feature observed in the acetone TPD (Fig. 2) was investigated by deconvolution of the TPD spectra [33]. The integrated TPD areas for each layer, corresponding to the relative amount of acetone molecules adsorbed at 25 L exposure, are plotted as a function of heat treatment tempera-ture in Fig. 3. As can be seen in Fig. 3, the capacity
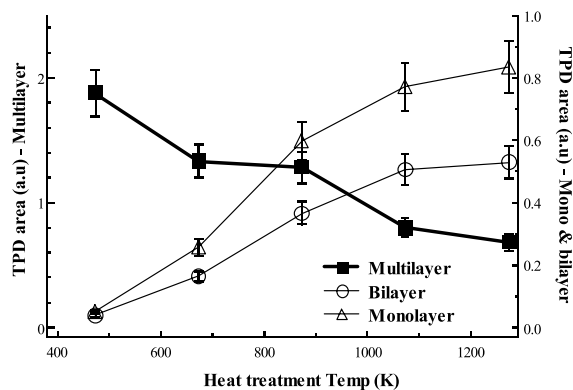

Fig. 3. Area of monolayer, bilayer, and multilayer features in acetone TPD spectra from HOPG treated at different temper-atures. All areas were obtained by deconvolution of TPD spectra corresponding to 25 L exposure.

of the monolayer and bilayer states eventually saturates at 25 L for treatment temperatures above 1000 K. As the sample is treated at higher tem-perature, the amount of acetone adsorbed directly on the HOPG surface (monolayer) increases as well as the amount adsorbed on the monolayer of acetone (bilayer). Both features appear to level off for heat treatment above 1000 K. The saturation behavior of the monolayer adsorption uptake of acetone, Fig. 3, for outgassing temperatures above 1000 K suggests that a heat treatment temperature of at least 1000 K is needed to remove the majority of air-formed functional groups from the surface and prepare a clean HOPG surface.

To investigate the effect of surface functional-ities on acetone uptake, the total TPD area as a function of heat treatment, for 473 and 1273 K, is shown in Fig. 4. The amount of acetone adsorbed on functional group-containing HOPG (473 K treatment) increases linearly through the entire exposure range. The TPD area for HOPG an-nealed at 1273 K increases linearly until about 7 L at which point the bilayer begins to grow and the slope of the TPD area increase becomes steeper, consistent with the results reported in our previous study [32]. The initial uptake slope, i.e., before the bilayer and multilayer begin to grow, is about a factor of two smaller for the 1273 K annealed HOPG sample than for the 473 K treated HOPG sample. This means that the sticking probability of
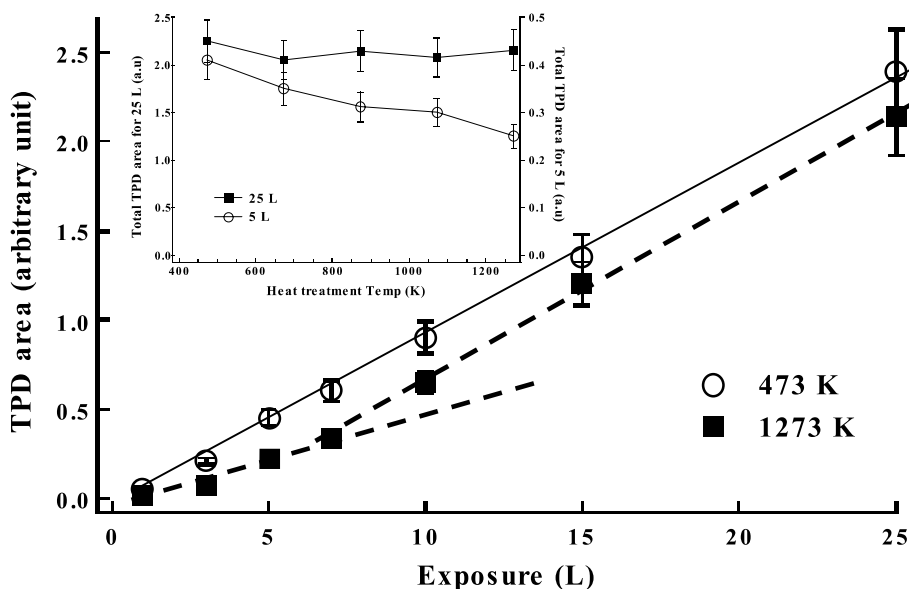
Fig. 4. Total area of acetone TPD spectra from HOPG treated at 473 and 1273 K as a function of exposure. Inset shows total area of acetone TPD spectra for 5 and 25 L exposure as a function of HOPG heat treatment. Overall, the total uptake of acetone at 25 L exposure remained constant over the entire range of HOPG heat treatment. For 5 L exposure, however, the uptake decreases by a factor of about two with increasing heat treatment.

acetone on the bare HOPG surface is a factor of two lower than on the surface containing functional groups. Once the acetone bilayer on 1273 K treated HOPG begins to form, the rate of TPD area increase becomes similar to the rate of TPD area increase for 473 K treated HOPG. This result suggests that the majority of functional groups on HOPG surface are polar, because the sticking probability of acetone on acetone, a polar organic compound, and on the HOPG surface containing functional groups is similar. This hypothesis is also supported by the observation that the total TPD area for high exposure (e.g., 25 L) remains approximately constant for all heat treatment temperatures as can be seen in the inset of Fig. 4. In this case, the contribution from each individual TPD peak changes with the removal of functional groups, while the overall adsorption remains constant. On the other hand, the TPD area for low exposure (e.g., 5 L) decreases, by almost a factor of two, as the pre-treatment temperature increases (inset in Fig. 4). Such behavior clearly demonstrates that the sticking probability of acetone on functionalities or an acetone layer already present

on the HOPG surface is higher that that on a functional group-free HOPG surface.

Qualitatively similar behavior was seen in the study of acetic acid and *n*-octane adsorption on HOPG surface [34]. Acetic acid and *n*-octane shows distinct mono- and multi-layer TPD features after thermal treatment of the HOPG to 500 K. Increasing the treatment temperature up to 1050 K led, at constant exposure, to a decrease in the multilayer feature and a concomitant enhancement of the magnitude of the monolayer feature. These results support our observation that increasing the treatment temperature leads to removal of functionalities and increasing access to the bare HOPG surface, resulting in an increase in the number of direct adsorption sites for these molecules on HOPG.

Intercalation of acetone molecules into HOPG layers is unlikely given the size of the molecule and the low pressures employed in this investigation. Furthermore, intercalation of acetone molecules should not result in saturation of all HOPG layers with such low acetone exposures, about 10 L after 1273 K heat treatment. The similarity of TPD

spectra for heat treatment above 1000 K and those from a previous study involving desorption of acetone from a monolayer of graphitic carbon grown on a Pt(1 1 1) surface [30], further supports the hypothesis that acetone molecules do not intercalate into HOPG layers, because a monolayer of graphitic carbon on Pt does not offer any layers for intercalation.

Our previous studies of adsorption of a non-polar organic, propane, on HOPG following heat treatment shows quite different behavior [24]. In the case of propane, the initial uptake capacity was very low. Heat treatment to over 1270 K increased the total adsorption capacity on HOPG by more than an order of magnitude. This indicates that the air-formed functional groups on HOPG interact more favorably with polar compounds compared to non-polar adsorbates. This is consistent with reports that air-formed functional groups are polar, e.g., carboxyl groups [14]. The presence of these oxygen-containing functional groups would result in higher adsorption capacity of carbonaceous surfaces for polar organic molecules (acetone) than non-polar (propane), because carbonaceous surfaces exposed to ambient conditions typically contain the kind of functionalities encountered in this study [29].

3.1. Energetics of acetone desorption

The activation energy for acetone desorption from a clean HOPG surface can be determined through the analysis of the desorption rate $(-\mathrm{d}\theta/\mathrm{d}T)$, which is commonly described by Eq. (1)

$$-\frac{\mathrm{d}\theta}{\mathrm{d}T} = \frac{v}{\beta}\theta^n \exp\left(-\frac{E_\mathrm{d}(1+\alpha\theta)}{RT}\right) \qquad (1)$$

where v is the pre-exponential factor, θ is the adsorbate coverage, β is temperature ramping rate $(\mathrm{d}T/\mathrm{d}t)$, n is the order of the desorption process, and E_d is the activation energy for desorption at zero coverage [35]. The variable α is an intermolecular interaction parameter. Positive values of α reflect attractive intermolecular interactions and negative values of α reveal repulsive intermolecular interactions.

In order to determine v, E_d and α, the acetone TPD spectra, for HOPG treated at 1273 K, were simulated for exposures ranging from 1 to 7 L. The best fits of Eq. (1) to the experimental data shown in Fig. 5 were obtained with $n = 1$, a pre-exponential factor of $10^{20\pm1.5}$ s^{-1}, an activation energy of 55.5 ± 3.0 kJ/mol and an intermolecular interaction parameter of 0.045 monolayer^{-1} for the acetone monolayer. The error range indicate the spread of parameters for which acceptable fits were generated. The pre-exponential factor obtained from this fit is much higher than the usually assumed value of 10^{13} s^{-1} [36]. High pre-exponential factors for desorption of organic molecules on HOPG surface were also reported in studies which investigated the desorption kinetics of n-alkanes and alkane derivatives from HOPG [34, 35]. Large pre-exponential factors have also been reported for desorption of physisorbed alkanes from Al$_2$O$_3$ [37].

The use of 10^{13} s^{-1} as the pre-exponential factor in the fitting procedure failed to achieve reasonable fits of experimental TPD data, as shown in Fig. 5(a). The 10^{13} s^{-1} pre-exponential factor results in a TPD peak that is twice as broad as that observed experimentally. While the similar leading edges of the TPD spectra at different exposures suggest zero order desorption, TPD peak line shape simulation using zero order reaction fails to predict significant trailing feature of the experimental data as shown in Fig. 5(b).

In addition to using the simulation method described above to assess the desorption parameters, acetone TPD experiments were performed using different heating rates at 3 and 7 L acetone exposure to independently determine the acetone desorption parameters [38]. The TPD profiles at different heating rates for acetone exposure of 7 L shown on Fig. 6 clearly illustrate that an increase in the heating rate leads to an increase in the peak amplitude and a shift in the peak location to higher temperature. These experiments allow the determination of the pre-exponential factor and activation energy using first order kinetics, via Eq. (2)

$$\frac{E_\mathrm{d}}{RT_\mathrm{p}^2} = \left(\frac{v}{\beta}\right)\exp\left(-\frac{E_\mathrm{d}}{RT_\mathrm{p}}\right) \qquad (2)$$
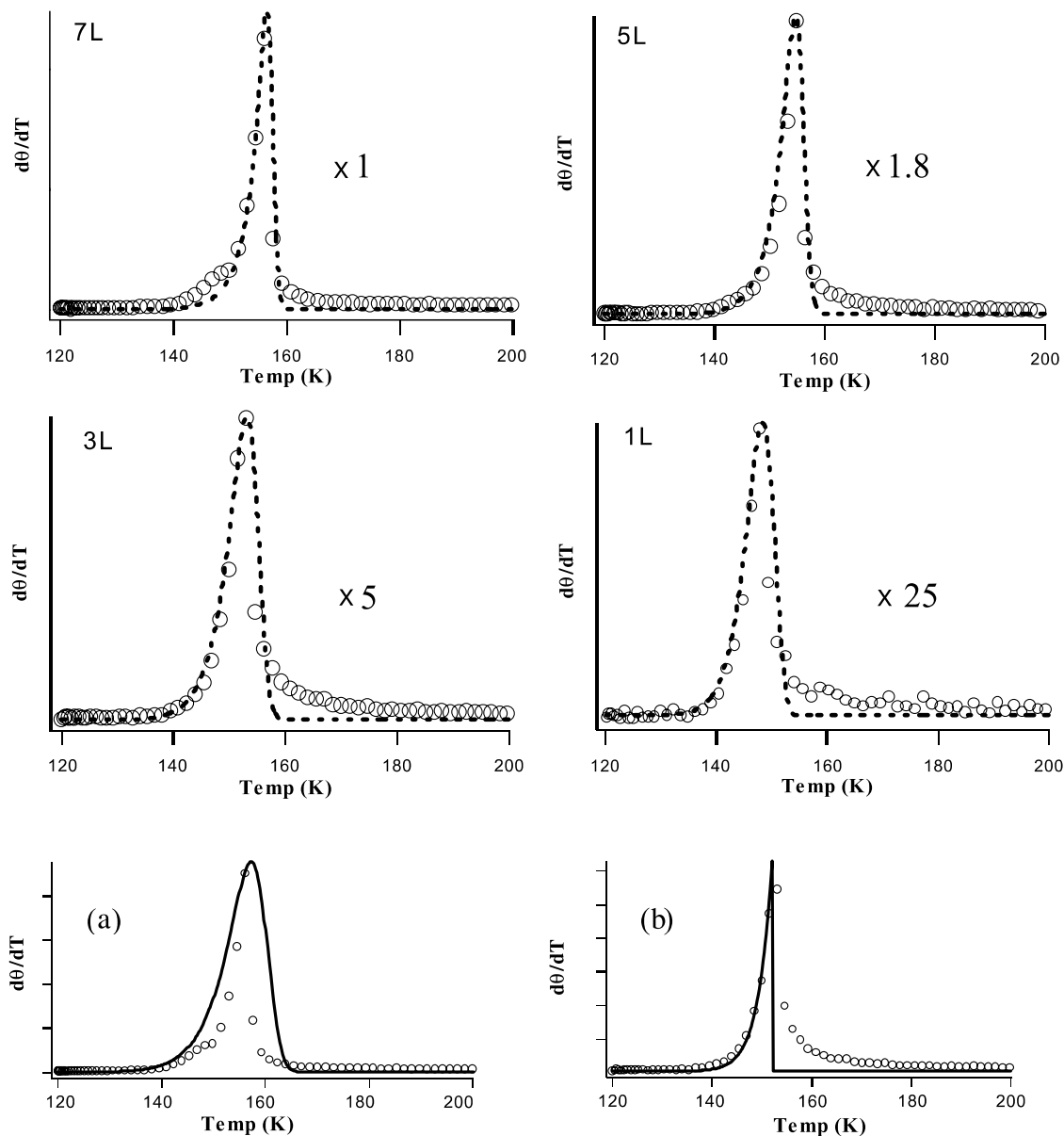
Fig. 5. Experimental (symbols) and simulated (lines) TPD spectra for acetone monolayer on HOPG treated at 1273 K. All lines were generated with common values of v (10^{20} s^{-1}), E_d (55.5 kJ/mol) and α (0.045 monolayer^{-1}). To show better images for TPD spectra at low exposures, data were multiplied by the constant shown in the figures. (a) Simulated TPD peak obtained with a conventional pre-exponential factor of 10^{13} s^{-1} for 7 L exposure; (b) Simulated TPD peak obtained using zero order desorption kinetics for 3 L exposure.

where T_p represents the temperature where the desorption rate maximum occurs [38]. Eq. (2) can be transformed to Eq. (3) to allow direct estimation of the pre-exponential factor and activation energy by plotting $\ln(\beta/T_p^2)$ versus $1/T_p$ [35,36]

$$v = \frac{\beta E_d}{RT_p} \exp\left(\frac{E_d}{RT_p}\right) \tag{3}$$

Such plots for 3 and 7 L exposure are shown in the inset on Fig. 6, where the slope of the straight line
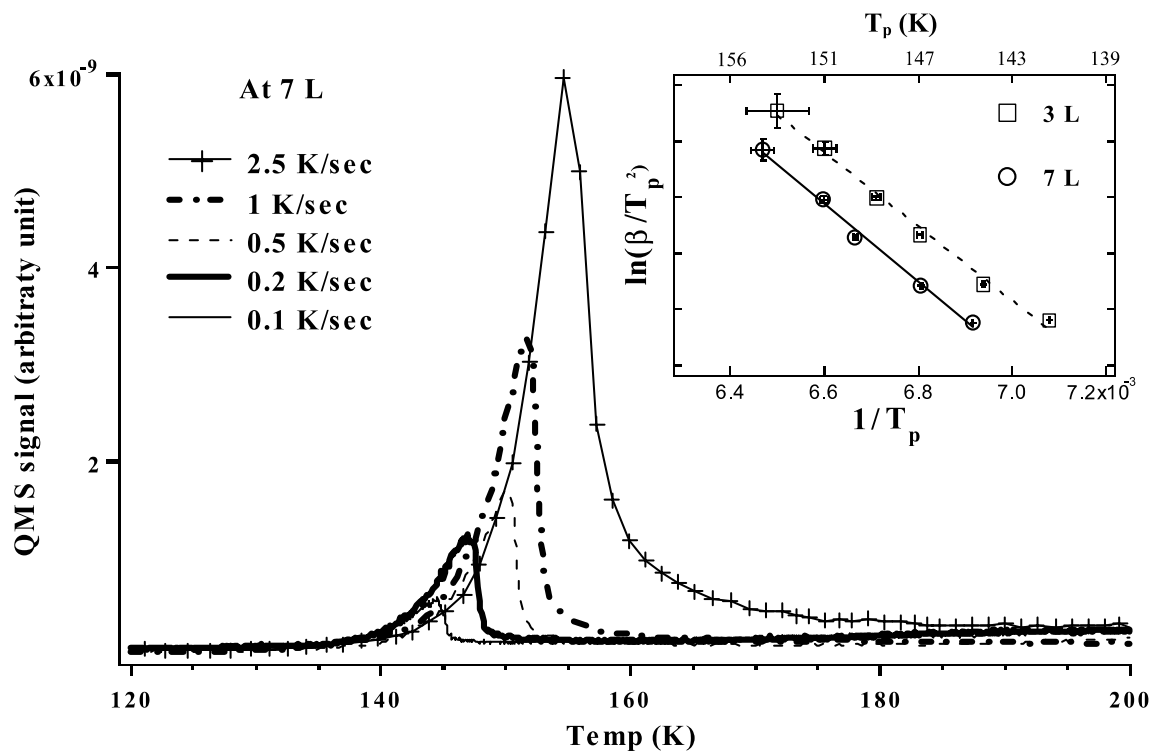
Fig. 6. Acetone TPD spectra from clean HOPG for 7 L exposure at different heating rates. The inset shows a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ for desorption experiments at 3 and 7 L exposure.

is equivalent to $(-\Delta E_d/R)$. A linear regression performed on the data yielded activation energy of 57.7 ± 2.5 kJ/mol for 7 L and 54.9 ± 2.5 kJ/mol for 3 L and a common pre-exponential factor of $10^{19 \pm 1}$ s^{-1}. These values are similar to those obtained from the line-shape analysis of acetone TPD shown on Fig. 5. This agreement provides confidence in the desorption parameters reported here in spite of the high values of the pre-exponential factor. Furthermore, the increase of the activation energy with increasing coverage is consistent with attractive interactions between acetone molecules in the monolayer on the HOPG surface.

The activation energy of the acetone monolayer on HOPG estimated in this study can be compared with other studies of acetone physisorption on metal surfaces, which also revealed three narrow TPD peaks for acetone desorption from Au(1 1 1), Ag(1 1 1) and C/Pt(1 1 1) [30,39,40]. While the desorption temperatures reported in the earlier studies are similar to those we observed, the re-

ported activation energies are different. We attribute this difference to the use of a "typical" pre-exponential factor of 10^{13} s^{-1}. Our experiments and analysis suggest that this may not be a good assumption for physisorption. Acetone desorption from other metals (e.g., Cu and Pt) did not show distinct bilayer feature, suggesting that the adsorption mechanism is different from that on HOPG, Ag and Au [41].

4. Conclusion

The presence of oxygen-containing functional groups, formed after cleaving HOPG in air dramatically affects the nature of the accessible sites for a simple polar organic compound. The removal of these groups by thermal treatment provides access for acetone to a clean carbonaceous surface without a significant change in the total capacity of the surface for that polar organic

adsorbate. The presence of surface functional groups appears to increase the sticking coefficient in the monolayer state by about a factor of two. These results suggest that carbonaceous surfaces should be thermally treated at temperatures above 1000 K to provide access to a non-functionalized surface. Practical carbon sorbents may benefit from surface passivation for the effective adsorption of polar organics as the presence of surface functionalities reduces the binding energy and the uptake kinetics. Acetone monolayer desorption from clean HOPG surface reveals a high pre-exponential factor for desorption. This appears to be a characteristic of physisorbed organic monolayers, both polar and non-polar.

Acknowledgements

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