Chlorination of Lanthanum Oxide

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ABSTRACT: The reactive system La2O3(s)−Cl2(g) was studied in the temperature range 260−950 °C. The reaction course was followed by thermogravimetry, and the solids involved were characterized by X-ray diffraction, scanning electron microscopy, and energy dispersive spectroscopy. The results showed that the reaction leads to the formation of solid LaOCl, and for temperatures above 850 °C, the lanthanum oxychloride is chlorinated, producing LaCl3(l). The formation of the oxychloride progresses through a nucleation and growth mechanism, and the kinetic analysis showed that at temperatures below 325 °C the system is under chemical control. The influence of diffusive processes on the kinetics of production of LaOCl was evaluated by studying the effect of the reactive gas flow rate, the mass of the sample, and the chlorine diffusion through the boundary layer surrounding the solid sample. The conversion curves were analyzed and fitted according to the Johnson−Mehl−Avrami description, and the reaction order with respect to the chlorine partial pressure was obtained by varying this partial pressure between 10 and 70 kPa. The rate equation was obtained, which includes the influence of the temperature, chlorine partial pressure, and reaction degree.

1. INTRODUCTION

Direct chlorination is a potential dry method for the production of rare earth chlorides, which allows further isolation of metals from ores and concentrates.6,7 The combination of chlorination and chemical vapor transportation is a method for recovery and separation of rare earths from oxide mixtures and sludges.2,3 Although there are several studies about chlorination with NH4Cl4,5 and CCl46−10 of lanthanum oxide and other lanthanum compounds, none have paid special attention to the kinetic research on direct chlorination of rare earth oxides,11−14 and to study the chlorination of La2O3 in order to determine the rate equation, the mechanism of the reaction, and the kinetics parameters. The aim of this work is to continue with the kinetic research on direct chlorination of rare earth oxides,11−14 and to study the chlorination of La2O3 in order to determine the rate equation, the mechanism of the reaction, and the kinetics parameters.

An electro-balance was used to follow the course of the reaction, and the resulting solids were analyzed with X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). The studies showed that LaOCl is the only existing solid phase after direct chlorination of La2O3 at the working temperature range. This compound has several potential uses as it is becoming of great interest within various industries due to its capability and potential to be used as a catalyst in the oxidative methane coupling, oxidative dehydrogenation of ethane, oxidative chlorination of methane, conversion of ethane and ethylene to vinyl chlorides and in the destruction of chlorinated hydrocarbons, toxins of the environment.8,15−19 Its nanomaterial can be used as a luminescent material and gas sensor.20−22

2. MATERIALS AND METHODS

The materials used were a lanthanum hydroxide [La(OH)3] powder 99.98% (Fluka), chlorine (Cl2) 99.8% purity (Indupa, Bahía Blanca, Argentina), and argon 99.99% purity (AGA, Buenos Aires, Argentina). The particle size distribution of the La(OH)3 powder measured by laser diffraction showed that 90% v/v of the particles have a size lower than 10 μm and 45% v/v have sizes between 2 and 6 μm (Mastersizer, Malvern Instruments Limited).

Solids were analyzed by X-ray diffraction (Philips PW 1310-01, with Ni filtered Cu Kα radiation), scanning electron microscopy (SEM 515, Philips Electronic Instruments), and energy dispersive spectroscopy (EDAX Genesis 2000).

The chlorination reactions were carried out using a thermogravimetric system.23 It consists of an electro-balance (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 ±0.01 mg 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 silica glass crucible (7.8 mm inner diameter and 3.3 mm deep), which hangs from one of the arms of the electro-balance through a silica glass wire. The reactor is a hang-down silica glass tube (4.6 cm inner diameter) which carries the gases (Ar/Cl₂) to the sample. The temperature was measured using a Pt–Pt (10% Rh) encapsulated thermocouple which was placed 5 mm below the crucible. Flows of Ar and Cl₂ were controlled by flow meters, and they were dried by passing them through silica gel and CaCl₂, respectively. The La₂O₃ samples (product of the La(OH)₃ decomposition) were heated in flowing Ar until the reaction temperature was reached. After temperature stabilization, chlorine was admitted into the reactor while mass changes were monitored every 2.5 s. The acquired data were carefully analyzed to determine the reaction zero time.

2.1. Production of La₂O₃ by La(OH)₃ Decomposition.
The lanthanum oxide used in the chlorinations was obtained by La(OH)₃ thermal decomposition under Ar atmosphere. The thermal treatment was a heating of 40 min until 850 °C and 20 min at this temperature. Figure 1 shows a thermogravimetric curve of the La(OH)₃ decomposition. The curve indicates three steps of weight loss, with these steps being associated with the following reactions:

\[
\text{La(OH)}_3(s) \rightarrow \text{LaOOH}(s) + \text{H}_2\text{O}(g) \\
[\approx 240–360^\circ C] \\
\text{LaOOH}(s) \rightarrow \frac{1}{2}\text{La}_2\text{O}_3(s) + \frac{1}{2}\text{H}_2\text{O}(g) \\
[\approx >440^\circ C] \\
\text{La}_2\text{O}_2\text{CO}_3(s) \rightarrow \text{La}_2\text{O}_3(s) + \text{CO}_2(g) \ [\approx >630^\circ C] \\
\]

The presence of a small amount of lanthanum oxide carbonate (La₂O₂CO₃) in the starting material and the formation of LaOOH during the decomposition was verified by XRD (La₂O₂CO₃: reference pattern, 37-804; hexagonal; space group, P6₃/mmc; space group number, 194. LaOOH: reference pattern, 19-656; crystal system, monoclinic; space group, P2₁/m; space group number, 11).

The final relative mass loss of the curve corresponds to the global reaction of La₂O₃ production by La(OH)₃ decomposition (≈0.142). The final product of the treatment was analyzed by XRD obtaining only the diffraction lines of La₂O₃ (reference pattern, 73-2141; hexagonal; space group, P-3m1; space group number, 164). These results are in good agreement with those obtained by Neumann et al.²⁵

The sample of La₂O₃ obtained was left in the reactor and subsequently chlorinated.

3. RESULTS AND DISCUSSION
3.1. Thermodynamic Considerations.
The following reactions are possible in the La₂O₃–Cl₂ reactive system:

\[
\text{La}_2\text{O}_3(s) + \text{Cl}_2(g) \rightarrow 2\text{LaOCl}(s) + \frac{1}{2}\text{O}_2(g) \\
(4) \\
\frac{1}{3}\text{La}_2\text{O}_3(s) + \text{Cl}_2(g) \rightarrow \frac{2}{3}\text{LaCl}_3(s, l) + \frac{1}{2}\text{O}_2(g) \\
(5) \\
\text{LaOCl}(s) + \text{Cl}_2(g) \rightarrow \text{LaCl}_3(s, l) + \frac{1}{2}\text{O}_2(g) \\
(6) \\
\text{LaOCl}(s) \rightarrow \frac{1}{3}\text{La}_2\text{O}_3(s) + \frac{1}{3}\text{LaCl}_3(s, l) \\
(7)
\]

The physical properties reported for lanthanum compounds are the following: La₂O₃ (Tm = 2313 °C);²⁶ LaOCl (Td = 934 °C (in vacuum));²⁷ LaCl₃ (Tm = 858 °C, Tc = 1747 °C).²⁶ Tm, Td, and Tc are the melting, decomposition, and vaporization temperatures.

The calculations were performed with HSC 6.12 Software,²⁸ and the reactions were taken per mole of chlorine.

The results can be compared, assuming that the reactions are independent from each other. The curves show that the chlorination reactions of La₂O₃ to produce LaOCl and LaCl₃ have negative ΔG° values, and the formation of the oxychloride is thermodynamically more feasible to occur. Then, LaOCl could be chlorinated (reaction 6) or decomposed (reaction 7). The chlorination of LaOCl has negative ΔG° values for temperatures below 580 °C, and has lower ΔG° values than the LaOCl decomposition reaction (compared per mole of LaOCl).

The phase stability diagram of the La–O–Cl system at 400 °C is shown in Figure 3.²⁸ The axes are the partial pressure of O₂ and Cl₂. The diagram indicates that La₂O₃ and LaCl₃ do not have a thermodynamic equilibrium, and LaOCl has to be formed previous to the formation of LaCl₃ from La₂O₃.

3.2. Nonisothermal Chlorination Experiments.
Nonisothermal chlorination experiments were carried out in order...
to determine both the reactivity with temperature and the reaction products. Figure 4 shows the relative mass change \((\Delta m/m_0)\) vs temperature for this system under Ar−Cl₂ atmosphere from 100 to 1000 °C.

The sample undergoes a mass gain starting from a temperature of about 260 °C. The mass change rate increases quickly until the mass change reaches a maximum value of \(\Delta m/m_0 = 0.18\), very close to the relative mass change expected for reaction 4.

The average composition, taking into account only La and Cl, for six measurements (two for each sample) was 52 ± 3 for La and 48 ± 3 for Cl (% at).

The thermodynamical analysis showed that LaOCl is the compound thermodinamically more feasible to be formed from La₂O₃ chlorination (Figure 2) and LaCl₃ is the more stable final product under the experimental conditions used (Figure 3). The DRX analyses of the final condensed products in the whole temperature range (260–950 °C) showed that LaOCl was the only phase present. This behavior is indicating that conversion of LaOCl to LaCl₃ is kinetically limited.

Therefore, the results indicate that the reaction taking place is reaction 4:

\[
\text{La}_2\text{O}_3(s) + \text{Cl}_2(g) \rightarrow 2\text{LaOCl}(s) + \frac{1}{2}\text{O}_2(g) \tag{4}
\]

The conversion degree is defined as:

\[
\alpha = \frac{m_{\text{La}_2\text{O}_3} - m_{\text{La}_2\text{O}_3}}{m_0}
\tag{1}
\]

where \(m_0\) and \(m_{\text{La}_2\text{O}_3}\) are the weights of La₂O₃ at zero time and time \(t\), respectively.

The mass change measured in the thermo-balance \((\Delta m)\) includes the weights of La₂O₃ and LaOCl. After relating these weights with conversion, an expression is obtained for \(\alpha\) as a function of \(\Delta m\):

\[
\alpha = \frac{\left(\frac{\Delta m}{m_0}\right)}{\left(\frac{PM_{\text{LaOCl}}}{PM_{\text{La}_2\text{O}_3}} - 1\right)} \cong \frac{\Delta m}{m_0} \cdot 0.169
\tag{II}
\]

where 0.169 is the final relative mass change of reaction 4.

The formation of LaOCl as the intermediate solid reaction product in the production of LaCl₃ by La₂O₃ chlorination with NH₄Cl and CCl₄ has been observed by several authors (NH₄Cl;⁴️,⁵️ CCl₄⁶⁻⁹).

3.3. Isothermal Thermo-Gravimetric Experiments. The isothermal chlorination experiments performed at temperatures between 260 and 950 °C (\(m_{\text{La}_2\text{O}_3}, 10\) mg; \(p\text{Cl}_2, 35\) kPa; \(Q_{\text{Ar-Cl}_2}, 4\) L/h) showed that the system has different kinetic behavior depending on the temperature range (Figure 6). For temperatures below 325 °C, the reaction rate is the fastest of the overall reaction, which is a different behavior compared to the reactions performed at lower temperatures where the reaction rate at the
beginning of the reaction is nearly zero (transformations which follow a nucleation and growth mechanism have a theoretical initial rate equal to zero).

For temperatures in the range 350–500 °C, the beginning of the reaction proceeds through a fast stage and the formation of LaOCl is subsequently completed by a slower kinetic stage. For temperatures above 600 °C, the production of LaOCl is fully performed by the fast stage, being rate independent of the temperature.

Chlorination experiments performed at temperatures above 850 °C showed that after the formation of LaOCl the system progresses with mass loss (Figure 7). The XRD analyses of the solid residues of these reactions showed that LaOCl is the only compound present.

Reactions 6 and 8 occur at temperatures above 850 °C. Reaction 8 is faster than reaction 6, causing LaCl3 to not be present as a condensed product after the chlorinations.

3.4. Morphological Analysis. Figure 8 shows SEM images with 10000x magnification of (a) starting La(OH)3, (b) La2O3 obtained by La(OH)3 decomposition, (c) LaOCl produced at 325 °C, and (d) LaOCl produced at 950 °C. It can be observed that there are few morphological differences between La(OH)3 and La2O3. The sample of LaOCl formed at 325 °C has a smaller grain size than the La2O3, which is in accordance with the behavior expected for a nucleation and growth mechanism (several LaOCl nuclei are formed inside the La2O3 grains). The morphology of the lanthanum oxychloride is quite different at temperatures below and above the melting point of LaCl3 (858 °C). At temperatures below 858 °C, the LaOCl grains are smaller than those obtained at higher temperatures (Figure 8c and d).

3.5. Effect of the Gas Phase Mass Transfer. The kinetics in gas–solid reactions can be affected by two gas phase phenomena: convective mass transfer through the boundary layer and reacting gas supply.37 The first process is analyzed by comparing the calculated chlorine molar flow diffusing through the boundary layer surrounding the solid sample with the measured chlorine molar flow (obtained from thermo-gravimetric curves and assuming a given reaction stoichiometry). The second one can be evaluated by studying the influence of the total flow rate (supply rate of chlorine) on the reaction rate.

The molar flow of Cl2 by diffusion (and assuming no starvation) can be estimated by using the Ranz–Marshall correlation34 (the development of eq III is detailed in ref 31):

$$\frac{dn_{\text{Cl}_2}}{dt} = \frac{D_{\text{Ar}-\text{Cl}_2} (2 + 0.6 N_R) \nu^{1/3}}{L} \left( \frac{P_{\text{Cl}_2,0} - P_{\text{Cl}_2,S}}{A} \right)$$

where \(dn_{\text{Cl}_2}/dt\) is the chlorine molar flow, \(D_{\text{Ar}-\text{Cl}_2}\) is the binary diffusion coefficient for \(\text{Ar} - \text{Cl}_2\), \(N_R = U L / \nu\) represents the Reynolds number (\(U\) is the linear fluid velocity, \(L\) is the characteristic dimension of the test system), \(A\) is the sample external surface (considered equal to the crucible transversal area), \(R_g\) is the gas constant, \(P_{\text{Cl}_2,S}\) is the chlorine partial pressure, and the subscripts 0 and S represent the bulk gas stream and sample surface, respectively.

The values of \(dn_{\text{Cl}_2}/dt\) calculated by eq III and those obtained from thermo-gravimetric curves, for temperatures between 300 and 700 °C, are shown in Table 1. Reaction 4 was assumed as irreversible, since the values of the equilibrium constants are nearly zero (transformations which follow a nucleation and growth mechanism have a theoretical initial rate equal to zero).

The values of \(P_{\text{Cl}_2,S}\) employed in the calculation is zero. The \(\nu\) and \(D_{\text{Ar}-\text{Cl}_2}\) values were obtained from the Chapman–Enskog theory.35,36 The experimental conditions considered were \(p_{\text{Cl}_2} = P_{\text{Cl}_2,0} = 35\) kPa, \(Q_{\text{Ar}-\text{Cl}_2} = 4\) L/h.

Equation III gives approximate values of \(dn_{\text{Cl}_2}/dt\). This equation is valid for a pellet in a freely flowing gas and not for a sample contained in a crucible. Hills32 and Halvøoert37 con-
cluded that values obtained using the Ranz and Marshall correlation are more than 1 order of magnitude higher than mass transfer rates for samples contained within crucibles. The criterion used in this work to conclude that the convective mass transfer of chlorine to the surface of the sample is not influencing the reaction rate is when the measured chlorine flow is at least 2 orders of magnitude smaller than the one obtained by using eq III. The results shown in Table 1 indicate that for temperatures below 350°C the reaction kinetics are not affected by this diffusive process.

Table 1. Comparison between Calculated and Measured Molar Flow of Chlorine

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>(1) d(n_{Cl_2}/dt) [calculated](^a) (mol of Cl(_2)/s)</th>
<th>(2) d(n_{Cl_2}/dt) [measured](^c) (mol of Cl(_2)/s)</th>
<th>(1)/(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>4.05 × 10^{-6}</td>
<td>2.72 × 10^{-8}</td>
<td>1487</td>
</tr>
<tr>
<td>350</td>
<td>4.31 × 10^{-6}</td>
<td>3.30 × 10^{-8}</td>
<td>131</td>
</tr>
<tr>
<td>400</td>
<td>4.55 × 10^{-6}</td>
<td>2.40 × 10^{-7}</td>
<td>19</td>
</tr>
<tr>
<td>500</td>
<td>5.02 × 10^{-6}</td>
<td>1.22 × 10^{-6}</td>
<td>4.1</td>
</tr>
<tr>
<td>700</td>
<td>5.88 × 10^{-6}</td>
<td>1.68 × 10^{-6}</td>
<td>3.5</td>
</tr>
</tbody>
</table>

\(^a\)Data used for the calculations: \(L = 0.74\) cm; \(A = 0.43\) cm\(^2\); \(p_{Cl_2} = 35\) kPa; \(Q_{Ar-Cl_2} = 4\) L/h. \(^b\)Calculated from eq III. \(^c\)Obtained from the thermogravimetric curves at the higher slope (stoichiometry of reaction 4).

Figure 8. SEM images of (a) starting La(OH)\(_3\); (b) La\(_2\)O\(_3\) produced by La(OH)\(_3\) decomposition; (c) LaOCl formed at 325 °C; (d) LaOCl formed at 950 °C.

Figure 9. Effect of Ar–Cl\(_2\) flow rate on the kinetics of La\(_2\)O\(_3\) chlorination at 350 °C. Two curves of 4 L/h are presented to show the reproducibility of the system.

Diffusion of the gas species (reactants and products) through pores between solid particles can affect the reaction rate. This process was analyzed by studying the effect of the reaction bed thickness, which was varied by changing the mass of La\(_2\)O\(_3\). The reaction rate decreases as the bed thickness increases when the interparticle void diffusion is playing a role in the rate control.

Figure 10 shows thermo-gravimetric curves of chlorination experiments performed at 325 °C and initial masses of 2 and 10 mg. The reaction rate does not depend on the sample size at this temperature; therefore, the mass transfer through the
interparticle voids is not affecting the overall reaction rate and hence an initial mass of 10 mg was used in the kinetic analysis.

3.7. Kinetic Analysis for \( T \geq 350 \, ^\circ\text{C} \). For temperatures above 350 \( ^\circ\text{C} \), the beginning of the reaction proceeds by a fast stage. The kinetics of this stage are affected by the gas phase mass transfer (Table 1, section 3.5); therefore, it is not possible to obtain intrinsic kinetic parameters.

The extension of the fast stage is raised as the temperature (Figure 6) and initial mass are increased. Figure 11 shows the effect of the initial mass of \( \text{La}_2\text{O}_3 \) on the kinetics of chlorination at 450 \( ^\circ\text{C} \). The extension of the fast stage is \( \alpha = 0.19, 0.74, \) and \( 0.97 \) for \( m_0 = 10, 30, \) and \( 40 \) mg, respectively. The same behavior was observed at 500 \( ^\circ\text{C} \). Figure 11 also shows that the time necessary to reach a given conversion depends on the initial mass. For example, a value of \( \alpha = 0.91 \) is reached in 300 and 62 s for 10 and 40 mg, respectively.

This behavior is not the most common in gas–solid kinetics. An increment in the reaction bed thickness generally causes the following, depending on the relative importance of the diffusion through the sample pores: (1) a diminution in the reaction rate for systems affected by this diffusion; (2) no change in the kinetics for systems which are not influenced by this process transfer. The increase of the fast stage extension and the reaction rate with the initial mass could be related to the formation of highly reactive gas intermediates. The chlorine radical (Cl•) is a probable species to be produced in the \( \text{La}_2\text{O}_3–\text{Cl}_2 \) interaction. The chlorine radicals react readily with the oxide to form the oxychloride. As the reaction thickness of the bed increases, the reaction probability before the recombination to form \( \text{Cl}_2 \) increases. When the reaction thickness diminishes, the radicals have a lower residence time in the bed and the probability of escaping from the sample is higher. Although the behavior can be explained with the proposal of the chlorine radical formation, the presence of this species should be demonstrated. Pasquevich et al.\textsuperscript{38,39} observed the same kinetic behavior in the carbochlorination of \( \text{ZrO}_2 \) (enhancement of the conversion with the increase of the initial mass) and verified by modulated-beam mass spectroscopy the formation of chlorine radicals.

3.8. Kinetic Analysis and Determination of the Equation Rate for \( T \leq 325 \, ^\circ\text{C} \). The intrinsic kinetic parameters of \( \text{La}_2\text{O}_3 \) chlorination that produces \( \text{LaOCl} \) and \( \text{O}_2 \) (reaction 4) are determined in this section. The results analyzed in previous sections showed that the reaction at temperatures below 325 \( ^\circ\text{C} \) follows a unique kinetic behavior and the reaction rate is not affected by gas phase and interparticle void mass transfer (\( Q_{\text{Ar}}–\text{Cl}_2, 4 \text{L/h} \); \( m_0, 10 \) mg). Therefore, the kinetics are under chemical control and the reaction rate can be expressed as a \textit{function of separate variables} \( (T, p, \alpha) \):

\[
\frac{d\alpha}{dt} = k(T)p_{\text{Cl}_2}G(\alpha)
\]

(IV)

where \( k(T) \) refers to an Arrhenius equation, \( F(p_{\text{Cl}_2}) \) expresses the dependence of reaction rate on \( p_{\text{Cl}_2} \) (it is related to the adsorption/desorption phenomena), and \( G(\alpha) \) is a function that describes the morphological evolution of the solid reactant.

3.8.1. Reaction Order with Respect to \( p_{\text{Cl}_2} \). Figure 12 shows the effect of the chlorine partial pressure on the reaction rate at 300 \( ^\circ\text{C} \), varying \( p_{\text{Cl}_2} \) between 10 and 70 kPa.

The reaction order is obtained from the integration of eq IV between \( \alpha = 0 \) and \( \alpha = \alpha \) and \( t = 0 \) and \( t = t \). The temperature is constant (300 \( ^\circ\text{C} \)), and it is assumed that dependence on \( \alpha \) and \( p_{\text{Cl}_2} \) can be separated.

\[
\int \frac{d\alpha}{G(\alpha)} = \int k(T)p_{\text{Cl}_2} \, dt
\]

(V)

\[
g(\alpha = \alpha) − g(\alpha = 0) = k(T)p_{\text{Cl}_2}H(\alpha)
\]

(VI)
where $g(\alpha)$ is commonly called the integrated conversion function and $t(\alpha)$ is the time to reach a conversion degree $\alpha$ at a given temperature and reactive gas partial pressure.

Assuming that $F(pCl_2) = B \cdot pCl_2^2$:

$$g(\alpha) - g(0) = k(T)B \cdot pCl_2^x \cdot t(\alpha)$$  \hspace{1cm} (VII)

$$1/t(\alpha) = \frac{k(T)B}{g(\alpha) - g(0)} \cdot pCl_2^x$$  \hspace{1cm} (VIII)

$$-\ln t(\alpha) = \ln \left[ \frac{k(T)B}{g(\alpha) - g(0)} \right] + x \ln pCl_2$$  \hspace{1cm} (IX)

The function inside brackets, at constant temperature, depends only on $\alpha$:

$$-\ln t(\alpha) = H(\alpha) + x \ln pCl_2$$  \hspace{1cm} (X)

The reaction order for a given $\alpha$ and $T$ is obtained by plotting $-\ln t(\alpha)$ vs $pCl_2$ and calculating the slope of the curve. Figure 13 shows these plots, obtaining an average value of 0.23. It was considered an experimental scattering error of 10% in the time to reach a given conversion.

### Table 2. Values of $n$ and $K$ Obtained from a Nonlinear Least Squares Fitting of Conversion Curves with eq XI

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$n$</th>
<th>$K$ ($s^{-1}$)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>$1.471 \pm 0.001$</td>
<td>$(2.148 \pm 0.001) \times 10^{-5}$</td>
<td>0.9988</td>
</tr>
<tr>
<td>270</td>
<td>$1.525 \pm 0.001$</td>
<td>$(3.901 \pm 0.002) \times 10^{-5}$</td>
<td>0.9981</td>
</tr>
<tr>
<td>280</td>
<td>$1.396 \pm 0.0005$</td>
<td>$(6.577 \pm 0.001) \times 10^{-5}$</td>
<td>0.9998</td>
</tr>
<tr>
<td>290</td>
<td>$1.377 \pm 0.001$</td>
<td>$(8.804 \pm 0.003) \times 10^{-5}$</td>
<td>0.9976</td>
</tr>
<tr>
<td>300</td>
<td>$1.540 \pm 0.002$</td>
<td>$(1.266 \pm 0.007) \times 10^{-4}$</td>
<td>0.9958</td>
</tr>
<tr>
<td>325</td>
<td>$1.457 \pm 0.002$</td>
<td>$(3.817 \pm 0.003) \times 10^{-4}$</td>
<td>0.9981</td>
</tr>
</tbody>
</table>

The average value of $n$ obtained was $1.461 \pm 0.066$. The value of $n$ is dependent on the nucleation and growth mechanisms. The types of growth considered in the JMA description are volume diffusion controlled and interface controlled. Interface controlled can occur in the absence of compositional changes (e.g., in cases of allotropic phase transformations), and volume diffusion can occur upon phase transformations where long-range compositional changes take place. Kempen et al. demonstrated numerically that intermediate values of the JMA exponents are possible for combination of the different nucleation models and volume diffusion growth: (I) between 1/2 (one-dimensional growth) and 3/2 (three-dimensional growth) for site saturation and (II) between 3/2 (one-dimensional growth) and 5/2 (three-dimensional growth) for continuous nucleation.

The obtained value for the JMA exponent could be consistent with a three-dimensional growth and site saturation. Figure 15 shows a magnification of Figure 8c, showing the detail of the LaOCl nuclei. It can be observed that these nuclei had a three-dimensional growth. The nucleation mechanism of site saturation assumes that the number of supercritical nuclei does not change during transformation; all nuclei are present at zero time. A possible mechanism, coherent with the results analyzed in section 3.7, is the following: at the beginning of the reaction, the Cl$_2$ molecule is destructively adsorbed and some...
of the generated Cl atoms diffuse into the La$_2$O$_3$ bulk. These atoms react and produce all LaOCl nuclei, which subsequently grow. Lanthanum oxide is widely used as a reactive substrate in the low temperature destruction of chlorinated hydrocarbons. A feature of these reactions is the facile oxygen diffusion from the bulk to the surface to undergo O/Cl exchange.

The function $G(\alpha)$ can be obtained by combining eqs IV and XI, and the average value of $n$ in the range of temperature analyzed was 1.46:

$$G(\alpha) = n(1 - \alpha)[-\ln(1 - \alpha)]^{(n-1)/n} \quad (n = 1.46)$$  \hspace{1cm} \text{(XIII)}$$

3.8.3. Activation Energy. The activation energy in the temperature range of 260–325 °C was calculated from the values of the global rate constant $K(T)$ obtained by the application of the JMA model (Table 2). Figure 16 shows the plot of ln $K$ vs $1/T$, from which a value for the intrinsic activation energy of 113 ± 5 kJ/mol was obtained. Table 3 shows the comparison with the intrinsic activation energies obtained for the same reaction using other rare earths. These reactions were studied in the same experimental system. The lower $E_a$ belongs to the lanthanum oxide chlorination, being consistent with the use of this compound for the destruction of chlorinated hydrocarbons.

4. CONCLUSIONS

The chlorination of La$_2$O$_3$ begins at temperatures above 260 °C and leads to the formation of solid LaOCl. At temperatures above 850 °C, the lanthanum oxychloride is chlorinated to lanthanum trichloride, but the rate for the LaCl$_3$(l) production is lower than its evaporation rate and thermo-gravimetric experiments show a loss of mass. Kinetic analysis showed that the reaction is under chemical control for temperatures below 325 °C. The formation of LaOCl proceeds through a nucleation and growth mechanism, and the conversion curves were analyzed with the Johnson–Mehl–Avrami description. The JMA parameters obtained were $n = 1.46$ and $E_a = 113$ kJ/mol. According to the JMA description and SEM images, the value of $n$ is consistent with a three-dimensional growth and site saturation nucleation of the LaOCl phase. An overall rate equation was obtained, which includes the effects of the parameters analyzed (a pre-exponential factor was obtained for each temperature by combining eqs IV, XI, and XII and calculating the average):

$$\frac{d\alpha}{dt} = 1.2 \times 10^6 (\text{seg} \cdot \text{kPa}^{0.23})^{-1} \exp\left(-\frac{112 \text{ kJ/mol}}{R_g T}\right) \times p\text{Cl}_2^{0.23} \{1.46(1 - \alpha)[-\ln(1 - \alpha)]\}^{0.3}$$

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


**Table 3. Activation Energies for Reaction RE$_2$O$_3$(s) + Cl$_2$(g) = 2REOCl(s) + 1/2O$_2$(g) (RE: Rare Earth)**

<table>
<thead>
<tr>
<th>RE</th>
<th>$E_a$ (kJ/mol)</th>
<th>temperature range (°C)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>113 ± 5</td>
<td>260–325</td>
<td>this work</td>
</tr>
<tr>
<td>Sm</td>
<td>130 ± 5</td>
<td>270–350</td>
<td>12, 13</td>
</tr>
<tr>
<td>Y</td>
<td>187 ± 3</td>
<td>575–800</td>
<td>14</td>
</tr>
</tbody>
</table>

**Figure 15.** SEM image of LaOCl obtained from La$_2$O$_3$ chlorination at 325 °C.

**Figure 16.** Plot of ln $K$ vs $1/T$. The $K$ values were obtained from the JMA analysis.