



Short communication

Kinetic analysis of dechlorination and oxidation of PrOCl by using a non-isothermal TG method[☆]H.C. Yang^{*}, H.C. Eun, Y.Z. Cho, H.S. Lee, I.T. Kim

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ABSTRACT

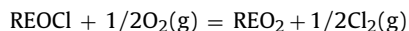
Thermal dechlorination and oxidation process of praseodymium oxychloride, PrOCl, was studied from the view point of reaction kinetics. On the basis of data of thermogravimetry under different oxygen partial pressures at various heating rates, a kinetic analysis was performed using an isoconversional method and a master plot method. The results of the isoconversional method of TG data suggested that the dechlorination and oxidation of PrOCl followed a single step with activation energy of $112.6 \pm 3.4 \text{ kJ mol}^{-1}$, and from master plot methods, the reaction was described by a linear-contracting phase boundary reaction.

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1. Introduction

Praseodymium oxide, also called praseodymia, is used as an ingredient of color glasses and enamels. As an important additive, praseodymium oxide is used as a yellow pigment in photonic applications. Glass containing praseodymium oxide is used to manufacture didymium glass, which is a colorant for welder's goggles. A thin praseodymium oxide film is widely used in the sensor, semi-conducting, and ceramic industries. An increased industrial use of pure praseodymium and its oxide requires more advanced separation technologies.

An electrochemical separation and an electrochemical synthesis in molten chloride salts are promising technologies for obtaining pure metals and oxides of rare earth elements [1–4]. By-products of these electrochemical processes include rare earth oxychlorides (REOCl). Pure RE oxides are obtained by a thermal treatment of the RE oxychlorides to emit gaseous chlorines in the presence of oxygen as:



Kinetic studies of the above reaction for GdOCl and NdOCl were performed by using a non-isothermal thermogravimetric (TG) method [5,6]. Detailed kinetics of a dechlorination and oxidation

of PrOCl have not been reported in the literature as yet. A non-isothermal TG study has an advantage in that a wide range of temperatures are covered with a single experiment [7–9]. This study investigated the kinetics of a thermal dechlorination and oxidation of PrOCl by using a non-isothermal TG method. The objectives of this study were to establish a detailed kinetic model and the kinetic parameters of the dechlorination and oxidation reaction of PrOCl under high-temperature oxidizing atmospheres. The results of this study will be used to determine the operating conditions for a thermal treatment furnace for the dechlorination and oxidation of PrOCl.

2. Experimental methods

2.1. Synthesis and analysis of PrOCl and its thermal oxidation products

Powdered PrOCl was synthesized in LiCl–KCl eutectic molten salt. The experimental apparatus for synthesizing the PrOCl is found elsewhere [5,6]. Anhydrous PrCl_3 with a purity of 99.99% was premixed with a LiCl–KCl solid salt with a purity of 99.9% (LiCl: 44.2 wt.%, eutectic point: 633 K) in an alumina crucible. The crucible containing the mixture was heated up to 723 K in a stainless-steel column and oxygen was sparged into it from the bottom. After a 10-h oxygen sparging, the mixture of the precipitate was sampled and dissolved in distilled water. A pure sample powder of PrOCl was then obtained by a vacuum filtration. SEM (Leo 1455VP; KBSI) photographs of the obtained PrOCl powder and its thermal oxidation product, PrO_2 powder, are shown in Fig. 1. Speciation of the

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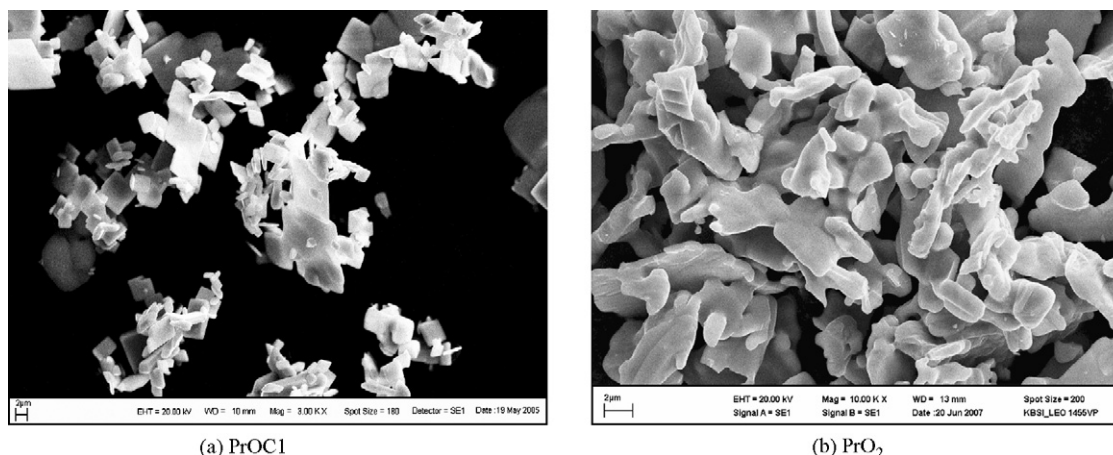


Fig. 1. SEM photograph of synthesized PrOCl (a) and its post-TG product, PrO₂ (b).

obtained samples before and after a thermal oxidation was performed by a powdered XRD (D8 Advance; KBSI) pattern analysis and the results are shown in Fig. 2.

2.2. TG analysis

Non-isothermal TG analyses by using TG/DTA (SDT-2960, TA instruments Inc.) were performed from room temperature to 1673 K. The temperature of the furnace was programmed to rise from room temperature to 1073 K with a heating rate of 50 K min⁻¹. About 15 mg of the obtained powdered PrOCl was loaded onto the platinum sample pans on the TG furnace. After an initial rapid heating, the furnace was slowly heated from 1073 to 1673 K with heating rates of 2.5, 5, 7.5 and 10 K min⁻¹. At each heating rate condition, four oxygen partial pressures were tested: $P_{O_2} =$

21, 50, 75 and 100 kPa and the remainder consisted of pure nitrogen ($P_{N_2} = 99.9$ kPa).

3. Results and discussion

3.1. Conversion patterns of the PrOCl

The conversion as a function of the temperature of the PrOCl powders at different heating rates under a fixed O₂ condition and

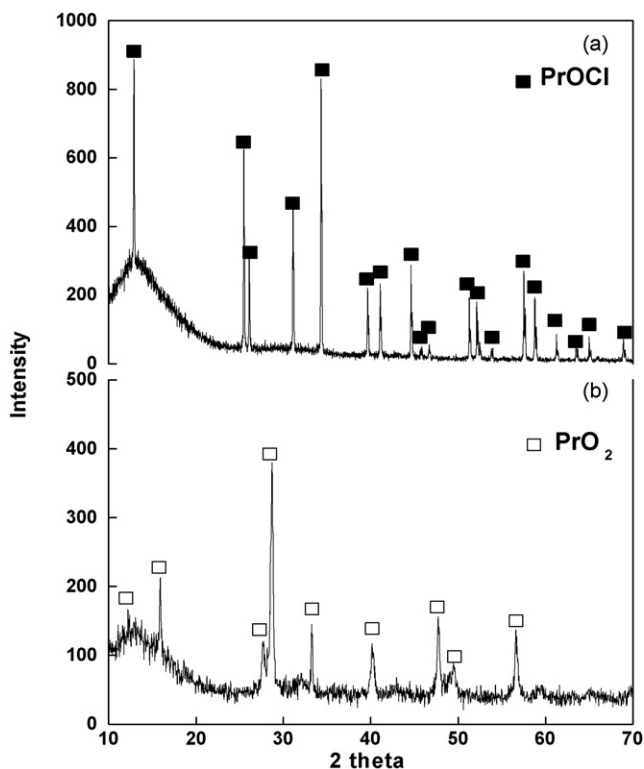


Fig. 2. Powdered XRD patterns of synthesized PrOCl (a) and its post-TG product, PrO₂ (b).

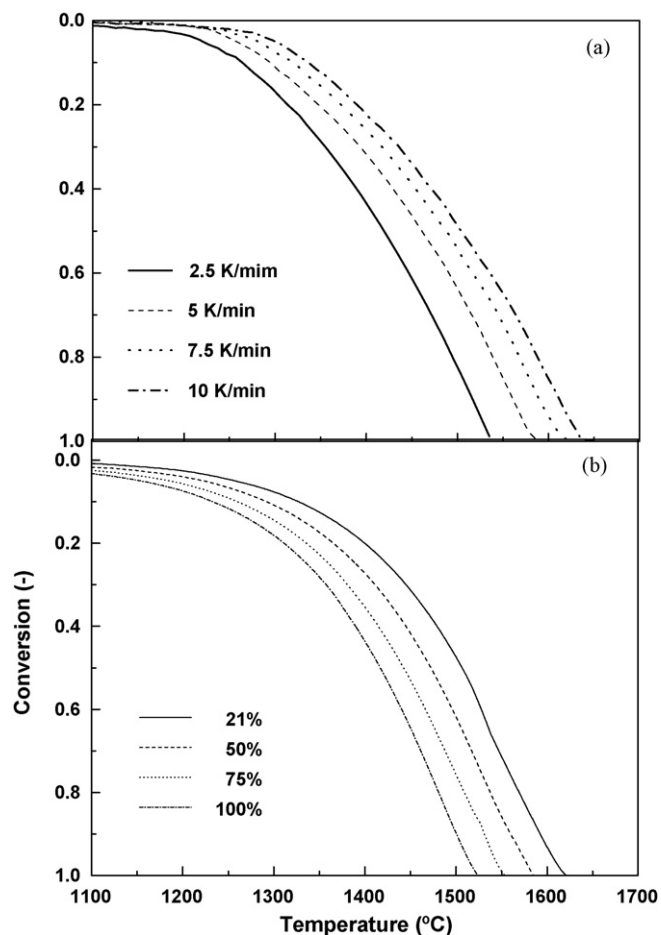


Fig. 3. Typical mass loss patterns of PrOCl at various heating rates under a fixed oxygen partial pressure ($P_{O_2} = 50$ kPa) (a) and at a fixed heating rate (5 K min⁻¹) under various O₂ partial pressures (b).

Table 1

Kinetic model equations examined in this study.

No.	Symbol	Reaction model	$f(\alpha)$	$g(\alpha)$
Avrami–Erofeev				
1	A1/2	$n = 0.5$	$(1/2)(1-\alpha)[- \ln(1-\alpha)]^{-1}$	$[- \ln(1-\alpha)]^2$
2	A3/2	$n = 1.5$	$(3/2)(1-\alpha)[- \ln(1-\alpha)]^{1/3}$	$[- \ln(1-\alpha)]^{2/3}$
3	A2	$n = 2$	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
4	A3	$n = 3$	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
5	A4	$n = 4$	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
Phase boundary controlled reaction				
6	R1	Contracting linear	1	α
7	R2	Contracting area	$2(1-\alpha)^{1/2}$	$1 - (1-\alpha)^{1/2}$
8	R3	Contracting volume	$3(1-\alpha)^{2/3}$	$1 - (1-\alpha)^{1/3}$
Diffusion				
9	D1	One-dimensional	$(1/2)\alpha$	α^2
10	D2	Two-dimensional	$1/[- \ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha) + \alpha$
		Three-dimensional		
11	D3	Jander equation	$3(1-\alpha)^{1/3}/2[1 - (1-\alpha)^{1/3} - 1]$	$[1 - (1-\alpha)^{1/3}]^2$
12	D4	Ginstling–Brounshtein	$(3/2)[(1-\alpha)^{-1/3} - 1]$	$(1 - 2\alpha/3) - (1-\alpha)^{2/3}$
Power law				
13	P1	$n = 1/4$	$4\alpha^{3/4}$	$\alpha^{1/4}$
14	P2	$n = 1/3$	$3\alpha^{2/3}$	$\alpha^{1/3}$
15	P3	$n = 1/2$	$2\alpha^{1/2}$	$\alpha^{1/2}$
16	P4	$n = 3/2$	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
Chemical reaction				
17	F1	First order	$1 - \alpha$	$-\ln(1-\alpha)$
18	F3/2	Three-halves order	$(1-\alpha)^{2/3}$	$2[(1-\alpha)^{-1/2} - 1]$
19	F2	Second order	$(1-\alpha)^2$	$(1-\alpha)^{-1} - 1$
20	F3	Third order	$(1-\alpha)^3$	$(1/2)[(1-\alpha)^{-2} - 1]$

those at a fixed heating rate under different O₂ conditions are plotted in Fig. 3. Increasing the heating rate or decreasing the gaseous oxygen concentration resulted in a decrease in the conversion rate. This indicates that the conversion of PrOCl into PrO₂ is an oxygen-dependent endothermic reaction.

3.2. Model free analysis

Dechlorination and oxidation reaction for PrOCl can be described with an Arrhenius equation and a power law approach, respectively. The reaction rate is thus described as:

$$\frac{d\alpha}{dt} = k_0(P_{O_2})^n \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (1)$$

where α is the extent of a conversion, k_0 the reaction rate constant ($s^{-1} Pa^{-n}$), P_{O_2} the oxygen partial pressure (Pa) and n the power dependency of the oxygen partial pressure. The function $f(\alpha)$ is the reaction model which represents the influence of an extent of conversion on the conversion rate. Widely used models for solid-state reactions are listed in Table 1 [6]. Rearranging Eq. (1) and integrating both sides of the equation gives,

$$g(\alpha) = \frac{ZE}{BR}p(y) \quad (3)$$

in which $g(\alpha)$ is the result of an integral on the left hand side of Eq. (2), $Z = k_0(P_{O_2})^n$, and $p(y)$ is a function of the temperature integral on the right hand side of Eq. (2):

$$p(y) = \int_{y_0}^{y_c} \frac{e^{-y}}{y^2} dy = \frac{e^{-y}}{y^2} + \int_{y_0}^{y_c} \frac{e^{-y}}{y} dy \quad (4)$$

in which $y = -E/RT$ [11–14]. A simple mathematical treatment provides the activation energy of the reaction as [10,15]:

$$E = \frac{-R}{1.001450} \left(\frac{d \ln(B/T^{1.894661})}{d(1/T)} \right) \quad (5)$$

Obtained TG data was analyzed to determine the activation energy for different levels of a conversion by using Eq. (5). Slopes of the regression lines in the conversional plots [5,6] were used to calculate the activation energy at each conversion degree. Determined activation energies for all the different conditions are plotted in Fig. 4. It was observed from Fig. 4 that the activation energy was not really changed and nearly independent with respect to the level of a conversion. This suggests that the dechlorination and oxidation reaction of PrOCl follows a single step reaction. Mean value of activation energy was determined as 112.6 ± 3.4 (standard deviation) $kJ mol^{-1}$. It should be noted that these results were obtained without any knowledge of the reaction model $f(\alpha)$.

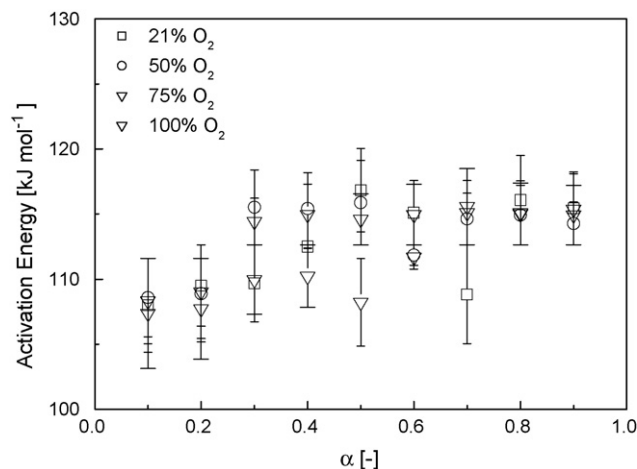


Fig. 4. Determined activation energy of the dechlorination and oxidation of PrOCl under different oxygen partial pressures, as a function of conversion.

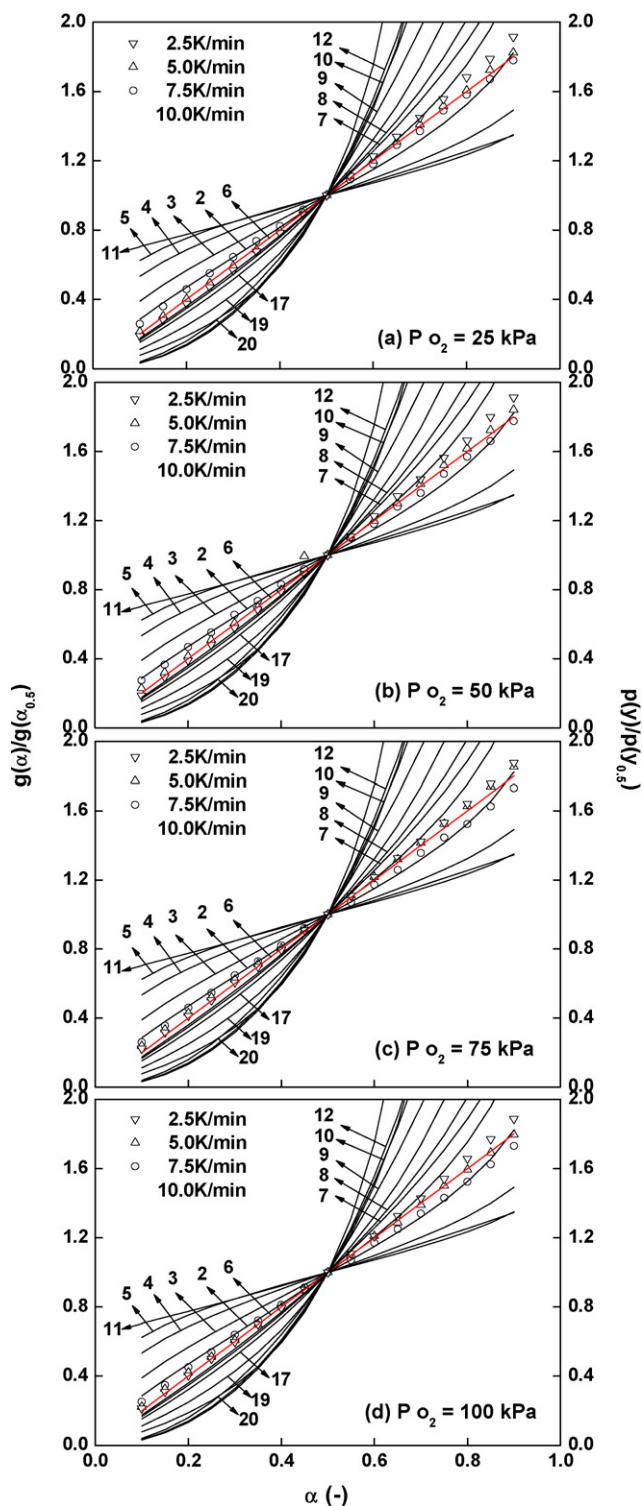


Fig. 5. Master plots of theoretical $g(\alpha)/g(\alpha_{0.5})$ against α for various reaction models (solid lines, as enumerated in Table 1) and experimental values of $p(y)/p(0.5)$ for different O_2 conditions (symbols).

3.3. Kinetic model determination

Following the evaluation of the activation energy, a conversion model was determined by means of master plots methods. By using the determined value of the activation energy E as a function of α for all the different conditions, the experimental master plots were constructed according to Eq. (4) as shown in Fig. 5. The theoretical

master plots of the various kinetic functions listed in Table 1 are also plotted as solid lines in Fig. 5. The plots related to different heating rates under various oxygen partial pressures are practically identical. The comparison of the experimental master plots with the theoretical ones indicates that none of the existing theoretical master plots matched the experimental ones perfectly. An acceptable kinetic model was selected based on the standard deviation (S.D.);

$$S.D. = \sqrt{\frac{\sum_j^n \sum_i^m [g_k(\alpha_i)/g_k(0.5) - p_j(y_i)/p_j(y_{0.5})]^2}{(n-1)(m-1)}} \quad (6)$$

where m and n are the numbers of points and heating rates, respectively [6]. The A2 and R1 models appear to be appropriate models for describing the reaction because they had smaller S.D. values, when compared to other models. Determined S.D. values of the model A2 and R1 were 1.43 and 0.949, respectively. Fisher F -tests, for the variances of models A2 and R1, were used to determine if two models were significantly different. Based on the standard deviations, variances were determined as 2.045 and 0.900 for models A2 and R1, respectively. Determined F value was 2.272. As shown in Fig. 5, both sample groups have the same sample size of 272 and the degree of freedom was 271. For this case, the critical reason for a rejection of the null hypothesis starts at a value of 1.22 for a 95% level of confidence. Thus the R1 and A1 models do not fail the 95% of confidence test that they are significantly different. Finally, the R1 model, a linear-contracting phase boundary reaction ($g(\alpha) = \alpha$), could be selected as an acceptable kinetic model for a ProCl dechlorination and oxidation.

By introducing the determined reaction model, $g(\alpha) = \alpha$, into Eq. (3), Eq. (6) is obtained.

$$\alpha = \frac{ZE}{BR} p(y) \quad (6)$$

The plots of $g(\alpha)$ against $(E/BR)p(y)$ for all the different conditions are presented in Fig. 6 and the determined Z values obtained by the linear regressions of all the data are shown in Table 2. All the plots fitted well linearly and all the linear regression coefficients were over 0.994. These results indicated that determined kinetic model, $g(\alpha) = \alpha$ is in agreement with all experimental data. Increasing values of Z with an increasing oxygen partial pressure indicated that the oxidizing atmosphere enhances the dechlorination reaction of ProCl.

4. Conclusion

The kinetics of the thermal dechlorination and oxidation reaction of ProCl powder originating from a molten salt process could

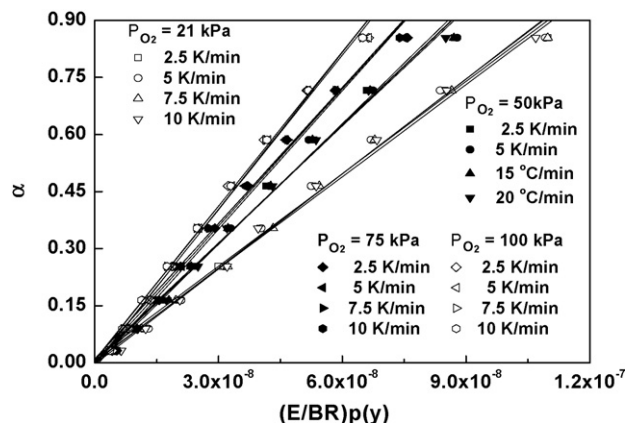


Fig. 6. Plot of $g(\alpha)$ against $(E/BR)p(y)$ for different O_2 conditions.

Table 2
Results of linear regression of the plot α vs. $(EP(y)/BR)$.

O ₂ condition	Heating rate (°C min ⁻¹)	$Z \times 10^6$ (min ⁻¹)	r
21% O ₂	5	8.2779	0.9974
	10	8.1294	0.9972
	15	8.2921	0.9955
	20	8.2471	0.9960
50% O ₂	5	10.462	0.9971
	10	10.462	0.9952
	15	10.374	0.9944
	20	10.437	0.9949
75% O ₂	5	12.106	0.9974
	10	12.055	0.9977
	15	11.991	0.9963
	20	11.863	0.9950
100% O ₂	5	13.657	0.9982
	10	13.666	0.9983
	15	13.451	0.9971
	20	13.531	0.9957

Z is the slope and r is linear regression coefficients.

be established by using non-isothermal TG analyses under various oxygen partial pressures. The conversion of PrOCl into PrO₂ started at over around 1100 K. The conversion appeared to be an oxygen-dependent endothermic and a single step reaction. The dechlorination and oxidation reaction of PrOCl followed a single step with an activation energy of 112.6 ± 3.4 kJ mol⁻¹, and from master plot methods, the reaction was described by a linear-contracting phase boundary reaction.

Proper treatment conditions of the furnace for obtaining pure rare earth oxides from the by-products of an electrochemical separation process of rare earth ores are given in this study. More

oxidizing atmosphere enhances the dechlorination reaction of PrOCl. The furnace should be maintained with at over around 1100 K and a proper external heating capacity must be provided for maintaining this temperature and supplying the required energies for the conversion determined in this study.

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