Thermochimica Acta 509 (2010) 100–110

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Carbochlorination of yttrium oxide

J.P. Gaviría [a,b,*], A.E. Bohé [a,b,c]

[a] División Cinética Química - Complejo Tecnológico Pilcaniyeu, Centro Atómico Bariloche - Comisión Nacional de Energía Atómica, Av. Bustillo km 9500 (8400), S.C. de Bariloche, Río Negro, Argentina
[b] Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina
[c] Centro Regional Universitario Bariloche, Universidad Nacional del Comahue, Argentina

ARTICLE INFO

Article history:
Received 31 March 2010
Received in revised form 4 June 2010
Accepted 9 June 2010
Available online 16 June 2010

Keywords:
Yttrium oxide
Carbochlorination
Yttrium oxychloride
Carbon–chlorine interaction
YCl_3 evaporation

ABSTRACT

The reaction of chlorination of a mixture composed by Y_2O_3 and sucrose carbon was studied by thermogravimetry over a temperature range of 550–950 °C. The reaction proceeds through several successive stages. The first of them is the formation of solid yttrium oxychloride (YOCl) and subsequently the YOCl is carbochlorinated to produce YCl_3 (solid or liquid, depending on the temperature) in two stages. The stoichiometries of the first stage and the global reaction were estimated by mass balances, taking into account the chlorine adsorbed by the remainder carbon. The results showed that the reactions involved progress with the formation of CO_2 and CO in the temperature range of 600–775 °C. The interaction between sucrose carbon and chlorine was analyzed by thermogravimetry in order to quantify the amount of chlorine which is adsorbed on its surface. It was studied the effect of the temperature and initial mass of carbon. The morphological analysis performed by SEM of partially reacted samples showed that the formation of YOCl proceeds through a mechanism of nucleation and growth. For temperatures above 715 °C the final product of the carbochlorination is liquid YCl_3, whose evaporation is observed in the thermogravimetry. The evaporation kinetics was analyzed in argon atmosphere and from the thermogravimetric curves was determined a value of 250 kJ/mol for the heat of evaporation of YCl_3. This value is consistent with a partial dimerization of the gaseous chloride.

1. Introduction

The carbochlorination of metallic oxides is a very important process in the industrial production of pure metals. There are many metallic oxides that can be transformed to metals through a process which consist of three stages [1–3]. In the first, the carbochlorination stage, the oxide reacts with chlorine in presence the carbon to produce the metallic chloride. Subsequently, the metal is obtained from the reduction of the chloride. Finally, the metallic sponge is purified by high temperature vacuum distillation.

Reductant species like carbon or carbon monoxide decrease the potential of oxygen, favoring the formation of the chloride. Carbon has catalytic activity sites where it is possible the formation of highly reactive gas intermediates, such as monoatomic chlorine ($Cl^\bullet$) [4,5], phosgene ($COCl_2$) [6] or oxychlorides [7]. Most of the authors propose that the carbochlorination reaction happens through gas intermediates. Bergholm [8] and Barin and Schuler [4] demonstrated that the direct contact between oxide and carbon particles is not necessary for the progress of the reaction. Several authors propose that $Cl^\bullet$ is the most probable intermediate; Barin found that the kinetic effect of the carbon in the carbochlorination of TiO_2 disappears when the distance between the particles of oxide and carbon is higher than the mean free path of $Cl^\bullet$. Amorebieta and Colussi [9] and Pasquevich [10] studied the interaction between Cl_2(g) and sucrose carbon by mass spectroscopy and verified the presence of $Cl^\bullet$ in the gas phase at temperatures below 1000 °C. Pasquevich detected them at 900 °C, an approximate temperature since the chlorine atoms can be recombined on the glass walls, which conducted the reactor gases to the spectrometer. Amorebieta utilized passive glass and found $Cl^\bullet$ from 677 °C.

There are in literature only a few works concerning to the chlorination or carbochlorination of yttrium oxide or minerals containing this rare earth. Miller et al. [11] presented a method to synthesize anhydrous rare earth chlorides, included YCl_3. The method is based on the reaction between oxides or mixture of oxides with gaseous carbon tetrachloride (CCl_4) in a temperature range of 500–650 °C. In a previous work [12] we analyzed the kinetics of the chlorination of yttrium oxide. The results showed that yttrium oxychloride is formed in an initial stage. For temperatures above 800 °C, the YOCl is chlorinated leading to the production of liquid YCl_3. The chloride has a considerable vapor pressure, and the evaporation rate

---

* Corresponding author at: División Cinética Química - Complejo Tecnológico Pilcaniyeu, Centro Atómico Bariloche - Comisión Nacional de Energía Atómica, Av. Bustillo km 9500 (8400), S.C. de Bariloche, Río Negro, Argentina.
Tel.: +54 02944 445293; fax: +54 02944 445293.
E-mail address: gaviriaj@cab.cnea.gov.ar (J.P. Gaviría).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.06.009

is higher than its production rate. Braginski et al. [13], Gimenes and Oliveira [14] and Augusto and Oliveira [15] studied the carbochlorination of the yttrium oxide and xenotime (mineral rich in heavy rare earths, [16]). They found that the YOCl is an intermediate product previous to the formation of the YCl_3.

The reactions proposed by these authors are the followings:

Braginski (1100 °C):

$$Y_2O_3(s) + C(s) + Cl_2(g) \rightarrow 2YOCl(s) + CO(g) \quad (1)$$

$$YOCl(s) + C(s) + Cl_2(g) \rightarrow YCl_3(l) + CO(g) \quad (2)$$

Gimenes (600–950 °C):

$$2YPO_4(s) + C(s) + 2Cl_2(g) \rightarrow 2YOCl(s) + P_2O_5(s) + COCl_2(g) \quad (3)$$

$$2YOCl(s) + C(s) + 2Cl_2(g) \rightarrow 2YCl_3(s,l) + CO_2(g) \quad (4)$$

Augusto (600–900 °C):

$$YPO_4(s) + 1/2CCl_4(g) \rightarrow YOCl(s) + 1/2P_2O_5(s) + 1/2COCl_2(g) \quad (5)$$

$$YOCl(s) + 1/2CCl_4(g) \rightarrow YCl_3(s,l) + 1/2CO_2(g) \quad (6)$$

The objective of this work is to elucidate the reaction stages of the carbochlorination of Y_2O_3, to analyze the influence of the temperature on these stages and to propose their stoichiometry. The final product of the reaction is liquid YCl_3, which has a considerable vapor pressure at the temperatures studied. The kinetics of its evaporation was analyzed and the evaporation heat was obtained.

2. Experimental

2.1. Materials

Solid reactants used were an yttrium oxide powder 99.99 pct (Aldrich Chemical Company, Inc., Milwaukee, MI) and sucrose carbon. The mean particle size of the oxide measured by laser diffraction was 10 μm and showed a size distribution highly homogeneous (Mastersizer, Malvern Instruments Limited, Worcestershire, UK). Carbon was obtained from the pyrolysis of sucrose (Fluka Chemie AG) in inert atmosphere at 980 °C during 48 h and sieved to a size of 400 mesh (ASTM, square aperture of 37 μm). Carbon characteristics are well described by Gonzalez et al. [17]. Amorebieta and Colussi [9] and Pasquevich [10] utilized sucrose carbon and determined by mass spectroscopy that this type of carbon does not have volatile organic residues at the reaction conditions. The oxide and carbon powder have a BET surface area of 3.7 and 7.2 m^2/g, respectively (Digisorb 2600 Micrometeritics Instrument, Norcross, GA). Respective amounts of the solid reactants were weighed and mixed mechanically to obtain mixtures of Y_2O_3–C in the range of 6.7–16.7 pct (w/w, carbon mass/total mass).

Gases used were Cl_2 99.8 pct purity (Indupa, Bahía Blanca, Argentina) and Ar 99.99 pct purity (AGA, Buenos Aires, Argentina).

Solids were analyzed by X-ray diffraction (XRD) (Philips PW 1310-01), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) (SEM 515, Philips Electronic Instruments).

2.2. Thermogravimetric system

The measurements were performed using a thermogravimetric analyzer (TGA), which has been described elsewhere [18]. It consists of an electrobalance (Cahn 2000, Cahn Instruments, Inc., Cerritos, CA) adapted to work with corrosive atmospheres, a vertical tube furnace, a gas line, and a data acquisition system. The sensitivity of the system is ±5 μg while operating at 1000 °C under a gas flow rate of 9 L/h, measured at normal temperature and pressure. Each sample was placed in a cylindrical quartz crucible (7.8-mm inner diameter, 3.3-mm deep), which hangs from one of the arms of the electrobalance through a quartz wire. A quartz hangdown tube (4.6-cm diameter) carried the gases to the sample. The temperature of the sample was measured using a Pt–Pt (10 pct Rh) thermocouple encapsulated in quartz, which was placed 2 mm below the crucible. Flows of Ar and Cl_2 were controlled by means of flow meters and they were dried by passing through silica gel and $CaCl_2$, respectively. The mass changes were acquired every 2.5 s.

2.3. Procedure

Non-isothermal and isothermal measurements were made. In the non-isothermal runs the samples were kept 1 h under flowing Ar to purge the gas line and heated at 100 °C to eliminate water. Then the chlorine gas was introduced to the reaction zone and the samples were heated in the Ar–Cl_2 mixture up to 950 °C. The linear heating rate used was 3.8 °C/min. Mass changes and temperature were continuously monitored during the heating and the apparent mass change was taken into account to correct the experimental data [18]. In the isothermal runs the samples were heated in flowing Ar until the reaction temperature was reached. Once the temperature was stabilized, chlorine was admitted into the hangdown tube while mass changes were continuously monitored. The data were carefully analyzed to determine the reaction zero time.

3. Results and discussion

3.1. Thermodynamic considerations

The following reactions are possible in the Y_2O_3–C–Cl_2 system:

$$Y_2O_3(s) + Cl_2(g) \rightarrow 2YOCl(s) + 1/2O_2(g) \quad (7)$$

$$Y_2O_3(s) + 1/2C(s) + Cl_2(g) \rightarrow 2YOCl(s) + 1/2CO_2(g) \quad (8)$$

$$Y_2O_3(s) + C(s) + Cl_2(g) \rightarrow 2YOCl(s) + CO(g) \quad (9)$$

$$1/3Y_2O_3(s) + Cl_2(g) \rightarrow 2/3YCl_3(s,l) + 1/2O_2(g) \quad (10)$$

$$1/3Y_2O_3(s) + 1/2C(s) + Cl_2(g) \rightarrow 2/3YCl_3(s,l) + 1/2CO_2(g) \quad (11)$$

$$1/3Y_2O_3(s) + C(s) + Cl_2(g) \rightarrow 2/3YCl_3(s,l) + CO(g) \quad (12)$$

The production of $COCl_2(g)$ was not proposed due to two reasons: (1) it was not detected in the carbochlorination reactions with sucrose carbon [10], (2) $COCl_2$ decomposes forming CO and Cl_2 at temperatures above 650 °C [19].

The reduction of the oxide by carbon is not considered since it has a very highly value of ΔG^0 at the range of temperature used in this work (1082 and 865 kJ/mol for 600 and 1000 °C, respectively [20]). Nevertheless, the interaction between Y_2O_3 and sucrose carbon in argon atmosphere was analyzed by thermogravimetry at 950 °C and no mass change was observed. The XRD analysis of the sample after the treatment showed only the diffraction lines of Y_2O_3.

Fig. 1 shows the standard Gibbs free energy for the above reactions mentioned except reaction (10) which is the only one that has a positive value of ΔG^0. The calculations were performed with the HSC 6.12 Software [20] and the reactions were taken per mole of chlorine. The YOCl thermodynamic data used were extrapolated from values reported by Patrikeev et al. [21].

The reactions can be compared, assuming that the reactive systems involved are independent from each other. The curves show that the carbochlorination of Y_2O_3 to produce YOCl (reactions (8) and (9)) are more feasible to occur than: (1) direct chlorination