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Synthesis of cordierite by dolomite and kaolinitic clay chlorination. Study of the phase transformations and reaction mechanism

P. Orosco [a,b,*], M. del C. Ruiz [a], J. González [a,c]

[a] Instituto de Investigaciones en Tecnología Química (INTEQUI–CONICET), Chacabuco y Pedernera, 5700, San Luis, Argentina
[b] Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, Chacabuco y Pedernera, 5700 San Luis, Argentina
[c] Instituto de Ciencias Básicas, Universidad Nacional de Cuyo, Parque General San Martín, 5500 Mendoza, Argentina

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ABSTRACT

The focus of analysis in this work has been the study of the synthesis of cordierite using a pyrometallurgical route which involved thermal treatment in a chlorine atmosphere of a kaolinitic clay and dolomite mixture as raw material. The reaction mechanism was also investigated. Isothermal and non-isothermal chlorination assays were conducted in experimental equipment adapted for working in corrosive atmospheres. The temperature effect on the reactions yielding cordierite were studied. Both reagents and products were analyzed by X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA). The experimental results have shown that cordierite starts to be produced at 700 °C, and that the elimination of iron, which is present as an impurity, begins at about 700 °C. The most favorable chlorination temperature was 900 °C, since at this temperature a selective production of cordierite and an efficient elimination of iron were achieved.

1. Introduction

Cordierite is a magnesium aluminosilicate composed of a ternary system of oxides ($MgO:Al_2O_3:SiO_2$) in a 2:2:5 ratio. In nature, it generates as a product of the thermal metamorphosis of clay rocks; crystallizes in an orthorhombic system, and it has a pseudo-hexagonal habit; its density is 2.53 g/cm^3, and its fusion point is 1470 °C [1–3].

This ceramic material has been the focus of attention over the last years due to its properties, such as low thermal expansion coefficient, low dielectric constant, low dielectric loss, high specific resistivity, high thermal shock resistance, and high temperature stability. These properties make cordierite an ideal material for use in the electronic industry [4,5]. One of the most significant applications of cordierite is as catalysts support in diverse processes, some of which can be found in the petrochemical industry, the selective reduction of alcohol, the control of automobile emissions, and the control of volatile organic compounds.

Cordierite is a mineral which is not abundant, or pure enough in nature; for this reason, it is necessary to synthesize it. The typical processes for cordierite synthesis are: sol–gel technique, glass crystallization technique, and reactions in solid state. The latter two techniques use natural mineral resources as raw material [5,6]. In industry, the production of cordierite is carried out by the process of reactions in solid state.

Several investigations [7–11] have been conducted in the last two decades with the aim of reducing the formation temperature of cordierite. These studies were carried out with the purpose of reducing the cost of processing, and improving the properties of cordierite. To this end, auxiliary minerals such as bismuth oxide and phosphorus pentoxide were used in the process of reactions in solid state [7,8]. The sol–gel method using aluminum acetate gel, tetraethyl orthosilicate, magnesium acetate solution, ethanol and phenol–formaldehyde resin [9] and non-hydrolytic sol–gel route [10] were investigated. Also the mechanical activation method to reduce the formation temperature of cordierite has been reported [11]. However, cordierite has not been possible to synthesize below 1000 °C by using the above mentioned methods so far.

A few researchers have been able to produce the pure cordierite phase, but only by using high synthesis temperatures which range from 1300 °C to 1400 °C [3,4]. Different studies [5,12–14] have shown that cordierite can be crystallized at about 950 °C by using the glass crystallization technique. However, this technique requires an additional energetic cost for the previous treatment applied to the raw materials with the aim of melting the precursors.

The presence of some impurities increases the thermal expansion coefficient and confers the color to the cordierite. Iron which is generally present in cordierite is one of the main elements increasing the thermal expansion coefficient, and it is also responsible for giving the material an undesirable reddish color, as well as for reducing its refractory properties [15,16]. Vitreous silica formed during the processing of phyllosilicates (talc, kaolin, kaolinitic clay, etc.), which are generally used for obtaining cordierite, also produces a considerable increase in

* Corresponding author at: Instituto de Investigaciones en Tecnología Química (INTEQUI-CONICET), Chacabuco y Pedernera -5700- San Luis, Argentina. Tel: +542664426711; fax: +542664426711.
E-mail address: porosco@unsl.edu.ar (P. Orosco).

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the thermal expansion coefficient [6,17]. Therefore it is necessary to remove or to avoid the presence of iron and vitreous silica.

The pyrometallurgic process of chlorination can be used to reduce the temperature of cordierite synthesis and eliminate the impurities which affect the thermal expansion coefficient, color and refractory properties. This method has been effectively used in the extraction of various metals from oxides and minerals in the last decades. This is due to the high reactivity of the chlorinating agent, the selectivity of the reaction, the simple treatment of effluents, and the low cost of the processes. Further, various studies have reported the effect of thermal treatment in chlorine atmosphere on the phase transformations of some materials, such as oxides and minerals, as well as the fact that the formation of intermediate chlorinated compounds favors the generation of products whose obtention by other means requires a more energetic treatment [18–20]. Although this information, there are no bibliographic data about the cordierite synthesis by mixture of minerals chlorination.

The previous studies referred to phase transformations during the thermal treatments of the chlorination of refractory clays and talc provided important information to investigate the synthesis of cordierite from the mixture of kaolinitic clay and dolomite [21,22].

This study has been devoted to studying the mechanism of chlorination of a mixture of kaolinitic clay and dolomite with chlorine gas in order to synthesize cordierite. The phase transformations occurring during the chlorination were also investigated. The knowledge of the process that occurs when the mixture is calcined in Cl_2 is crucial to optimize the synthesis of cordierite and improve the properties of this ceramic material. This study was done in order to reduce the working temperature of cordierite synthesis, exploit Argentinian natural resources, and eliminate the impurities that affect the thermal expansion coefficient, color, and refractory properties.

2. Materials and methods

2.1. Materials

The solid reagent used in the synthesis of cordierite by chlorination was a mixture of dolomite and kaolinitic clay, both of Argentine origin. The mixture of these minerals, denominated M, was prepared in a ratio of the 70% w/w of kaolinitic clay and 30% w/w of dolomite. This ratio was selected taking into account the stoichiometric composition of the cordierite and the impurities contained in the starting minerals. The preparation of the mixture was made in a disk mill, and the mixing time was 4 min.

Table 1
Chemical composition (w/w%) of the starting minerals and the M sample.

	Mineral		Sample
	Kaolinitic clay	Dolomite	M
Al_2O_3	28	–	20
SiO_2	53	–	36
Fe_2O_3	3.5	–	2.5
CaO	1.3	33.2	8.6
MgO	1.2	19.5	7.2
TiO_2	0.7	-	0.5
LOI	11.85	48.23	14.2

The primary minerals which are present in the mixture under study were identified by X-ray diffraction (XRD). The diffractogram of the mixture of dolomite and kaolinitic clay (Fig. 1) shows the presence of kaolinite (JCPDS 89–6538), dolomite (JCPDS 89–5862), calcite (JCPDS 86–2340) and quartz (JCPDS 89–8939).

The chemical composition of the minerals and the M sample were determined by X-ray fluorescence (XRF). The results obtained are presented in Table 1. The table shows that the mixture contains iron, which comes from the impurities of the clay. Iron can be found as either a phase separate from kaolinite or adsorbed on its surface as colloidal iron in the form of hematite (Fe_2O_3), limonite (FeOOH), or ferric hydroxide ($Fe(OH)_3$) [19,21].

In order to determine some of the mineral phases of iron present in the mixture, an analysis was performed by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

SEM image obtained with back-scattered electrons is shown in Fig. 2. The brilliant particle indicated with an arrow was analyzed by EPMA (Table 2). The composition of hematite has also been reported in the table with comparative purpose. The composition of this particle suggests that it is probably a hematite particle.

The gasses used in the different assays were chlorine 99.5% v/v as reactive gas, provided by Cofil, and nitrogen 99.99% v/v as diluent and purge gas, provided by Air Liquid.

2.2. Equipment

The experimental chlorination assays were performed in a thermogravimetric system designed in our laboratory [23]. The dispositive is provided of a reactor of quartz placed inside an electric furnace equipped with a temperature controller. The sample was contained in a quartz

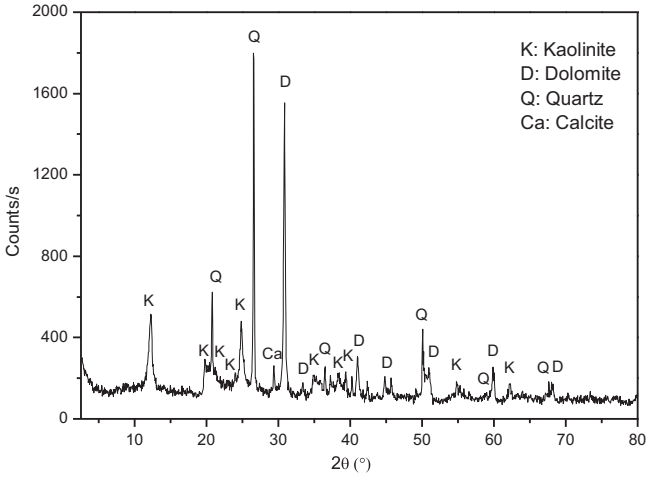

Fig. 1. Diffractogram of the M sample.

Fig. 2. SEM micrograph corresponding to particles of the M sample.