Temperature Programmed Desorption Approach in Understanding the Development of Semiconductors and Catalyst

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Abstract: *This comprehensive article review delves into the extensive utility of temperature-programmed desorption (TPD) as a valuable technique for understanding the intricate development of semiconductors and catalysts. TPD serves as a powerful tool that provides profound insights into the surface chemistry of materials, enabling researchers to gain a comprehensive understanding of various crucial aspects. The article covers a wide range of TPD aspects, including the analysis of surface functional groups, system temperature control, the impact of oxidation and surface treatment, the significance of heat treatment, the dynamics of adsorption and desorption processes, the thermodynamics underlying TPD measurements, surface group characterization techniques, accurate analysis, and measurements considerations, and the importance of sequential surface treatment. By comprehending these multifaceted aspects, researchers can effectively optimize the performance of semiconductors and catalysts, as well as develop novel materials with enhanced properties. Ultimately, the article emphasizes the remarkable versatility and power of TPD in the dynamic realm of semiconductor and catalyst development.*

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1.0 Temperature Programmed Desorption

Temperature-programmed desorption (TPD) is a valuable technique used to study surface interactions and reactions involving adsorb molecules on a substrate, particularly in catalysis applications. The method involves the regulation of surface temperature to explore catalytic processes like desorption, surface reactions, and adsorption function (Rakić and Damjanović, 2013). During TPD, a small amount of catalyst is placed in a reactor, and an inert gas is allowed to flow through the reactor. Next, a probe gas is deposited on the catalyst's surface, and the rate at which a carrier gas flows through the catalyst is increased linearly. Downstream, a detector monitors the changes in the inert gas stream, while a thermocouple near the catalyst measures the temperature. The mass spectrometer is a reliable TPD detector that examines the effluent stream's composition concerning the catalyst's temperature (Ishii & Kyotani, 2016; Krasnikova et al., 2019). One advantage of TPD is that it allows for the study of oxygen-containing functional groups that thermally break down at different temperatures to produce oxygen-containing gases. By monitoring the effluent stream's composition and the catalyst's temperature, TPD can be used to monitor oxygen-containing functional groups in real time. TPD can also provide insight into the rate of desorption, adsorption, and surface reactions, which are essential in catalysis applications (Falconer & Schwarz, 1983; Ishii & Kyotani, 2016).

2.0   Understanding the Surface Functional Group

In temperature-programmed desorption, the surface functional groups are typically identified by monitoring the release of adsorbed molecules, such as water, carbon dioxide, or ammonia, from the surface as the temperature is increased (Herold et al., 2022) The desorption temperature of these molecules is related to the strength of their interaction with the surface functional groups (Jentoft, 2013). In the field of carbon material analysis, the Temperature Programmed Desorption (TPD) technique has been extensively used to investigate the surface functional groups and their behavior under different experimental conditions, including the ramping heating rate, the type of experimental atmosphere, and the temperature (Schmid et al., 2023a). To obtain valuable information, it is crucial to consider the relationship between the experimental conditions, the process, the functional group, and the apparatus used. Factors such as the material's texture, heating rate, and experimental setup geometry may influence the peak temperatures observed during the TPD analysis (Rocha et al., 2023). Therefore, it is essential to carefully design and control these experimental parameters to obtain reliable and accurate data. Moreover, TPD analysis can be coupled with other analytical techniques such as X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR) to provide a more comprehensive understanding of the surface functional groups and their behavior (Ishii & Kyotani, 2016). For example, if a surface is functionalized with carboxylic acid groups, the adsorbed water molecules will be released at a lower temperature compared to a surface without these groups, because carboxylic acid groups form stronger hydrogen bonds with water molecules than non-functionalized surfaces. Therefore, the desorption temperature of water molecules can be used to identify the presence of carboxylic acid functional groups on a surface.

3.0   Understanding the Temperature of the system

Temperature-programmed desorption (TPD) is a widely used technique for also for the analysis of surface functional groups on carbon materials (Rocha et al., 2023). The TPD pattern of a commercial activated carbon will show that CO_2 and CO are adsorbed at $0^{o}C$, and as the temperature is increased, CO_2 will desorb first at 250 ^{o}C, followed by CO at $900^{o}C$. However, the desorption of both gases will decrease at a temperature of 1000 ^{o}C. The thermal decomposition of oxygen functional groups in carbon materials can occur when the material is heated up to a temperature of $1200^{o}C$. However, some researchers have reported higher desorption temperatures for CO and CO_2 due to the presence of extremely stable oxygen functional groups. For example, Pan and Yang, 1992 observed an increase in the desorption temperature of CO up to $1500^{o}C$ in oxidized graphite samples. Similarly, Fritz & Hüttinger, 1993 observed desorption temperatures above $1200^{o}C$ in PVC carbons. Therefore, the desorption temperature of CO and CO_2 can vary depending on the type of carbon material, the presence of oxygen functional groups, and the experimental conditions such as the rate of heating and the type of atmosphere (Petrovic et al., 2021). It is important to relate the experimental conditions to the process and functional groups being analyzed to obtain accurate and useful information. The texture of the material, the rate of heating, and the geometry of the experimental setup can all influence the peak temperatures observed in the TPD pattern. Therefore, careful consideration and control of the experimental parameters is necessary for the proper interpretation of TPD data.

Below are some ways in which the temperature of a system can affect the temperature programmed desorption experiment:

3.1   *Heating rate*

Modifying the linear temperature ramp rate during the desorption process results in a shift in the peak temperature. By reducing the temperature ramp rate, the time delay between the actual desorption temperature and the temperature detected becomes shorter. In other words, a slower increase in temperature allows for a more accurate representation of the true desorption temperature, minimizing any discrepancies between the two. This adjustment can be beneficial in ensuring the reliability and precision of desorption measurements(Altamira, 2022) (Schmid et al., 2023b) .

3.2   *Re-adsorption*

The process of re-adsorption introduces an additional time increment to the regular desorption time, causing a delay in the arrival of desorbing molecules at the detector. Consequently, molecules reaching the detector are recorded at incorrect temperatures, leading to erroneous temperature readings. This phenomenon occurs because the re-adsorbed molecules may carry residual heat from previous desorption cycles, which can distort the accurate temperature measurement. Therefore, accounting for the effects of re-adsorption is crucial to ensure precise and reliable temperature detection during desorption processes (Thomas, 2023) (Altamira, 2022).

3.3   *Initial coverage:*

In a second-order desorption process, as the initial surface coverage increases, there is a corresponding decrease in the temperature at which the peak occurs. This relationship between initial surface coverage and peak temperature can be observed due to the nature of the desorption reaction. A higher initial surface coverage implies a larger number of adsorbed molecules on the surface, leading to a higher concentration of desorbing species. As a result, the desorption reaction becomes more efficient, requiring less energy to overcome the activation barrier. This reduced energy requirement is reflected in the lower peak temperature observed during the desorption process. Therefore, in a second-order desorption process, an increase in initial surface coverage correlates with a decrease in the temperature at which the peak occurs (Pavan M. V. Raja & Andrew R. Barron, 2023) (Schmid et al., 2023b).

3.4   *Desorption activation energy:*

In a first-order desorption process, the temperature of the peak values will increase as the activation energy increases. This relationship between activation energy and peak temperature can be understood by considering the kinetics of the desorption reaction. A higher activation energy represents a higher energy barrier that the desorbing molecules must overcome in order to transition from the adsorbed state to the gas phase. As the activation energy increases, it becomes more difficult for the desorbing molecules to reach the necessary energy threshold for desorption. Consequently, higher temperatures are required to provide the additional energy needed to surpass the higher activation energy barrier. This results in an increase in the temperature at which the peak values occur during the desorption process. Therefore, in a first-order desorption process, an increase in activation energy is associated with an increase in the temperature of the peak values (Pavan *et al*., 2023). Therefore, the temperature of a system affects TPD by changing the desorption rate, which can be measured by detecting the evolved gas or monitoring the retained species. The heating rate, re-adsorption, initial coverage, and desorption activation energy are all factors that can affect the temperature-programmed desorption process.

4.0   Understanding the contribution of Oxidation of the system

In temperature-programmed desorption (TPD), oxidation of the system refers to the process of

introducing an oxidizing agent to react with the adsorbed species on the surface of a material. In a study to (Figueiredo *et al*., 1999) investigate the effect of oxygen on the TPD (temperature-programmed desorption) profile of five samples of activated carbon. The results showed that as the oxidation of the samples increased, there was a gradual increase in both CO and CO_2 peaks. The increase in peak size of CO was observed to be higher than that of CO_2, indicating that CO decomposed at a higher rate than CO_2. Figure 2a and 2b in the study shows the TPD spectra of a sample oxidized in the gas phase, 5% O_2 in N_2, to different extents of CO and CO_2 evolution. The spectra show that there is a threefold increase in peak size going from the original sample (A1) to the sample with lower oxidation (A2). Furthermore, the increase in peak size continues from A3 to A5. This indicates that there is a gradual increase in oxidation as we move from A1 to A5. The study also found that there is a large increase in the ratio of CO/CO_2 from the spectra. This ratio increases as the oxidation of the sample increases, indicating that the rate of decomposition of CO is higher than that of CO_2. However, it is important to note that the increase in peak size may not always be three-fold as the oxidation of the sample increases. Therefore, the studies demonstrated that the TPD profile of activated carbon is affected by the presence of oxygen (Figueiredo et al., 1999). The increase in peak size of CO and CO_2 with increasing oxidation indicates the rate of decomposition of CO is higher than that of CO_2. The results suggest that the TPD technique can be useful in characterizing the degree of oxidation of activated carbon samples.

The effect of oxidation on TPD can vary depending on the specific system and the nature of the adsorbed species. Here are a few general effects that oxidation can have on TPD (Herold *et al*., 2022).

4.1   Desorption temperature shift

Oxidation can affect the desorption temperature of adsorbed species. Some species may require higher temperatures to desorb after oxidation due to increased binding energy resulting from the formation of stronger chemical bonds. In such cases, the desorption peaks in the TPD curve would shift to higher temperatures (Schmid *et al*., 2023b).

4.2   Enhanced desorption

In certain cases, oxidation can promote the desorption of adsorbed species. Oxidation reactions can break weaker bonds between the adsorbate and the surface, making it easier for the species to desorb. This can result in increased desorption rates and higher desorption yields in the TPD analysis (Deng *et al*., 2019).

4.3   Change in desorption profile

Oxidation can alter the desorption profile in TPD. It can introduce new desorption peaks or modify the relative intensities of existing peaks. The appearance of new peaks can indicate the formation of new species through oxidation reactions, while changes in peak intensities can reflect alterations in the surface coverage of different species (Deng *et al*., 2019).

4.4   Complete removal of adsorbates

Strong oxidation may lead to the complete removal of adsorbates from the surface. This can result in the disappearance of desorption peaks associated with specific species in TPD. The absence of desorption peaks after oxidation suggests that the adsorbates have been completely converted into gaseous products or removed from the surface (Kim et al., 2022).

4.5   Interaction with the support material

In TPD experiments, the adsorbed species are typically supported on a solid material. The

oxidation of the system can affect the interaction between the adsorbed species and the support material. This can lead to changes in the strength of adsorption, the stability of the

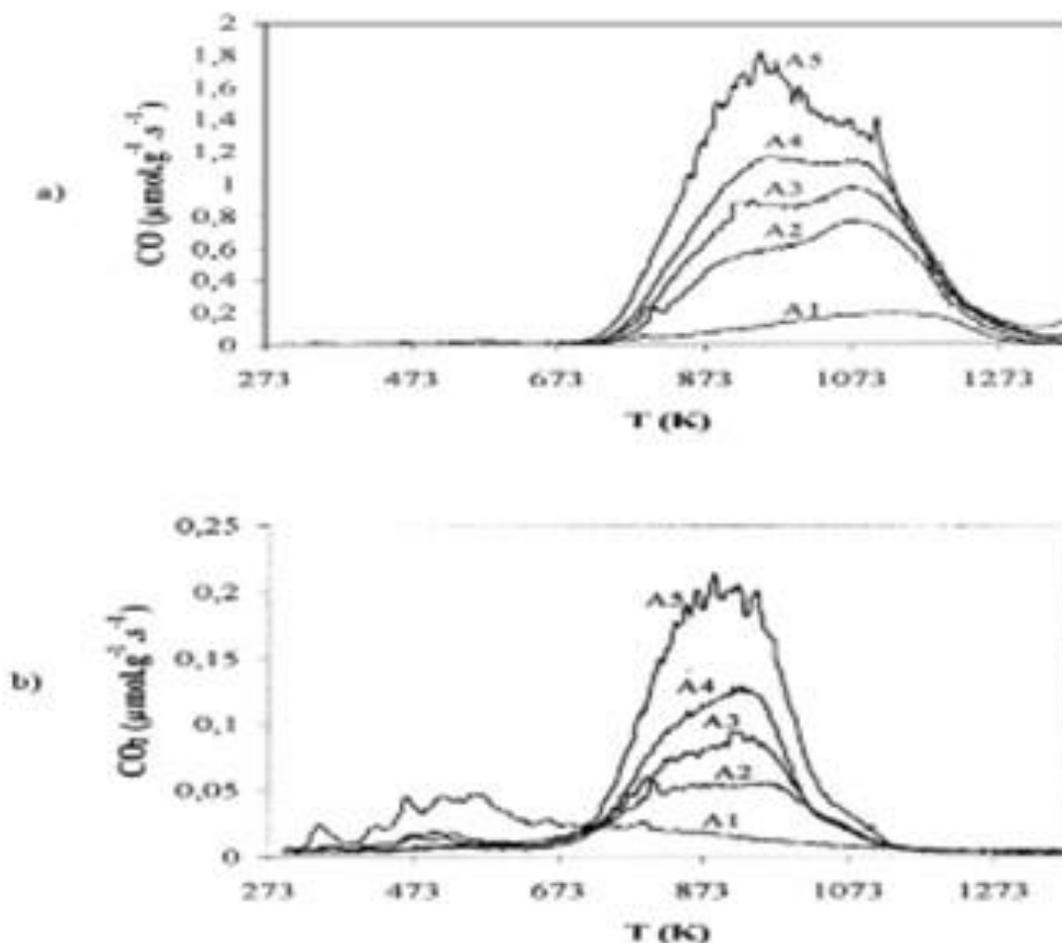adsorbed species, and the desorption behavior (DeRita et al., 2017).

Fig 2 (a and b): The TPD spectra for oxidized samples in a gas phase regarding (a) CO and (b) CO₂ evolution; reproduced from (Figueiredo et al., 1999)

4.6   *Oxidation of adsorbed species*

In TPD, the desorption process involves the removal of adsorbed species from the surface. If the system undergoes oxidation, it can lead to the oxidation of the adsorbed species as well. For example, the oxidation of adsorbed CO by hydroxyl groups on the surface of the support material has been observed (Langhammer *et al*., 2022. It's important to note that the specific effects of oxidation on TPD can vary significantly depending on the nature of the adsorbates, the oxidizing agent used the

temperature and duration of oxidation, and other experimental conditions. Therefore, it is necessary to carefully design and control the oxidation process to achieve the desired effects and accurately interpret the resulting TPD data (Rodriguez et al., 2022).

5.0   Understanding the contribution of Surface Treatment in the system

From the TPD spectra in Fig 3 (a and b), the before and after oxidizing treatment and the increase in the amount of surface oxygen

groups is evidence that there is an increase in the CO and CO_2 peak. With liquid phase treatment, the evolution of CO_2 is increased at low temperatures (373K to 673K, A1, A12, and A11), when the gas phase is oxidized CO_2 peak is increased at higher temperatures (673 to 1073K, A4, and A9). There is the evolution of CO peaks at 900K to 1070K with gas phase treatment. Liquid treatment can be done with nitric acid and gas treatment can be done with a suitable gas. The treatment process can reduce the contamination of the substances. Gas treatment can increase the yield of

anhydride, lactone, phenol, and carbonyl/quinone surface groups, which affect the increase in the concentration of hydroxyl and carbonyl surface groups, while nitric acid treatment can also increase the yield or concentration of carboxylic acid group. When the activated carbon is treated with gas, there is much more CO peak than when it is treated with nitric acid. In both cases, there are two maxima TPD peaks in the CO and CO_2 spectra at around 900K to 1070K (Figueiredo et al., 1999) due to the presence of carbonyl/quinones, ethers, and phenols.
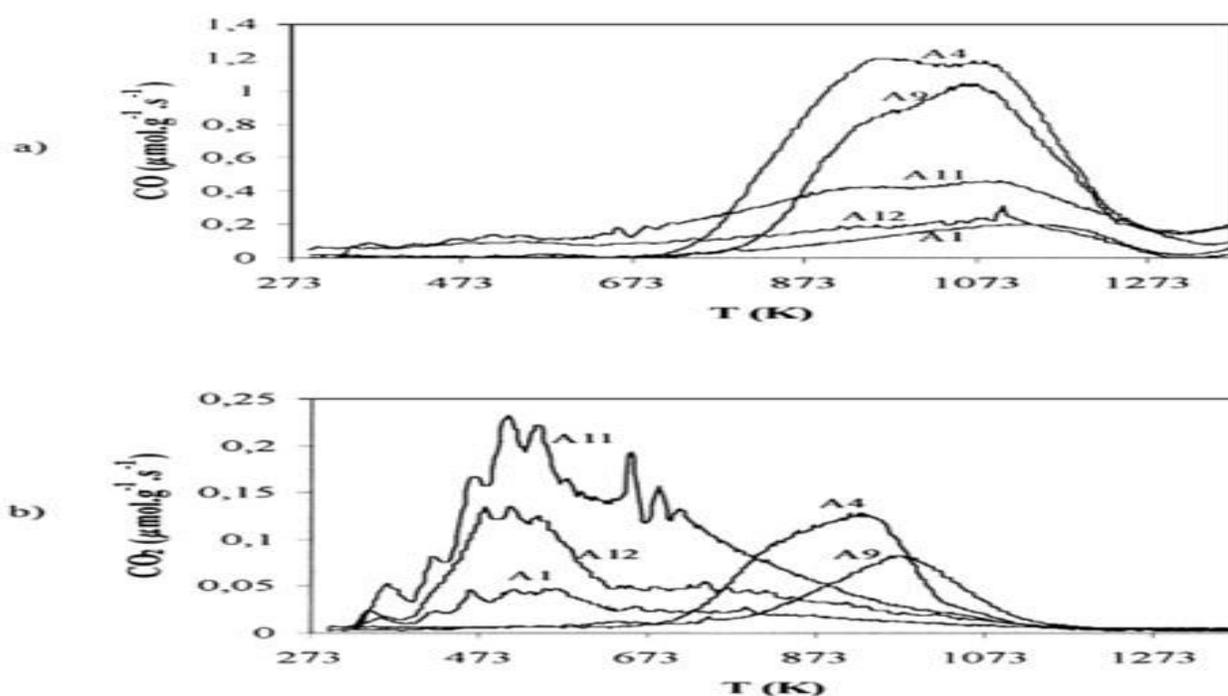

Fig 3 (a and b): TPD Spectra for the oxidizing treatment with liquid phase and gas phase on CO and CO_2; reproduced from (Figueiredo et al., 1999)

6.0 Understanding the contribution of Heat Treatment to the system

In another study, researchers (Belhachemi & Addoun, 2011) describe the significant alteration in surface chemistry by oxidation and thermal treatment. (a) Carbon dioxide (CO_2) and (b) carbon monoxide (CO) desorption profiles for the various activated carbons in the range of 298 to 1273K temperature range are

shown in both figures below. This table below makes it quite evident that carbon S49N has the most oxygen surface groups (with the highest concentration in CO – 3.53 mmol. g^{-1} and CO_2 – 1.51 mmol.g^{-1}), with these groups primarily evolving as CO. (Figueiredo et al., 1999; Rios *et al*., 2007).

Table 1: Amount of CO_2 and CO evolved during the TPD experiments on the as-synthesized, oxidized, and heat-treated activated carbons (Figueiredo *et al*., 1999; Rios *et al*., 2017)

Sample	CO, mmol.g^{-1}	CO_2, mmol.g^{-1}	CO/CO_2
C16	0.89	0.41	2.1
C16N	1.5	0.38	3.9
C16NT	0.82	0.27	3.0
C37	1.17	0.43	2.7
C37N	2.55	1.05	2.4
C37NT	0.92	0.14	6.5
C50	1.22	0.39	3.1
C50N	2.67	1.04	2.5
C50NT	0.74	0.06	12.3
S34	0.90	0.40	2.2
S34N	3.23	1.15	2.8
S34NT	0.59	0.10	5.9
S49	0.95	0.40	2.3
S49N	3.53	1.51	2.3
S49NT	0.49	0.09	5.4

However, the breakdown of ethers, phenols, and carbonyls causes the CO evolution profile to show a significant peak at higher temperatures in the 973 to 1123K range. Furthermore, as seen in the table above, the oxidized material displays a significant increase in the total quantity of surface oxygen groups that have evolved into CO_2 and CO, with the CO_2 groups exhibiting a larger improvement (lower CO/CO_2 ratio). The larger coverage area and more developed porosity of the beginning activated carbons with matching degrees of activation are to blame for the oxygen surface groups growing with increasing burn-off. In comparison with the samples from series C, samples from series S were better able to fix oxygen groups because of their wider microporosity with improved accessibility to the acid solution. However, C50NT displays a CO peak at high temperatures between 1073 K and 1273 K. (Fig 4 (a and b). These groups belong to basic structures of the carbonyl, quinone, pyrone, and chromone types. The presence of oxygen-containing groups and,

more importantly, of electron-rich oxygen-free sites at the carbon basal planes give thermally treated samples their fundamental properties(Leon *et al*., 1992). But for both samples (C50NT and S49NT), the amount of CO_2 that is evolved is essentially insignificant, and C50NT has the highest CO/CO_2 ratio. Since this was also observed in the parent activated carbons, that means the higher degree of activated carbons synthesized in conjunction with carbon dioxide is present in the most stable groups (Belhachemi & Addoun, 2011).

6.1 *Adsorption and Desorption of the System in Temperature Programmed Desorption*

Both gas adsorption, desorption, and diffusion are impacted by temperature. Methane desorption and diffusion are encouraged when the temperature of coal seams is raised. (c). According to a preliminary analysis, there is a chance that more coal gases could be desorbed at a greater heating rate. This is proof that rising temperatures have an impact on gas desorption, but this research is currently exploratory and qualitative. Isothermal desorption studies at high and low temperatures (95 and 20 °C) were carried out as part of extensive research (Wang & Zhu, 2021) to examine the methane desorption at these two temperatures under three adsorption equilibrium pressures (0.9, 1.5, and 2.1 MPa). Fig 5(a) depicts the desorption content-time curves from the testing, while Fig 5(b), depicts the desorption rate-time curves.

The figures show that for a given adsorption equilibrium pressure, higher desorption temperatures are associated with larger desorption contents and rates. Higher adsorption equilibrium pressure relates to higher desorption content and desorption rate at the same desorption temperature.
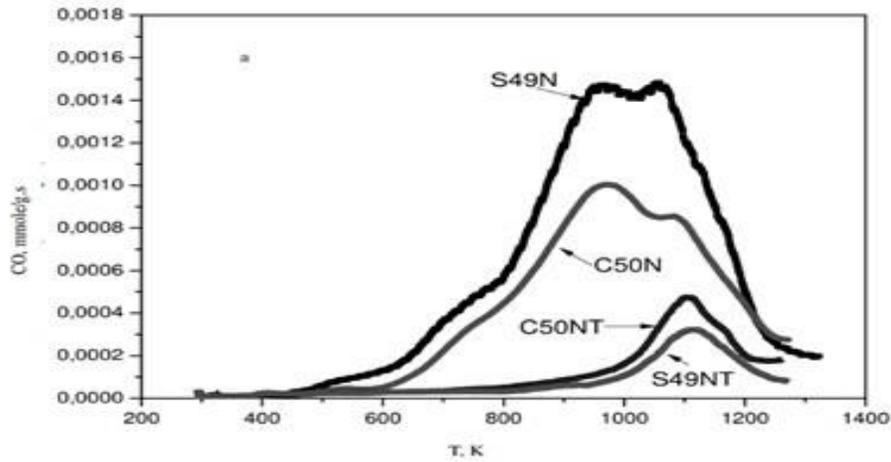
(a)
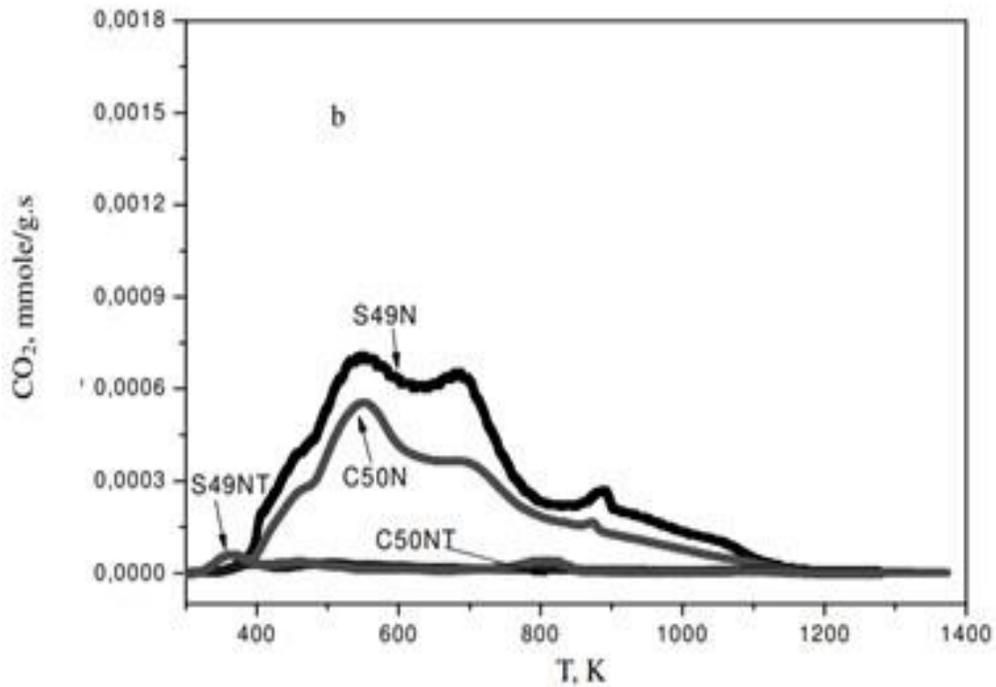
(b)

Fig. 4 (a and b): Evolution profiles of CO and CO_2 in TPD experiments for oxidized (carbon C50N and S49N) and heat-treated (carbon C50NT and S49NT) carbons; Reproduced from (Belhachemi & Addoun, 2011)
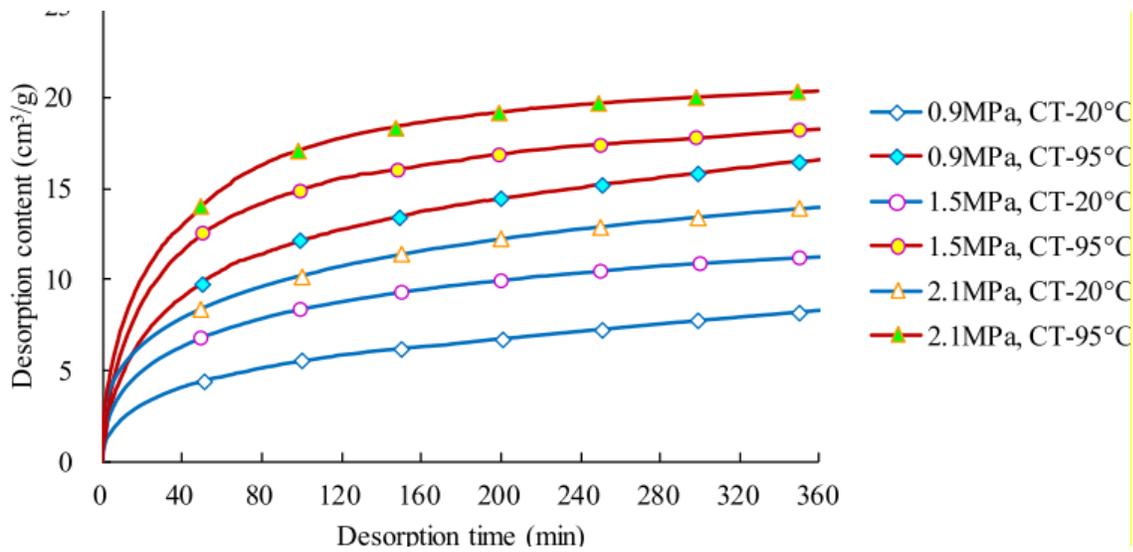
Figure 5a: Methane desorption content against time for tests conducted at 20 and 95 °C with 0.9, 1.5, and 2.1 MPa adsorption equilibrium pressures. Reproduced from; (Wang & Zhu, 2021)

Figure 5b: Methane desorption rate vs time for tests conducted at 20 and 95 °C using 0.9, 1.5, and 2.1 MPa as the adsorption equilibrium pressures. Reproduced from; (Wang & Zhu, 2021)

To explain methane desorption from coal and describe the link between the desorption time and the amount of desorbed methane, (Wang & Zhu, 2021) employed the dynamic diffusion model from equation 1. where $Q\infty$ denotes the total amount of methane desorption after infinite time, cm^3/g, and Q_t denotes the cumulative desorption amount of methane in time t, cm^3/g, t denotes time, s; D denotes the diffusion coefficient, cm^2/s. r_0 denotes the average radius of the coal particles, cm.

6.2   Understanding the contribution of Thermodynamics to the system

The variable D in equation 1 is expected to be a constant during desorption, although it is not a constant for methane desorption from coal. Due to fluctuations in methane concentrations and coal granule surface-to-volume ratios, the diffusion coefficient for methane-coal

desorption is time-dependent (Wang & Zhu, 2021).

$$\frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2\pi^2 D}{r_0^2} t\right)$$ (1)

The process taken into consideration in this study of methane desorption at various heating rates is rising temperature. When there are temperature changes during diffusion, the equivalent diffusion coefficient D_{eq} is frequently used to express the gas's diffusivity. The link between D_{eq} and temperature is given by the Arrhenius equation;

$$D_{eq} = D_{initial} \exp(-E_0/RT - 1.5)$$ (2)

where $D_{initial}$ stands for the D_{eq} value at the beginning (in units of m^2/s), T for thermodynamic temperature (in units of K), R for the universal gas constant (in units of kJ/mol K), and E_0 for the temperature

independent activation energy (in units of kJ/mol).

The diffusion coefficient is no longer treated as a constant and instead has a negative exponential relation with time, as indicated in the equation below, according to Li et al (2016), who defined the dynamic diffusion model equation used by (Wang & Zhu, 2021).

$$D(t) = D_0 \exp(-\beta t) \qquad (3)$$

where D_0 is the diffusion coefficient's starting value at time t = 0, cm^2/s; D(t) is the dynamic diffusion coefficient at time t, cm^2/s; t is the time, s; and is the diffusion coefficient's attenuation coefficient, s1. The dynamic diffusion model's equation is eqn 4.

$$\frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_0}{r_0^2 \beta}(1 - e^{-\beta t})\right) \qquad (4)$$

The authors (Wang & Zhu, 2021) were able to conclude that a greater temperature caused the methane to desorb more quickly and completely. The kinetic energy of methane molecules adsorbed to the coal matrix might increase at high temperatures. The likelihood that the molecules will have enough energy to break through the adsorption potential energy barrier and leave the coal matrix increases with increased energy. As a result, at greater temperatures, more methane is released. Methane desorption in coal is endothermic, thus raising the temperature of the coal can accelerate desorption by providing energy. The methane molecules can escape more readily because of the heat's consistent driving force for desorption. extended heating

6.3   Surface group characterization of the product

Kalijadis, et al (Kalijadis et al., 2011) aimed to describe the surface chemistry of various carbon materials with various porous textures. The surface chemistry of carbon materials has a significant impact on several applications. Chemisorbed oxygen, which can be bonded in the form of various functional groups, has a significant impact on several properties of carbon-based materials. The faces of basal planes and the margins of such layers make up the heterogeneous surface of carbons. The edge sites serve as active sites for oxygen chemisorption since they are substantially more reactive than the atoms within the basal planes. As a result, surface oxygen groups are mostly found there (Kalijadis et al., 2011; Kim Kinoshita, 1988). Titrations in aqueous solutions are typically used to determine the surface oxygen groups on carbon compounds. The Boehm method is one of the conventional approaches used. Also, techniques utilizing temperature-programmed desorption (TPD), diffuse reflectance FTIR (DRIFTS), or X-ray photoelectron spectroscopy (XPS) can be applied (Kalijadis et al., 2011). Due to the disintegration of surface oxygen complexes on carbon materials during heating and the subsequent emission of CO and CO_2, the TPD peaks of CO and CO_2 at different temperatures correlate to different oxygen groups. For instance, the disintegration of carboxylic or lactone groups produces CO_2 at 373 - 673K or 463 - 923K, respectively. CO and CO_2 peaks are formed when carboxylic anhydrides break down between 623 and 900K. Phenols, ethers, carbonyls, and quinones are the sources of CO at 973–1253 K. The amounts of CO and CO_2 released during the TPD trials match the total number of surface oxygen groups (Kalijadis et al., 2011). The binding force of oxygen-containing groups has an impact on the decomposition temperature. As a result, the location of the peak maximum at a particular temperature correlates to a particular oxygen complex at the surface. Qualitative data about surface oxygen groups is revealed by deconvolution of the TPD profiles. The Boehm method can be used to identify the oxygen groups on a carbon molecule that have both basic (phenol, lactone, and carboxyl) and acidic (carboxyl) surface qualities. By neutralizing

these groups with various solutions—HCl (for basic groups), $NaHCO_3$, Na_2CO_3, and NaOH—you can tell them apart because their acidities are different (for acidic groups) (Marchon et al., 1988; Nevskaia et al., 1999; Otake & Jenkins, 1993; Zielke et al., 1996)

6.4 Surface group analysis and Measurements in TPD

The nature and thermal stability of the surface oxygen groups of the carbon compounds were examined using the TPD technique and mass spectrometry. For temperature-programmed desorption, specially constructed equipment is being used. Titration techniques make it simple to identify the oxygen groups that have acidic or basic qualities on a carbon material surface. The Boehm method was used to determine the surface groups of the carbon compounds under investigation. Small amounts (0.1 g) of each carbon material were combined with 10 ml of various bases (0.1 M NaOH, 0.1 M $NaHCO_3$, or 0.05 M $NaCO_3$) in 25 ml beakers to identify the acidic sites. For 24 hours, the beakers were sealed and shaken. Following filtering, the solutions underwent a titration with 0.05 M H_2SO_4. Similar to the previous, the basic sites were identified by combining 10 ml of 0.1 M HCl with 0.1 g of each carbon material. With 0.1 M NaOH, the resulting solutions were titrated (Kalijadis et al., 2011). $CaCO_3$ and $CaCO_3$ mixed with GC ($CaCO_3$/GC) TPD profiles were taken to look into the potential for CO_2 reduction as a secondary reaction on a carbon surface. CO evolution might be caused by one of two potential reactions. Two examples are the reduction of CO_2 gas on the carbon material in the furnace of the TPD apparatus and CO^{2+} fragmentation in the mass spectrometer's ion source (Kalijadis et al., 2011). Figure 6a depicts a typical TPD profile for the thermal decomposition of calcium carbonate. The parent ion CO^{2+} is the source of the primary peak at m/z = 44, while the minor peak at m/z = 28 reflects CO^+ produced

because of CO^{2+} fragmentation in the ion source (Kalijadis et al., 2011).
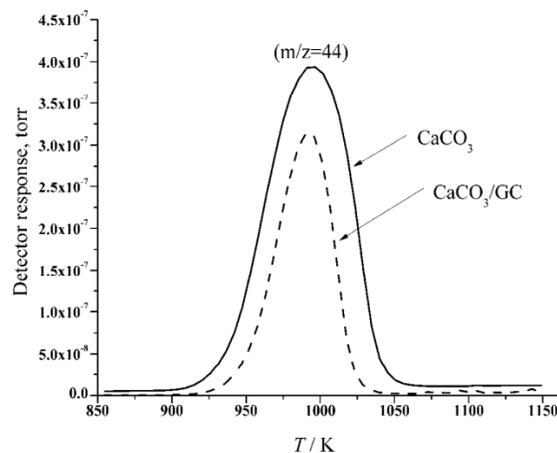
(a)
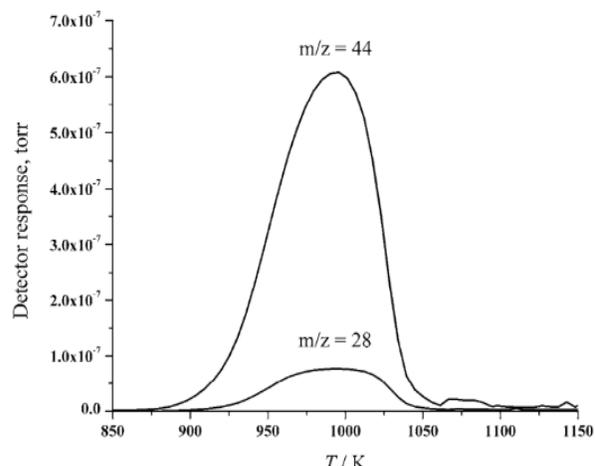
(b)

Fig 6a: Thermal decomposition of $CaCO_3$ TPD profile; reproduced from Kalijadis, *et al.*, (2011).
Fig 6b: Comparison of the decomposition of $CaCO_3$ and $CaCO_3$/GC; reproduced (Kalijadis *et al.*, 2011)

Figure 6b compares the TPD findings for $CaCO_3$ and $CaCO_3$/GC decomposition. In comparison to pure $CaCO_3$, the TPD Profile of the $CaCO_3$/GC combination revealed an increase in CO evolution and a concurrent decrease in CO_2 evolution. Both measurements for peak CO and CO_2 concentrations were determined (I_{CO} and I_{CO2}, respectively). I_{CO}/I_{CO2} was 0.13 for $CaCO_3$ breakdown, but in

the presence of GC, the ratio rose to 0.22 because more CO was liberated. Therefore, it may be argued that there was a decrease in CO_2 on the carbon surface (Kalijadis et al., 2011).

Kalijadis, et al.,(Kalijadis et al., 2011) conducted research on temperature-programmed desorption (TPD) profiles and identified the presence of local CO maximums at very low temperatures, specifically 600K, which were unexpected to be generated by the breakdown of oxygen complexes. The study suggests that the decrease in CO_2 on the carbon surface may be responsible for the formation of these peaks. The researchers propose that the decrease in CO_2 could be due to a decrease in the number of available oxygen sites for CO_2 to react with, leading to the formation of these local CO maximums. Additionally, the study suggests that the decomposition temperature is directly related to the strength of the link between a particular oxygen-containing group and the carbon surface. This means that the peak maximum at a given temperature correlates to a specific oxygen complex at the surface. The presence of these local CO maximums in TPD profiles at low temperatures can be attributed to changes in the availability and strength of oxygen complexes on the carbon surface. The research highlights the importance of understanding the role of oxygen-containing groups in the reactivity of carbon surfaces, and how they can affect the TPD profile.

6.5   Treatment of a surface

In Fig 7a, TPD experiments starting with various modified iron surfaces were recorded. Oxidation or chlorination or both are needed to control the reactivity of the iron surface. At room temperature and at 440 K, Fe(acac)$_2$ or Fe(acac)$_3$ was expected to desorb as a possible product, but were not. That is for the sputtered-cleaned iron surface that is exposed to acacH either at 440K or at room temperature, no iron-containing desorption products were observed. There was no acac (2,4-pentane dione or acetylacetone) containing products recorded,

and other acacH desorption starts at 500K. This suggests that the main pathway for acacH interaction with iron would be decomposition or desorption.
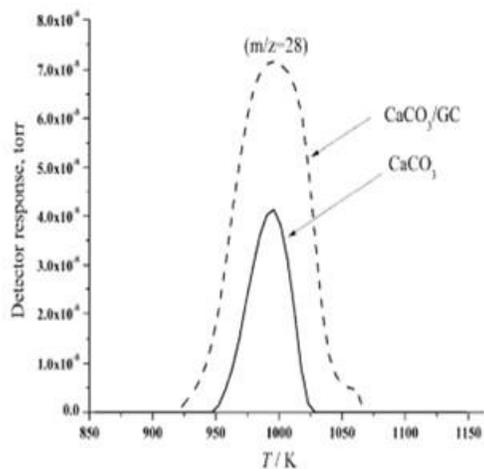

Fig 6c: Comparison of the thermal decomposition of CaCO$_3$ and CaCO$_3$/GC with respect to their TPD profile; reproduced from (Kalijadis et al., 2011)

7.0   Understanding the sequential

In Fig 7b, TPD results on the chlorinated partially oxidized surface clearly show that the TPD technique can be very useful for understanding Fe-containing products, which have several fragments containing both acac (2,4-pentane dione or acetylacetone) and Cl ligands that desorb from the surface. It was observed that the chlorinated partially oxidized iron surface exposed to acacH at 440K starts desorbing at around the temperature at which acacH is dosed initially. Also, the Fe(acac)$_3$ desorbs around the same temperature with water alongside some acacH. In Fig 7c, desorption was observed at different adsorption temperatures on the chlorinated partially oxidized iron surface exposed to acacH at room temperature. Therefore, desorption is enhanced in the order of surface oxidation, then chlorination, and finally reaction with acacH. TPD was used to explain the desorption patterns and all the possibilities associated with the thermal dry etching of iron in a two-step
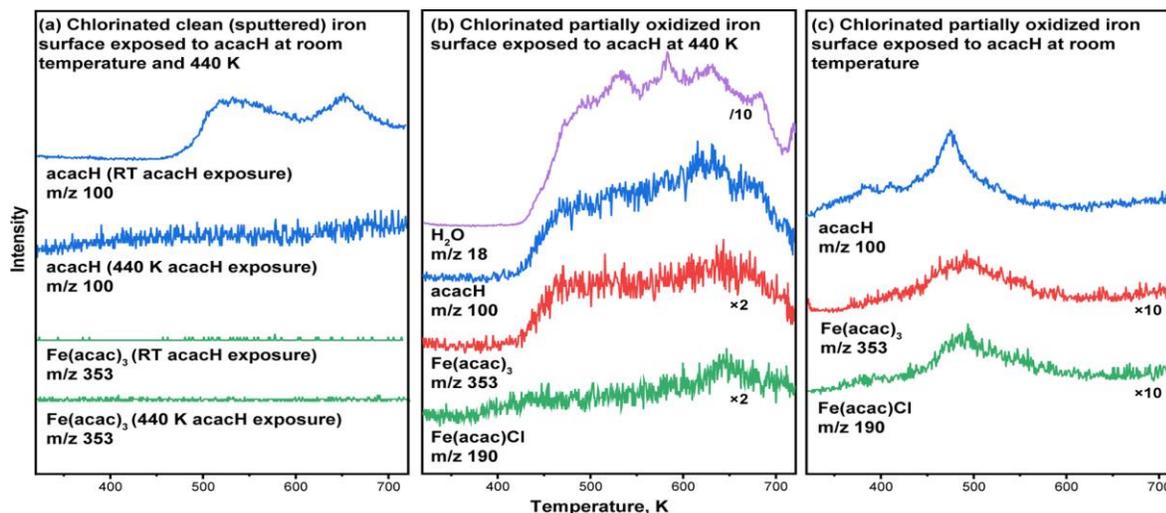
atomic layer etching process (Konh et al., 2021)

Fig 7: Temperature program desorption profile for thermal dry etching of iron in a two-step atomic layer etching process (Konh et al., 2021)

8.0   Conclusion

In conclusion, this article provides an in-depth exploration of the processes and advantages associated with temperature-programmed desorption (TPD) in the surface analysis of semiconductors and catalysts. TPD serves as a powerful and versatile tool for unravelling the intricate surface chemistry of materials, enabling researchers to gain valuable insights into various aspects of their behaviour and performance. One significant application of TPD discussed in the article is surface functional group analysis. By analyzing the desorption profiles of different functional groups, researchers can elucidate the surface composition and distribution of species, allowing for a comprehensive understanding of surface reactivity and the formation of active sites. This knowledge is crucial for optimizing the performance of semiconductors and catalysts, as well as designing new materials with enhanced properties. This article highlights the importance of system temperature characterization in TPD experiments. By precisely controlling the temperature ramping profile, researchers can

investigate the kinetics and energetics of adsorbate desorption, providing valuable information on the strength of surface interactions and the stability of adsorbates. This knowledge is essential for tailoring surface properties and designing materials with improved thermal stability and reactivity. This article also emphasizes the significance of TPD in the analysis of carbon-containing materials, which are widely employed in various industrial applications. Understanding the surface chemistry of these materials is crucial for optimizing their catalytic activity, adsorption properties, and electronic behaviour. TPD enables researchers to probe the desorption behaviour of carbon-based species, leading to insights into surface reactions, surface reconstruction, and the formation of carbon-based intermediates, all of which impact the material's performance. The article discusses the contribution of TPD to surface group characterization, group analysis, and sequential treatment of surfaces. By sequentially modifying the surface and performing TPD measurements, researchers can unravel the effects of different surface

treatments on the desorption behavior of species, shedding light on the reactivity and stability of surface functionalities. This knowledge aids in designing tailored surface modifications and optimizing the performance of materials in specific applications. In summary, this article highlights the versatility and power of TPD as a fundamental tool for surface analysis in the development of semiconductors and catalysts. By utilizing TPD techniques, researchers can delve into the intricate surface chemistry of materials, gaining valuable insights into surface functional groups, system temperature effects, oxidation and surface treatment, heat treatment, adsorption and desorption processes, thermodynamic contributions, and sequential surface modifications. These insights pave the way for optimizing material performance, improving catalytic activity, and developing advanced materials with enhanced properties for diverse industrial applications.

8.0   References

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Compliance with Ethical Standards Declarations

The authors declare that they have no conflict of interest.

Data availability

All data used in this study will be readily available to the public.

Consent for publication

Not Applicable

Availability of data and materials

The publisher has the right to make the data
Public.

Competing interests

Authors' contributions

The entire work was carried out by the author