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MASS EFFECTS ON THE SURFACE REACTION OF CHLORINE WITH CARBON

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ABSTRACT

The reaction of chlorine with carbon surfaces has been studied by thermogravimetric techniques. The carbon samples increase in mass at a rate which increases with sample mass. This effect is interpreted as being due to the adsorption of the HCl formed by the reaction of chlorine with chemically bound hydrogen.

INTRODUCTION

Thermogravimetric techniques have been used to study a large variety of phenomena, such as gas–solid reactions, thermal decomposition, phase transitions, adsorption phenomena, etc. In such studies, the interpretation of the results is frequently open to question as a very careful recognition of the many possible errors is vital, and, moreover, analysis of the effect of the experimental variables on the thermograms has to be performed. A great number of publications and papers deal with these errors, and with the analysis of the factors affecting the thermogravimetric curves [1–6]. One of these factors is sample mass. Coats and Redfern [7] have pointed out that for larger samples great temperature gradients can exist within the sample, and, for exothermic or endothermic reactions, the nominal linear temperature program is effectively altered and, also in these cases, the diffusion of reagent or product gases through the void spaces around the solid particles can be affected.

In the case of adsorption phenomena on powders, it is generally known that the sample mass affects only the rate of adsorption. The diffusion of the molecules in the free space between particles is normally the rate-controlling step [8]. Thermogravimetric curves of relative mass gain q, versus time frequently depend on sample mass, whereas the equilibrium value of the adsorbed mass usually depends only on temperature and the composition of the adsorbed gas, and is independent of the sample mass.

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In the study of the surface reaction between chlorine and sucrose char, we reported elsewhere [9] that upon reaction with chlorine at 950 ° C, the carbon samples show large mass increases. In the present paper we present new thermogravimetric measurements which show that this interaction is strongly mass dependent. We found that an increase in the sample mass not only produces the expected decrease in the reaction rate, but also an unexpected increase in q_m, the maximum value of q.

THE CHLORINE–CARBON REACTION

The reaction between chlorine and carbon has not been extensively studied. It is, however, known that the reaction is complex and may involve several different mechanisms. In a recent publication, Tobias and Soffer [10] mention that at high temperatures the reaction may involve both physical adsorption and chemisorption, reaction of the chlorine with chemibound hydrogen and diffusion in micropores. Carbon, furthermore, apparently has a catalytic activity on the dissociation of the chlorine molecules into atoms which may then be detected in the gas phase [11].

The presence of H–C bonds on the surface of carbon and graphite is unavoidable. There is hydrogen on the surface of even high purity graphites [12]. Significant quantities can still be detected after long periods of heating in a vacuum at temperatures as high as 2000 ° C [13,14]. Furthermore, it has been known that one of the mechanisms of the Cl_2–C interaction involves these superficially bound hydrogen atoms through the formation of HCl. The formation of this HCl can occur through the following reactions [10]

$$Cl_2 + H{-}C^{\star}{-}C^{\star}{-}H \rightarrow 2HCl(g) + C^{\star}{=}C^{\star} \tag{1}$$

$$Cl_2 + C^{\star}{-}H \rightarrow HCl(g) + Cl{-}C^{\star} \tag{2}$$

where the symbol $C^{\star}$ denotes a surface carbon atom.

The replacement of hydrogen by chlorine is irreversible. The adsorbed chlorine cannot be eliminated by heating alone [10].

The hydrogen content and the pore structure of any carbon depends strongly on its origin and history. The precursor and the heat treatment determine such structural properties. Marsh [15] points out that non-graphitisable carbons, which are prepared using precursors that do not traverse a fluid phase during carbonisation, usually have a microporous structure. Sucrose chars belong to this class of carbons. Sircar [16] has recently measured the micropore distribution in such chars, and found an average pore radius of 6.9 Å. Rouzad and Oberlin [17] have measured the H/C ratio in these carbons and have found that it depends strongly on the heat treatment: after vacuum degassing at 900 ° C, they found an atom ratio (H/C) of 0.09; after heating to 1500 ° C this ratio reduces to 0.01.

EXPERIMENTAL

The carbon used in this work was prepared by carbonisation of sucrose (Mallinckrodt Chemical Works). The charring was done by heating the sucrose in an argon atmosphere to 950 °C for 72 h. After milling the char, the resulting powder had a BET surface area of 17.5 m^2 g^{-1}. The gases produced during heating to 950 °C were analysed using an EMBA II (Extranuclear Laboratories) modulated beam mass spectrometer; this instrument has been described elsewhere [18].

The gases used in the study were chlorine, 99.9% purity (Indupa, Argentina) and argon, 99.99% (AGA, Argentina). Both gases were dried over H_2SO_4 and P_2O_5.

The Cl–C reaction was studied in a thermogravimetric analyser especially adapted for work with corrosive gases, described elsewhere [9]. It consists of a Cahn 2000 electrobalance, a gas line for the preparation of the gas mixtures and a data acquisition system. The experimental procedure is as follows: the samples are placed in a quartz crucible which hangs from the balance beam; they are heated and kept for 2 h at the desired temperature. Chlorine is then introduced, and mass changes and time are recorded through an interface to an IBM PC/XT computer. Measurements are corrected for apparent mass changes [9].

The gaseous species formed during the first few minutes of reaction were also determined by means of modulated beam mass spectrometer. The experimental set-up for these measurements has also been described elsewhere [11].

RESULTS

Thermogravimetry

The mass gains of the carbon samples under the action of chlorine were measured at two temperatures, 770 °C and 950 °C. The measurements were repeated for samples of different sizes at a total gas pressure of 700 Torr and a chlorine partial pressure of 490 Torr. Figure 1 shows the results for the first 150 s for three samples of 5, 14 and 25 mg. The data show that the relative mass gain, $q = (\Delta m/m_0) \times 100$ (where $\Delta m = m - m_0$ represents the mass gain and m_0 is the initial mass of the sample), strongly depends on m_0 in two different ways: the reaction rate is larger the smaller the samples; and q_m increases with m_0. The latter effect shows that the maximum observed in the q–t curves, being mass dependent, does not correspond to a thermodynamic equilibrium between the solid and the gas. At longer times than those represented in Fig. 1, under constant experimental conditions, a slow but continued mass loss sets in. Figure 2 shows q as a function of time for much

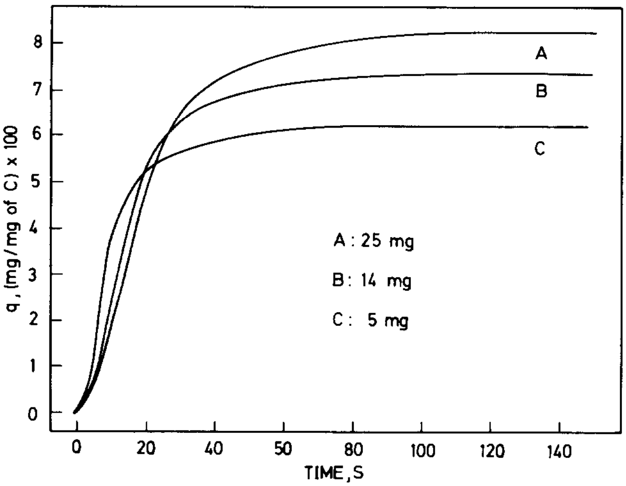

Fig. 1. Isothermal kinetics: relative mass-gain q during the first 150 s for different sample masses: A, 25 mg; B, 14 mg; C, 5 mg. Temperature, 950 ° C.

longer periods. During the first seconds the mass increases very rapidly up to the maximum value, q_m. This maximum is held for a few minutes after which a steady decreases sets in. Figure 2 also shows what happens when the chlorine flow is suddenly discontinued. It can be seen that the subsequent mass decrease is very slow. Figure 3 shows the same results at a lower temperature, 770 ° C, for two sample sizes. The behaviour of the samples is similar to that at the higher temperature. The differences are as expected: the mass gain is slower; the maximum of the curves is flatter and the

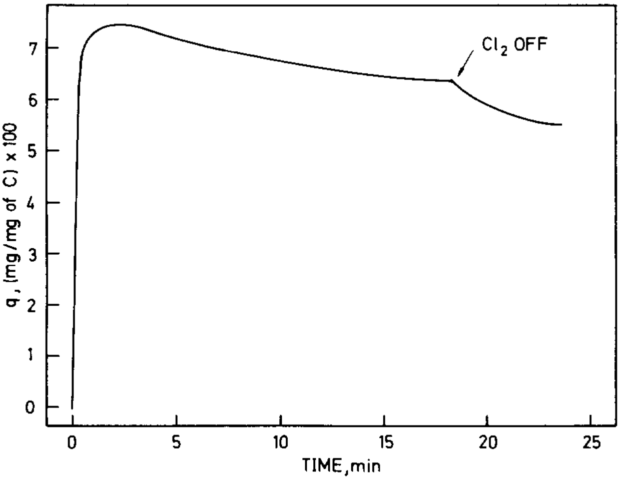

Fig. 2. Long-term isothermal variation of the relative mass gain q under constant Cl_2–Ar flow. Sample size, 14 mg; temperature, 950 ° C. The arrow indicates chlorine flow discontinuation.

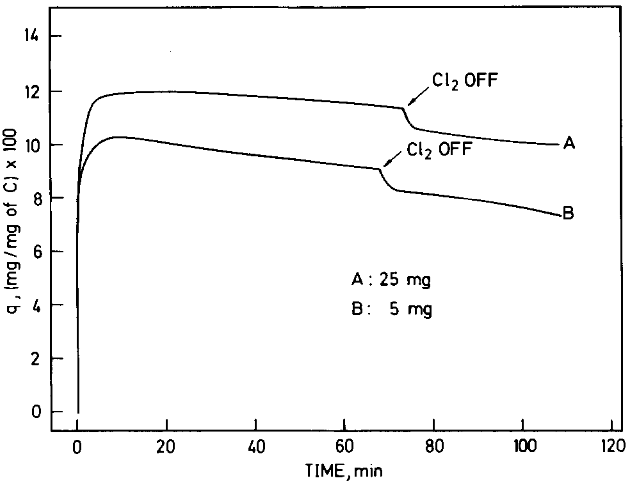

Fig. 3. Long-term isothermal variation of the relative mass gain q under constant Cl_2–Ar flow. Sample size: A, 25 mg; B, 5 mg. Temperature, 770 °C. The arrows indicate chlorine flow discontinuation.

subsequent decrease is also slower; and the absolute values of the mass gain are larger.

Mass spectrometry

The mass spectra indicate that the char, upon vacuum degassing, eliminates CO_2, CO, H_2O and H_2 which are normally chemisorbed even on high purity chars. It was also found that during the reaction with chlorine, noticeable quantities of HCl are rapidly formed. Other gases or fragments containing carbon were not detected.

DISCUSSION

In this paper we wish merely to discuss two results which by themselves show that the Cl_2–C interaction is no simple chemisorption. These are the increase of the mass gain with sample size and the excessive mass gain when compared with the BET surface area of the samples.

A simple calculation starting with the value of the BET surface area of the samples shows that if all the active sites of the carbon were occupied by chlorine, the maximum mass gain should be about 1.2% ($q = 1.2$). This value is several times smaller than those measured, as seen in the figures. This is what we mean when we say that the mass gain is excessive relative to the BET surface area.

Other cases are known where the gas uptake by a solid is larger than that expected from BET measurements. This phenomenon usually indicates that mechanisms other than normal adsorption are operating. These may be absorption, activated diffusion in micropores, or molecular sieve effects.

In the interpretation of our results, the first effect plays no role, since it is known that chlorine is not absorbed by carbon at temperatures below 1000 ° C [19]. The second mechanism, however, can be relevant, because of the microporosity of the sucrose chars.

Microporosity

Penetration of a gas into the structure of a solid can be extremely slow at 77 K (the temperature at which BET isotherms are measured). Such penetration can take hours or even days [20]. Temperature increase favours access to the internal surfaces of the micropores: by acceleration of the diffusion rate; by the opening of closed pores; or by the increase in the diameter of the channels [20]. In such cases, the gas adsorption by a microporous solid is favoured by temperature increases. In the Cl_2–C system, a micropore diffusion effect may occur. The adsorption at high temperatures may occur by means of the access of chlorine to micropores that are not accesible to N_2 at 77 K. Chlorine adsorption is further favoured relative to N_2 because its effective molecular diameter is smaller [10]. Chlorine can thus enter pores which are inaccessible to nitrogen.

The adsorption of chlorine in micropores may be important and may lead to a mass gain larger than that expected on the grounds of BET measurements. Nevertheless, we shall see presently that two other mechanisms may make an important contribution to the mass gain and permit an explanation of the observed sample mass effect.

Formation and chemisorption of HCl

It is known that the thermal treatment effected on the char eliminates most of the chemisorbed oxygen [10] as CO and CO_2 [21]. A significant amount of hydrogen remains, however, which cannot be removed in this way. This remaining hydrogen reacts with chlorine to form HCl. Mass spectra indicate that this HCl forms very quickly during the first phase of the reaction. As mentioned above, HCl can form by either of the mechanisms, eqns. (1) and (2), given above. Reaction (2) leads to a mass increase because H atoms are replaced by Cl atoms. The amount of this mass gain is thus independent of BET surface area and depends only on the availability of H atoms on the surface.

A third mechanism leading to mass gain might be associated with the adsorption of HCl. In fact, the adsorption of gaseous intermediates produced by gas–solid surface reactions may be significant and may induce errors in the analysis of surface studies [22]. Recent investigations have shown that HCl is rapidly and irreversibly adsorbed on carbon at high temperatures [23,24]. In the present work, we have not tried to determine the extent of this adsorption, but we estimate it to be important enough to account for the observed mass effects. The partial pressure of HCl in the pores might be quite high. It has been reported that gaseous intermediates, which originate in pores or between the particles, may develop pressures above 1 atm [25]. Other studies have shown that the polar character of the HCl molecule ($\mu = 1$ Debye) favours its rapid adsorption on microporous carbon, entering pores not accounted for by BET data [12]. This is because of the highly polar nature of the solid–gas attraction forces in the micropores.

Effect of sample size

Mass effects on the residence time of gaseous intermediates have been reported for several reactions, such as the thermal decomposition of $CaCO_3$ [26] and the reductions of metal oxides by carbon [27]. The larger the sample mass the longer the diffusion path of the product gas. In our system, the HCl that is formed in reactions (1) and (2) can suffer varied fates. It can be instantly adsorbed on the carbon surface; it may penetrate into the micropores; or diffuse towards the exterior of the sample and thus be removed from the system by the Ar–Cl_2 gas flow. Increasing the sample mass increases the diffusion path of HCl, and consequently the partial pressure is more likely to build up and hence raise the adsorption. This mass effect can explain the increase in q_m with m_0 shown in Figs. 1 and 3.

Desorption of HCl and Cl_2

For the measurements shown in Figs. 2 and 3, it can be seen that q, after reaching the maximum q_m, begins slowly to decrease. This mass loss may be because of HCl desorption. As the pressure of HCl in the sample pores decreases by diffusion into the surrounding atmosphere, HCl begins to desorb. Measurements show that this desorption is quite slow, as it should be if chemisorption is strong [23]. The decrease is faster at the higher temperature. Stopping the chlorine flow causes an immediate small drop in the q values, as shown by the arrows on the figures. This drop may be related to some reversible, high-temperature chemisorption [24]. The slow decrease that follows is related to the irreversibility of the chlorine chemisorption and the C–Cl bonds formed by reaction (2).

CONCLUSIONS

The interaction between chlorine and carbon is complex and involves several mechanisms: chemisorption, micropore adsorption and HCl formation. The excessive mass gain, relative to BET surface area, can be explained by the substitution of hydrogen by chlorine and by the adsorption of chlorine and HCl in the micropores. The mass effect results essentially from the adsorption of HCl in the micropores of the carbon particles. The magnitude of the HCl adsorption increases with the residence time of HCl in the micropores.

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