

Effect of the reaction temperature on the chlorination of a $\text{Fe}_2\text{O}_3\text{-TiO}_2\text{-C}$ mixture

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Received 11 June 1996; received in revised form 18 February 1997; accepted 5 March 1997

Abstract

The intrinsic kinetics of the chlorination of an hematite–titania–carbon mixture was studied by means of scanning electron microscopy and isothermal and non-isothermal thermogravimetry between 580 and 1123 K. It was observed that various reactions take place simultaneously and that a carbon surface deactivation occurs between 733 and 820 K. The latter was attributed to chemisorption of iron chlorides on the carbon surface. © 1997 Elsevier Science B.V.

Keywords: Chlorination; Hematite; Heterogeneous kinetics; Mechanism; Titania

1. Introduction

The chlorination of raw metallic oxides to produce the corresponding chlorides is applied in the extractive metallurgy of refractory metals [1–3]. Refractory oxides chlorination is thermodynamically favorable provided that it occurs in the presence of a reducing agent. When carbon is used, chlorination reaction is called carbochlorination. The process is applied for large scale production of Zr, Ti and Be from raw oxides.

The thermochemistry of carbochlorination of oxide mixtures is fairly well understood and thermodynamic data are available. However, the selectivity and the intrinsic kinetics of these reactions have not been extensively studied [4–7]. Selectivity is based upon the different chloride-forming affinity of oxides composing complex minerals. We recently have reported a study on the selectivity of the carbochlorination of a

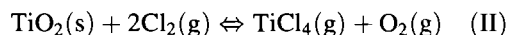
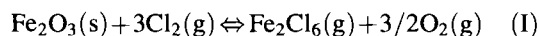
$\text{TiO}_2\text{-FeO}_3$ mixture [6]. Hematite was selectively converted into the respective chloride between 820 and 1033 K and both oxides were chlorinated simultaneously at higher temperatures [6].

The study of the carbochlorination of the $\text{Fe}_2\text{O}_3\text{-TiO}_2$ system presents both an academic and technological interest. The first is based upon the different chloride-forming affinity of each oxides and in the lack of kinetic information available in the literature. The second one takes into account the fact that the $\text{Fe}_2\text{O}_3\text{-TiO}_2$ system is found in minerals. For instance ilmenite, oxidized and leached during weathering contains up to 70% of TiO_2 and 30% of hematite [8]. Hence, a selective carbochlorination of the hematite at low temperatures and a subsequent TiO_2 carbochlorination at higher temperatures might be a suitable procedure for titanium extraction. Consequently, we present in this paper a study of the intrinsic kinetics of the carbochlorination of a $\text{Fe}_2\text{O}_3\text{-TiO}_2$ mixture. The occurrence of simultaneous reactions and the carbochlorination of each oxide are discussed in detail.

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1.1. Thermodynamic and kinetic aspects of carbochlorination reactions

Hematite and titania react with chlorine to form FeCl_3 , Fe_2Cl_6 and TiCl_4 , which are gases within the temperature range investigated in this study, that is, from 580 to 1123 K. However, the amount of $\text{FeCl}_3(\text{g})$ in equilibrium with the Fe_2Cl_6 is small at low temperatures [9,10]. Therefore the reactions of alone chlorine with these oxides, called direct-chlorinations, are well represented by:



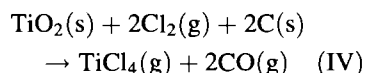
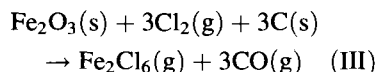
The corresponding standard Gibbs energy changes ($\Delta_r G^0$) per mole of chlorine are [11]:

$$\begin{aligned} \Delta_r G^0(\text{I})(\text{kJ mol}^{-1}) \\ = -0.02342 T + 53.27 \quad (500\text{--}1400 \text{ K}) \end{aligned}$$

$$\begin{aligned} \Delta_r G^0(\text{II})(\text{kJ mol}^{-1}) \\ = -0.02887 T + 85.97 \quad (500\text{--}1400 \text{ K}) \end{aligned}$$

where T represents absolute temperature. The lower value of $\Delta_r G^0$ (I) indicates the greater reactivity of the Fe_2O_3 .

When the chlorination of Fe_2O_3 or TiO_2 is performed in the presence of carbon, the reaction is called carbochlorination. The stoichiometry of the carbochlorination reactions is not well established because reaction products contain $\text{CO}_2(\text{g})$ and $\text{CO}(\text{g})$ whose amounts depend on the experimental conditions [12–15]. However, $\text{CO}(\text{g})$ is the principal co-product of the reaction [13,16,17], as supported by thermodynamic [16,17] and kinetics [12,13] results. In fact, it has been reported that the concentration ratio of CO_2 to CO can become lower than 0.04 for the carbochlorination of TiO_2 [16] or lower than 0.1 for carbochlorination of ZrO_2 [13,17]. For this reason, in a first approximation, the carbochlorination and the respective values of $\Delta_r G^0$ [11] can be represented by the following equations:



$$\begin{aligned} \Delta_r G^0(\text{III})(\text{kJ mol}^{-1}) \\ = -0.1120 T - 58.174 \quad (500\text{--}1400 \text{ K}) \end{aligned}$$

$$\begin{aligned} \Delta_r G^0(\text{IV})(\text{kJ mol}^{-1}) \\ = -0.1157 T - 25.48 \quad (500\text{--}1400 \text{ K}) \end{aligned}$$

The formation of both chlorides is thermodynamically favorable in the presence of carbon.

The intrinsic kinetics of carbochlorinations of pure oxides [12–14,18–20] and oxide mixtures [3,5,7] is not known. Most of the authors have suggested that carbochlorinations occur by means of gaseous intermediates formed at the carbon surface [12–14,18–20]. The proposed reaction intermediates are phosgene [18], free radicals [21] and chlorine atoms [13,14,19]. The existence of phosgene (COCl_2) is only possible at low temperatures since it dissociates into $\text{Cl}_2(\text{g})$ and $\text{CO}(\text{g})$ above 900 K. On the other hand, the formation of free radicals and chlorine atoms is possible at high temperatures [22]. Phosgene may be formed by reaction of $\text{Cl}_2(\text{g})$ with $\text{CO}(\text{g})$ adsorbed on carbon [18,23,24] whereas the chlorine atoms may be formed into the gaseous phase by the dissociation of Cl_2 on a carbon surface [22].

Carbon intervenes in the carbochlorination of a $\text{Fe}_2\text{O}_3\text{--TiO}_2$ mixture in three ways. First it eliminates the liberated oxygen in the direct-chlorination (equations I and II) through the formation of $\text{CO}(\text{g})$, avoiding the reverse reactions. Secondly, carbon plays a kinetic role (equations III and IV) since it forms the reaction intermediates into the gas phase above proposed, which act as chlorinating agents of the oxides. Thirdly, chlorine interacts with carbon through a complex mechanism that involves an exchange reaction with hydrogen present in the carbon surface [25,26]. This reaction, called $\text{Cl}_2\text{--C}$ reaction, was studied by thermogravimetry by using the same carbon of this research, as recently published [25]. The mass increases about 11% of the initial mass at 1000 K. This reaction, irreversible and thermally activated, involves the formation of $\text{HCl}(\text{g})$ into the gaseous phase [25,26].

Reactions of hematite with Cl_2 [27] and COCl_2 [27,28] have also been studied. In this case thermogravimetry [27] showed only mass loss during the chlorination process. The starting reaction temperatures of hematite with COCl_2 [27,28] and Cl_2 [27] were 550 and 800 K, respectively.

2. Experimental

2.1. Materials

Argon, 99.99% purity (AGA, Argentina), and Cl_2 , 99.8% purity (Indupa, Argentina) were used in this study. Powdered materials were Fe_2O_3 (Spex Industries, Inc., USA), TiO_2 (Mallinckrodt Chemical Works, USA) and carbon, which was obtained by thermal decomposition of sucrose (Mallinckrodt Chemical Works). This carbon powder was previously characterized [13,19]. Only CO , CO_2 , O_2 and H_2 are evolved during heating in vacuum up to 1273 K [13]. The hydrogen content of this carbon was not determined but it is known that sucrose carbon can have a H/C ratio of 0.09 at 1173 K [29]. The BET surface area of TiO_2 , Fe_2O_3 and C were 3.0; 9.4 and $17.5 \text{ m}^2 \text{ g}^{-1}$, respectively. Carbon powder [19] is composed of particles smaller than $200 \mu\text{m}$ with sharp edges and stepped surface as shown in Fig. 1. Titanium dioxide, Fe_2O_3 and a sample of TiO_2 (70 wt%)- Fe_2O_3 (30 wt%) were respectively mixed with carbon to obtain the following mixtures: TiO_2 (70 wt%)-C(30 wt%); TiO_2 (30 wt%)-C(70 wt%); Fe_2O_3 (70 wt%)-C(30 wt%); Fe_2O_3 (50 wt%)-C(50 wt%) and TiO_2 (49 wt%)- Fe_2O_3 (21 wt%)-C(30 wt%).

2.2. Procedure

Mass changes occurring during the chlorination of Fe_2O_3 , C, Fe_2O_3 -C, TiO_2 -C and TiO_2 - Fe_2O_3 -C were measured using a thermogravimetric analyzer (TGA), which has been described elsewhere [30]. It consists of an electrobalance (Model 2000, Cahn Instruments Inc.) suitable for working with corrosive atmospheres, a gas line, and a data acquisition system. This experimental set-up has a sensitivity of $\pm 5 \mu\text{g}$ while operating at 1373 K under a gas flowrate of 9 l h^{-1} , measured at normal temperature and pressure.

Samples of about 10 mg were placed in a quartz crucible and heated under flowing Ar to the desired temperature. Non-isothermal and isothermal measurements were performed. In non-isothermal experiments chlorine gas was introduced ($p_{\text{Cl}_2} = 33 \text{ kPa}$) at 598 K and the temperature was then increased in the Cl_2 flow at a linear rate of 2.7 K min^{-1} while measuring mass changes continuously. In the case of isothermal measurements, samples were heated in flowing Ar for 2 h at the reaction temperature. No mass loss was observed when samples were heated in argon. Chlorine was then introduced and mass changes were measured. In both cases the apparent mass changes were taken into account to correct the experimental



Fig. 1. Morphological aspect of unreacted carbon particles.

data. The reactions were stopped at selected conversions and a small fraction of each sample was examined by scanning electron microscopy (SEM) (SEM 515, Philips Electronic Instruments). Conversions at which reactions were stopped and solids analyzed by SEM are represented by the symbol • in the Figures showing the thermogravimetric data.

For convenience, mass changes were plotted as $\Delta M/M_i$ (the relation mass change, compared to the total initial mass) and $\Delta m/m_i$ (the relative mass change of the oxide compared to the initial oxide mass) ratios, which represent fraction mass change of mixture and oxide, respectively. The values of Δm were calculated from ΔM , according to the stoichiometry given in the previous chemical equations.

3. Results and discussion

3.1. Direct-chlorination and carbochlorination of hematite: Effect of the reaction temperature

Thermogravimetric curves obtained in the non-isothermal chlorination of carbon, Fe_2O_3 and Fe_2O_3 -C mixtures are shown in Fig. 2. Curve 'a' shows that C increases its mass when chlorine is introduced at 598 K. The mass gain which increases as the temperature raised, is due to the substitution of hydrogen by chlorine on the carbon surface, as demonstrated in previous studies [25,26]. This mass gain contrasts with

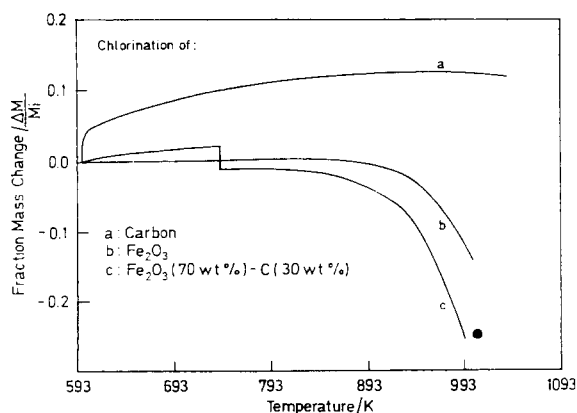


Fig. 2. Non-isothermal fraction mass changes involved in the chlorination of C, Fe_2O_3 and $\text{Fe}_2\text{O}_3(70 \text{ wt}\%)\text{-C}(30 \text{ wt}\%)$.

the mass loss expected for reactions (I) to (IV). In fact, mass loss shown in curve 'b' confirms that the $\text{Fe}_2\text{O}_3\text{-Cl}_2$ reaction only involves the formation of gaseous products. Direct-chlorination starts above 880 K, which agrees quite well with the starting reaction temperature observed in similar experimental conditions [27].

The non-isothermal chlorination of the hematite-carbon mixture is illustrated in curve 'c' of Fig. 2. Mass gain takes place as the temperature increases, but at 733 K a sudden mass loss of 4.5 wt% occurs. Then, negligible mass changes are observed in a temperature range of about 90 degrees. Above 820 K a continuous mass loss takes place, which is certainly due to the formation of gaseous products in accordance with chemical equation (III). On the other hand, the sharp mass loss observed at 733 K and the subsequent negligible mass changes observed between 733 and 820 K are not easy to understand. However, a comparison with curves 'a' and 'b' in which no mass loss is observed below 880 K (curve 'b') allows to conclude that mass loss at 733 K in curve 'c' must be also attributed to the beginning of the carbochlorination reaction of hematite. Based on the current hypothesis that the kinetic role of carbon is the formation of gaseous intermediates [14–18,20,25,30], we assume that mass loss at 733 K is due to the reaction of these species with the Fe_2O_3 . The identity of these intermediates and the physical meaning of the negligible mass changes observed between 733 and 820 K will be discussed later in the light of additional results.

A comparison of curves 'b' and 'c' also indicates that the hematite can be converted into the $\text{Fe}_2\text{Cl}_6(\text{g})$ in two ways above 880 K. The first is the direct reaction between Fe_2O_3 and Cl_2 , that is, direct-chlorination as shown by reaction (I) in which O_2 is also liberated. The second alternative, which involves the formation of gaseous reaction intermediates at the carbon surface [12–14,18–20], takes place by means of carbochlorination, in accordance with reaction (III).

Fig. 3 illustrates the mass loss involved in the isothermal chlorination of a $\text{Fe}_2\text{O}_3\text{-C}$ mixture at various temperatures. The mass loss rate increases as the reaction temperature rises, from 923 to 1123 K. The mass loss is attributed to both chlorination (reaction (I)) and carbochlorination (reaction (III)) of Fe_2O_3 , as supported by the fact that both reaction occur above 880 K (curve 'b' and 'c' of Fig. 2). The analysis of

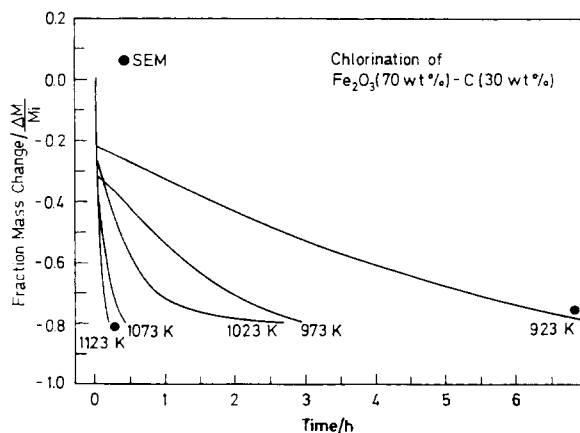


Fig. 3. Isothermal fraction mass loss corresponding to the chlorination of $\text{Fe}_2\text{O}_3\text{-C}$ (30%) at several temperatures.

chemical attack of carbon particles at 923 and 1123 K, both at a conversion of 0.8, is shown in Fig. 4(a) and (b), respectively. A comparison of Fig. 4(a) with Fig. 1 reveals a chemical attack characterized by pores, channels and cracks. The chemical attack is very similar to that observed in carbon particles when a $\text{ZrO}_2\text{-C}$ mixture was chlorinated [19]. From this comparison we assumed that Fig. 4(a) shows the chemical attack generated by the carbochlorination reaction. In Fig. 4(b) is visible stronger and more aggressive chemical attack than that observed in Fig. 4(a). Hence, at high temperature, the chemical attack probably is a consequence of the oxygen produced in the direct-chlorination of Fe_2O_3 (equation I).

3.2. Effect of the carbon fraction on the non-isothermal chlorination of $\text{Fe}_2\text{O}_3\text{-C}$ and $\text{TiO}_2\text{-C}$ mixtures

The effect of the carbon fraction on non-isothermal chlorinations of $\text{Fe}_2\text{O}_3\text{-C}$ and $\text{TiO}_2\text{-C}$ mixtures is shown in Fig. 5. The chlorination of $\text{Fe}_2\text{O}_3(70 \text{ wt}\%)\text{-C}$ (30 wt%) and $\text{Fe}_2\text{O}_3(50 \text{ wt}\%)\text{-C}$ (50 wt%) shows mass gain due to the $\text{Cl}_2\text{-C}$ reaction, then a sudden mass loss at 733 K, followed by a region until 820 K in which no mass loss are observed, and finally a continuous mass loss. The overall behavior is analogous to that shown in Fig. 2. Chlorination of $\text{TiO}_2(70 \text{ wt}\%)\text{-C}$ (30 wt%) and $\text{TiO}_2(30 \text{ wt}\%)\text{-C}$ (70 wt%) mixtures shows a similar qualitative behavior until 733 K. At this temperature a sudden mass

loss also occurs, but it continues as the temperature increases.

Fig. 5 shows that mass loss at 733 K increases as carbon fraction increases too. The mass loss is about 4% and 7% of hematite, for 30 and 50 wt% of carbon, respectively, and 2% and 2.3% of titania, for 30 and 70 wt% of carbon, respectively. The effect of carbon fraction on the oxides conversion is more evident at high temperatures, as calculated from curves of Fig. 5. After subtracting the mass gain expected for the $\text{Cl}_2\text{-C}$ reaction from mass changes involved in oxide carbochlorination, a Fe_2O_3 conversion of 11 and 23.5% at 903 K results for 30 and 50 wt% of carbon, respectively. At the same temperature, the conversion of TiO_2 is 49 and 81% for 30 and 70 wt% of carbon, respectively. Hence, two conclusion are obtained. Firstly, an increase in the carbon fraction leads to a greater conversion of both TiO_2 and Fe_2O_3 at each temperature. Secondly, a greater conversion degree for TiO_2 than for Fe_2O_3 is observed, which is in opposition to the different chloride-forming affinity of both oxides. This apparent contradiction will be explained later when Fig. 7 is discussed.

Morphological analysis of carbon particles were performed for conversions indicated in Fig. 5. In the chlorination of $\text{Fe}_2\text{O}_3\text{-C}$, the carbon particles show channelling and cavities similar to those shown in Fig. 4(a). In the TiO_2 carbochlorination, carbon particles were chemically attacked as shown in Fig. 6. We notice channellings and localized corrosion, which are very similar to those seen in Fig. 4(a) and those reported in ZrO_2 carbochlorination [19]. Since the chlorination of both $\text{ZrO}_2\text{-C}$ and $\text{TiO}_2\text{-C}$ mixtures involves only carbochlorination, morphological changes revealed in Fig. 4(a) are primary generated by the hematite carbochlorination. Consequently Fig. 4(b) must be interpreted as showing the chemical attack generated by the corresponding direct-chlorination of Fe_2O_3 (reaction I), as indicated above.

3.3. An approach to the intrinsic kinetics of the non-isothermal chlorination of a Fe_2O_3 (21 wt%)- TiO_2 (49 wt%)-C(30 wt%) mixture

The mass loss involved in the non-isothermal chlorination of $\text{Fe}_2\text{O}_3(21 \text{ wt}\%)\text{-TiO}_2(49 \text{ wt}\%)\text{-C}(30 \text{ wt}\%)\text{-C}$ mixture between about 700 and 943 K is shown in curve 'a' of Fig. 7. It shows a sudden mass loss, about

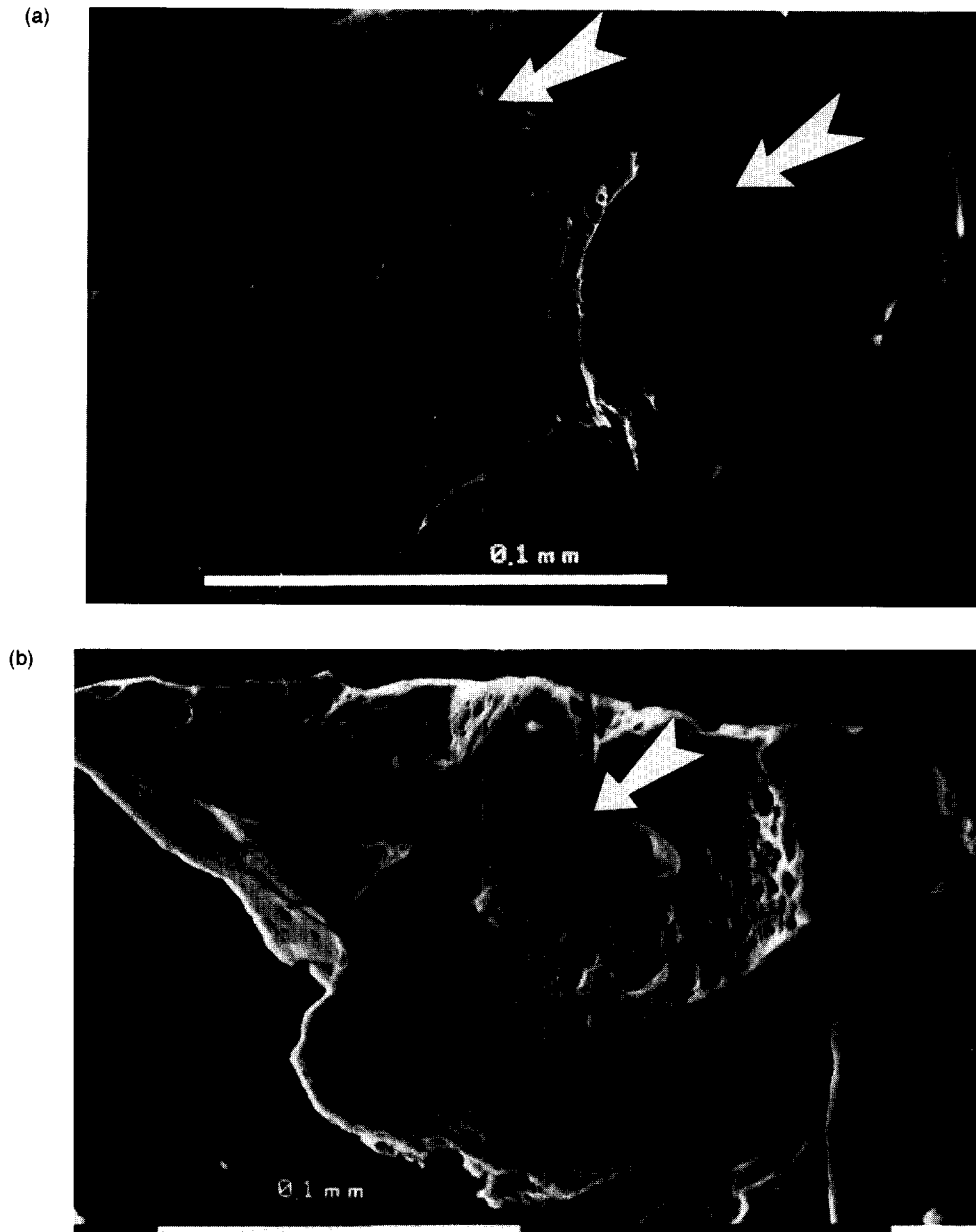


Fig. 4. (a) Typical chemical attack of carbon particles during the chlorination of $\text{Fe}_2\text{O}_3\text{-C}$ mixtures. The carbon particle corresponds to a sample with a conversion of 0.8 at 923 K. Arrows show channeling and pores. (b) Chemical attack of carbon particles during the chlorination of $\text{Fe}_2\text{O}_3\text{-C}$ mixtures at 1123 K. Arrow indicates a big channeling.

1 wt%, at 733 K and a continuous mass loss above 820 K. No mass loss was observed between 733 and 820 K. Mass loss above 820 K is due to the formation of gaseous products in accordance with reactions (I),

(III) and (IV), since the chlorination of a $\text{Fe}_2\text{O}_3(21 \text{ wt}\%)\text{-TiO}_2(49 \text{ wt}\%)\text{-C}(30 \text{ wt}\%)$ mixture involves the direct-chlorination of Fe_2O_3 and the carbochlorination of Fe_2O_3 and TiO_2 .

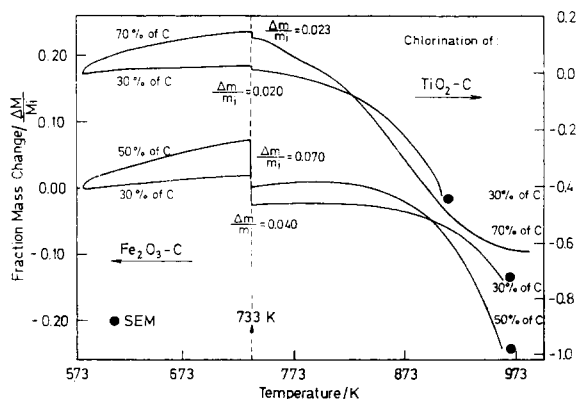


Fig. 5. Non-isothermal chlorinations of $\text{Fe}_2\text{O}_3\text{-C}$ and $\text{TiO}_2\text{-C}$ mixtures at two carbon fractions.

The continuous mass loss corresponding to the chlorination of the $\text{Fe}_2\text{O}_3(70 \text{ wt}\%)\text{-C}(30 \text{ wt}\%)$ mixture (curve 'b') starts at the same temperature as $\text{Fe}_2\text{O}_3(21 \text{ wt}\%)\text{-TiO}_2(49 \text{ wt}\%)\text{-C}(30 \text{ wt}\%)$, i.e. 820 K. In opposition, the continuous mass loss, corresponding to chlorination of the thermodynamically less reactive $\text{TiO}_2\text{-C}$ mixture, curve 'c', begins at 733 K. Hence, TiO_2 in the presence of carbon reacts

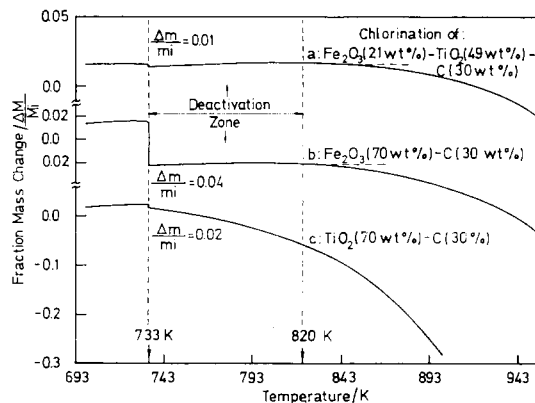


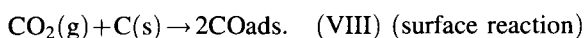
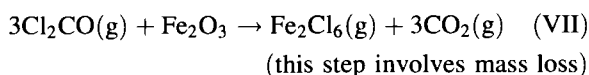
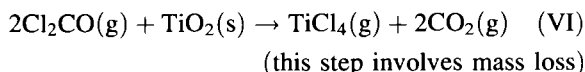
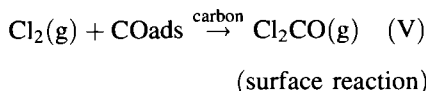
Fig. 7. Non-isothermal chlorination of $\text{Fe}_2\text{O}_3(21 \text{ wt}\%)\text{-TiO}_2(49 \text{ wt}\%)\text{-C}(30 \text{ wt}\%)$; $\text{Fe}_2\text{O}_3(70 \text{ wt}\%)\text{-C}(30 \text{ wt}\%)$ and $\text{TiO}_2(70 \text{ wt}\%)\text{-C}(30 \text{ wt}\%)$ mixtures between 693 and 943 K. Between 733 and 820 K a deactivation zone of the carbon in the $\text{Fe}_2\text{O}_3\text{-C}$ and $\text{Fe}_2\text{O}_3\text{-TiO}_2\text{-C}$ mixtures is indicated.

with chlorine above 733 K to produce TiCl_4 and CO in accordance with reaction (IV). This reactivity of TiO_2 contrasts with the fact that it does not react with chlorine when carbon and hematite are present, as shown in curve 'a'. The comparison between the three curves allows one to distinguish two kinetic features:



Fig. 6. Chemical attack of carbon particles during the chlorination of a $\text{TiO}_2\text{-C}$ mixture at 910 K.

the sudden mass loss at 733 K, which is common in the three curves, and the 'passivation zone' between 733 and 820 K observed in curve 'a' and 'b', in which mass loss should be expected. To interpret this mass loss at 733 K we must consider that the three mixtures have in common the presence of carbon and that the mass loss at 733 K is proportional to the carbon fraction, as shown in Fig. 5. Both features are in agreement with the role of carbon in carbochlorinations: to produce gaseous intermediates of high reactivity. Thus, a fast desorption of active species from carbon surfaces followed by a reaction with oxides to form gaseous chlorides might be the reason for the rapid mass loss at 733 K. The intermediates proposed in the literature have been phosgene, free radicals and chlorine atoms, as indicated earlier [12–14,18–20]. In this study, phosgene might be formed on the carbon surface at 733 K by reaction of Cl_2 with CO adsorbed on carbon [6]. Considering that CO is a common species adsorbed on carbon [25,31] and that the carbon used in this study eliminates $\text{CO}(\text{g})$ on heating until at least 1000 K [13,25], the mass loss observed at 733 K can be interpreted by the following reaction scheme:



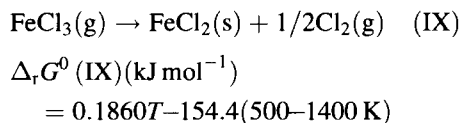
where COads represents CO adsorbed on the carbon surface. Thus, reaction (V) represents the formation and fast desorption of Cl_2CO at 733 K, which is supported by the fact that one procedure of phosgene synthesis is the reaction of Cl_2 with CO in the presence of carbon [23,24]. The sudden mass loss at 733 K might be attributed to the fast reactions (VI) and (VII), which progress with mass loss. This is consistent with the fact that Cl_2CO reacts rapidly with both oxides even at low temperature, as reported [27,28]. Reaction (VIII) implies that CO_2 formed in reaction (VI) and (VII) may partially react with carbon and regenerating CO adsorbed to form more Cl_2CO , in accordance with reaction (V). The foregoing mechanism also agrees

with assumptions of previous authors [18]. More details about this mechanism have been given elsewhere [6]. It is important to indicate that species that might act as reducing or chlorinating agents and that generally are eliminated by carbon in the presence of chlorine such as hydrocarbons, hydrogen and HCl were not taken into account by us to explain mass loss at 733 K by the following reasons: (a) hydrocarbons have not been observed in the sucrose carbon used in this study, as previously reported [13]; (b) hydrogen, which is certainly eliminated during heating does not react with TiO_2 at low temperature [11] and there is no evidence that allows to consider hydrogen as a gaseous intermediate in carbochlorination reactions; (c) HCl, which is formed in the $\text{Cl}_2\text{-C}$ reaction [25,26], does not react with TiO_2 since the reaction is thermodynamically unfavorable [11]. Moreover, other interpretations on the nature of the mass loss at 733 K such as direct-chlorination of oxides or elimination of spurious gases adsorbed on carbon surface were ruled out based on curves 'a' and 'b' of Fig. 2, in which no mass loss was observed at that temperature.

3.4. Deactivation zone

The TiO_2 carbochlorination progresses continuously above 733 K (curve 'c', Fig. 7) whereas the Fe_2O_3 mass loss is negligible between 733 and 820 K (curve 'b', Fig. 7). This contrasts with the fact that the chlorine-reactive of Fe_2O_3 is greater than that of TiO_2 . Moreover, a comparison between curve 'a' and 'c' indicates that the TiO_2 carbochlorination does not take place in the same temperature range (733–820 K) when it is mixed with hematite. Consequently a deactivation of carbon surface takes place when carbochlorination is performed in the presence of Fe_2O_3 . Poisoning of the carbon surface by chemisorption of gaseous products on the active sites is a rather common feature in solid–gas reactions [32,33]. Considering this hypothesis, poisoning of active sites of the carbon by chemisorption of $\text{Fe}_2\text{Cl}_6(\text{g})$ or deposition of $\text{FeCl}_2(\text{s})$ on the carbon surface might take place after the mass loss at 733 K. The first alternative is logically proposed from the fact $\text{Fe}_2\text{Cl}_6(\text{g})$ is produced in reaction (VII). The second one arises from the fact that small amounts of $\text{FeCl}_3(\text{g})$ are in equilibrium with $\text{Fe}_2\text{Cl}_6(\text{g})$ at 733 K [9,10]. The $\text{FeCl}_3(\text{g})$ species may

produce $\text{FeCl}_2(\text{s})$ on the carbon surface in accordance with the following reaction:



At 733 K the $\Delta_r G^0$ (IX) is negative, viz. $\Delta_r G^0$ (VII) = -18 kJ mol^{-1} . Moreover the reaction is probably kinetically favored on the carbon surface since the carbon has a strong affinity for Cl_2 . A decrease in the Cl_2 concentration might shift the reaction towards the formation of $\text{FeCl}_2(\text{s})$. Reaction (IX) is also supported by a study of the equilibrium composition based on a free enthalpy minimization program in which the formation of $\text{FeCl}_2(\text{s})$ in the presence of phosgene was demonstrated [28]. Therefore, both iron chlorides may adsorb on active sites of the carbon. However, the deactivation is not irreversible with the temperature and above 820 K the mass loss corresponding the carbochlorination started, as indicated by curve 'a' and 'b' (Fig. 7).

4. Conclusions

The chlorination of hematite-titania-carbon is very complex and involves the occurrence of four overall reactions which predominate in different experimental conditions: Cl_2 -C reaction, chlorination of Fe_2O_3 and carbochlorination of Fe_2O_3 and TiO_2 . The independent study of the intrinsic kinetics of each reaction would help to understand the reaction path involved in the chlorination of the mixture. The chemical activity of the carbon surface is largely decreased between 733 and 820 K when iron chlorides are formed. To determine the mechanism of deactivation it would be necessary to study the chemisorption of iron chlorides on carbon.

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