Journal of Alloys and Compounds 480 (2009) 702–705

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Solution combustion synthesis of α-cordierite

Robert Ianoş*, Ioan Lazău, Cornelia Păcurariu

"Politehnica" University of Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, P-ţa Victoriei no. 2, Timişoara 300006, Romania

ARTICLE INFO

Article history:
Received 3 December 2008
Received in revised form 31 January 2009
Accepted 7 February 2009
Available online 20 February 2009

Keywords:
Ceramics
Chemical synthesis
Thermal expansion
X-ray diffraction

ABSTRACT

The preparation of α-cordierite powders via combustion route was investigated. Urea, monoethanolamine and triethylenetetramine were used as fuels. The resulting powders were characterized by means of thermal analysis and XRD. Experimental results showed that SiO_2 behaves as an inert material, preventing the formation of $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ directly from the combustion reaction. Using a fuel mixture of urea and monoethanolamine yielded a poorly crystalline powder ($MgAl_2O_4$). The phase composition of powders after annealing at various temperatures has shown that the formation of α-cordierite occurs indirectly, via the solid state reaction of spinel and cristobalite. After annealing at 1300 °C for 1 h α-cordierite is virtually the only crystalline phase in the sample obtained with triethylenetetramine. In the sample prepared by using urea and monoethanolamine fuel mixture α-cordierite is the main crystalline phase, alongside traces of spinel and cristobalite. The intermediate formation of μ-cordierite was not observed.

1. Introduction

The general term of cordierite refers to solid solutions in the $MgO–Al_2O_3–SiO_2$ ternary system, which has a stoichiometry ranging from $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ to $MgO{\cdot}Al_2O_3{\cdot}3SiO_2$. The properties of these solid solutions are mainly determined by their chemical composition. From this point of view, $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ is one of the most commonly used compositions [1]. $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ melts incongruently at 1460 °C turning into mullite and a liquid phase. Cordierite has two allotropic modifications:

- α-cordierite, also known as indialite, which has a hexagonal symmetry and crystallizes above 1000 °C; this high temperature polymorph form may be found in nature as well as in various ceramic products [2];
- β-cordierite has a rhombic symmetry and crystallizes below 950 °C; González-Velasco et al. [3] mentioned that an intermediate structure between α-cordierite and β-cordierite exists;

Besides the two genuine polymorph modifications of cordierite, the existence of μ-cordierite (a meta-stable modification) is also reported in the literature [4]. μ-Cordierite is not an authentic allotropic modification of cordierite, but rather a high-quartz derivative solid solution resulting from the partial substitution of Si^{4+} by Li^{+}, Mg^{2+}, Al^{3+}. Usually, the complete transformation of μ-cordierite → α-cordierite takes place above 1100 °C [4].

μ-Cordierite may be prepared by glass devitrification, below 925 °C. Melscoet-Chauvel et al. [5] reported the positive effect of CeO_2, which inhibits the crystallization of μ-cordierite and enables the formation of α-cordierite. Chen [6] found that the replacement of MgO by CaO in the glass–ceramics fired at 900 °C also enables the crystallization of α-cordierite, whereas μ-cordierite becomes the secondary crystalline phase. Marghussian et al. [7] concluded that the mixture of V_2O_5 and BaO acts as an effective nucleation agent in the crystallization of cordierite glass–ceramics, promoting the crystallization of α-cordierite.

Among all its polymorph modifications, α-cordierite exhibits several valuable properties (excellent thermal shock resistance, refractoriness, electric insulator etc.) and it is widely used for: components for internal combustion engines, refractory coatings, electric insulators, microelectronic components, indialite glass–ceramics, membranes with micro-filtration function, retention filters for solid particles, missile nose cone material etc. [8–10]. One of the most important applications of cordierite aims the production of honeycomb catalysts for reducing the emissions of motor vehicles [11]. Moreover, cordierite is used as catalytic support in the petrochemical industry for selective reduction of nitrogen oxides, selective hydrogenation of alcohols, control of volatile organic compounds [3,5,12].

Overall, the production of low-porosity cordierite materials involves the synthesis of cordierite powder with favorable sintering behavior. On the other hand, the difficulty of obtaining single-phase α-cordierite powders represents a well-known issue. Mainly this is due to the fact that the annealing product of commonly used raw materials shows a complex phase composition consisting of cordierite – in one of its polymorph varieties – several crystalline byproducts (mullite, corundum, spinel, forsterite, clinoenstatite,

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* Corresponding author. Tel.: +40 256 404167.
E-mail address: robert_ianos@yahoo.com (R. Ianoş).

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doi:10.1016/j.jallcom.2009.02.022

cristobalite) and even a vitreous phase [13]. Moreover, the sintering of cordierite powders without any additives is an additional difficulty that originates in the narrow range of vitrification [14]. Because of this narrow range, products are prone to distortion during sintering and the resulting product has lower thermal shock resistance due to the occurrence of vitreous phase [15].

The traditional methods of cordierite powder preparation rely on annealing of suitable material mixtures (talc, clay, gibbsite, alumina, magnesite) above 1300 °C [16], or crystallization of some glasses having an appropriate composition [4,6,7]. Kurama and Kurama [17] used rice husk as raw material for the cordierite synthesis; they concluded that the formation of α-cordierite takes place at 1365 °C and is preceded by the intermediate formation of spinel and cristobalite. Chen et al. [18] prepared single-phase α-cordierite powders by annealing at 1400 °C for 5 h a stoichiometric mixture of MgO, Al_2O_3 and SiO_2.

Ribeiro et al. [19] obtained cordierite based ceramic materials by annealing (1350 °C) a mixture of diatomite, talc and industrial Al-rich sludge derived from the wastewater treatment of the aluminum anodizing process.

Due to the numerous difficulties related to the ceramic method, many researchers have resorted to the use of chemical synthesis methods in order to reduce the synthesis and sintering temperature of α-cordierite: precipitation [20], spray drying [21], pechini [22], emulsion processing [23], sol–gel [24], plasma spraying [25], combustion synthesis [26,27].

In this context, the aim of the present work is a study of the solution combustion synthesis of α-cordierite using new organic fuels. The inherent difficulties of cordierite formation via solid state reactions are discussed and an overcoming solution is suggested.

2. Experimental

Merck raw materials were used: $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, urea (CH_4N_2O), monoethanolamine (C_2H_7NO) and triethylenetetramine ($C_6H_{18}N_4$). Commercial Syloid with a BET specific surface area of 330 m^2/g was used as SiO_2 source. Stoichiometric metal nitrate/fuel ratios were used in all recipes (Table 1).

The starting raw materials were dissolved in warm distilled water (70 °C) under continuous stirring using a magnetic stirrer. Later on, the capsules with the concentrated solution were placed in the electric furnace preheated at 300 °C (samples 1 and 3), or directly at 1200 °C (sample 2) in order to initiate the combustion reaction.

After combustion reactions reached an end, the voluminous resulting powders were easily crumbled and then subjected to annealing at 900 °C, 1200 °C and 1300 °C with a soaking time of 1 h. No crumbling operation was performed in the case of sample 2.

Phase composition of the powders was established by X-ray diffraction, using a Bruker D8 Advance System ($Cu_{K\alpha}$ radiation). The heating behavior of samples was studied by thermal analysis using a Mettler Toledo instrument. The investigated temperature range was 25–800 °C. Thermal analysis were performed in alumina crucibles and static atmosphere (air) using a heating rate of 10 °C/min.

3. Results and discussion

The selection of the three recipes was done considering the premises, which represent the basis of cordierite formation. The ideal case would be that the cordierite formation takes place directly from the combustion process (1), without any additional thermal treatment.

Table 1
Recipes designed for solution combustion synthesis of cordierite.

Sample	Sample composition (molar ratio)						T_f[a] (°C)
	$Mg(NO_3)_2$	$Al(NO_3)_3$	SiO_2	CH_4N_2O	C_2H_7NO	$C_6H_{18}N_4$	
1	2	4	5	10	20/13	–	300
2	2	4	5	10	20/13	–	1200
3	2	4	5	–	–	80/21	300

[a] Furnace temperature used for the ignition of combustion reaction.

Table 2
Experimental observations concerning the evolution of combustion reactions.

Sample	Reaction time (s)	Combustion type	Powder color
1	60	Flame combustion	White
2	40	Flame combustion	White
3	600	Smoldering combustion	Black

$$2Mg(NO_3)_2 + 4Al(NO_3)_3 + 5SiO_2 + (20/13)C_2H_7NO + (10)CH_4N_2O \rightarrow Mg_2Al_4Si_5O_{18} + (170/13)CO_2 + (330/13)H_2O + (233/13)N_2 \quad (1)$$

However, this hypothesis is not very plausible, since SiO_2 (Syloid) is redox inert. As result, SiO_2 does not participate in the redox processes but acts as ballast, decreasing the temperature reached during the combustion reaction. In order to counteract the disadvantage of using redox inert SiO_2, a fuel mixture of urea and monoethanolamine (molar ratio 13:2) was used in samples 1 and 2, which is supposed to ensure the most exothermic combustion reaction. Our previous results have shown that starting from $Mg(NO_3)_2$, $Al(NO_3)_3$ (molar ratio 1:2) and a mixture of urea and monoethanolamine (molar ratio 13:2) leads to the formation of pure and well crystallized $MgAl_2O_4$ directly from the reaction of combustion [28].

In the case of sample 1 the combustion process was very energetic and lasted for about 60 s (Table 2), leading to the formation of a white and very voluminous powder. The strong exothermic nature of the combustion reaction is also confirmed by thermal analysis (Fig. 1). The endothermic effect (136 °C) accompanied by a weight loss can be attributed to the aluminum nitrate and urea partial decomposition. The two exothermic peaks present on the DTA curve suggest a two-stage combustion process. At 176 °C the combustion reaction aluminum nitrate and urea occurs, which stimulates the redox reaction of magnesium nitrate and monoethanolamine (290 °C).

The general profile of the XRD pattern of the powder resulting from the combustion reaction indicates a predominantly amorphous character (Fig. 2). However, the two less intense and very wide peaks suggest the intermediate formation of spinel, $MgAl_2O_4$. After annealing at 900 °C for 1 h, new amounts of $MgAl_2O_4$ are generated and the crystallization of SiO_2 (α-quartz) occurs. The XRD pattern of the powder thermally treated at 1200 °C for 1 h proves that a mixture of α-cordierite, spinel and cristobalite was formed (Fig. 2).

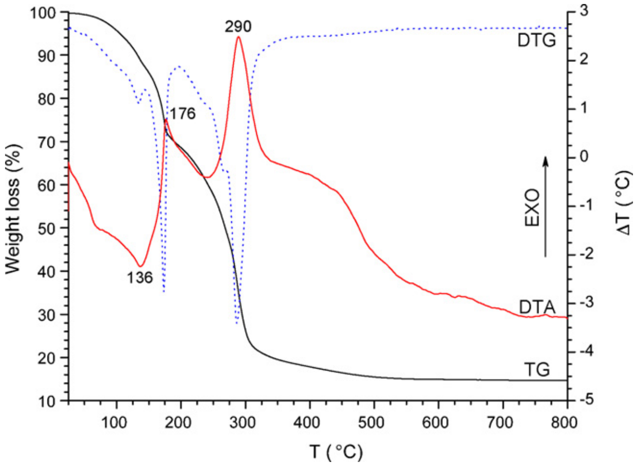

Fig. 1. Thermal analysis of the precursor mixture 1, consisting of magnesium nitrate, aluminum nitrate, Syloid, urea and monoethanolamine.

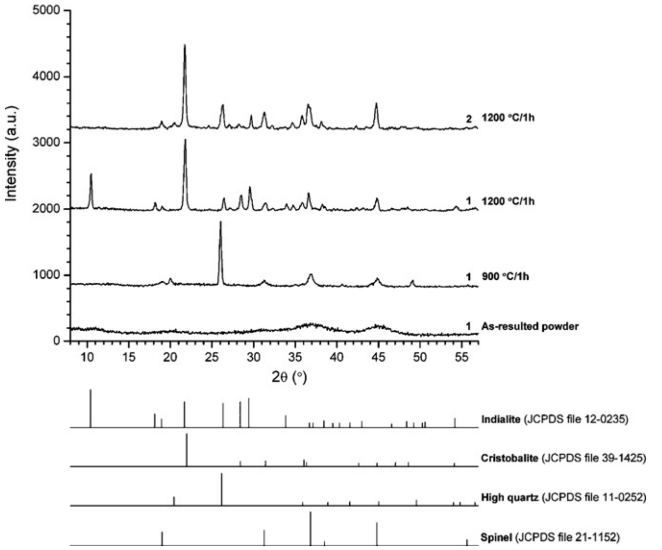

Fig. 2. XRD patterns of powders 1 and 2 after annealing at various temperatures.

In this context becomes clear that the formation of α-cordierite occurs indirectly, via the solid state reaction (2) of spinel and cristobalite, which is consistent with the results reported by other authors [8,13].

$$2MgAl_2O_4 + 5SiO_2 \rightarrow Mg_2Al_4Si_5O_{18} \quad (2)$$

Since the formation of α-cordierite (indialite) takes place at about 1200 °C, in the case of sample 2 the initiation of the combustion reaction was done by placing the capsule containing the same raw materials as in sample 1 in the preheated oven (1200 °C) followed by a heat treatment of 1 h at the same temperature. By igniting the combustion reaction in the preheated oven (1200 °C) the heat loss is minimized, whereas the combustion temperature increases and gets closer to the adiabatic temperature.

In addition, a number of unwanted processes and phenomena which usually occur during solid state reactions (recrystallization, grain growth, healing of structural defects and improving the crystalline degree, residual stress elimination—all of these being done on the expense of the final powder reactivity) would be considerably minimized or even avoided.

In the case of sample 2, the combustion reaction was faster and more vigorous than the one in the case of sample 1; the capsule broke due to the thermal shock. After combustion reaction was over, the capsule with the resulting powder was left for 1 h in the preheated oven at 1200 °C. The phase composition of the annealed sample consisted mainly of cristobalite and spinel (Fig. 2). The diffraction peaks of indialite (α-cordierite) were practically missing (Fig. 2). The other small diffraction peaks might be attributed to some magnesium silicates species. This behavior can be explained by the very large volume of the powder resulting from the combustion process, which is responsible for diminishing the contact area between the SiO_2 grains and the $MgAl_2O_4$ grains. As a matter of fact the volume of the powder produced from the combustion process was approximately 18 times larger than the volume occupied by the same powder but after crushing.

Because of the α-cordierite formation mechanism – that is the solid state reaction of spinel and cristobalite – the intermediate formation of a more reactive spinel phase, with higher surface area, which should provide a larger contact area with respect to the SiO_2 grains was aimed. Considering that triethylenetetramine is able to generate after annealing at 700 °C spinel powders with specific surface area as high as 175 m^2/g [29], in the case of sample 3 triethylenetetramine was used as sacrificial fuel (reaction (3)).

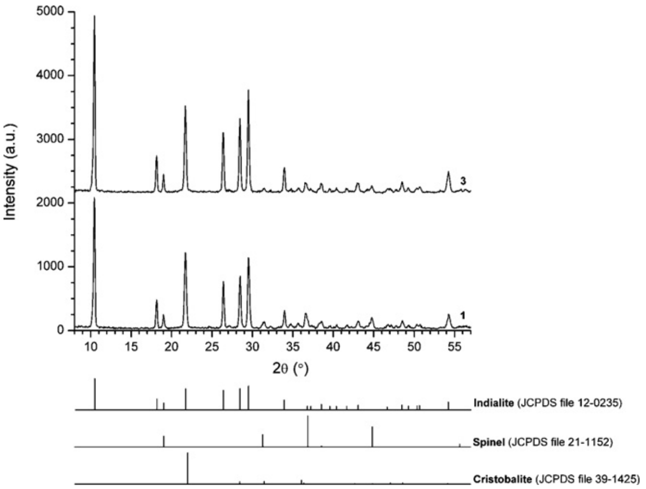

Fig. 3. XRD patterns of powders 1 and 3 after annealing at 1300 °C for 1 h.

$$2Mg(NO_3)_2 + 4Al(NO_3)_3 + 5SiO_2 + (40/21)C_6H_{18}N_4 \rightarrow Mg_2Al_4Si_5O_{18} + (80/7)CO_2 + (120/7)H_2O + (248/21)N_2 \quad (3)$$

In this case the combustion reaction evolved as a smoldering process and a gray amorphous powder was obtained. Remarkably, after crushing and annealing at 1300 °C for 1 h the phase composition of the powder consisted primarily of indialite (α-cordierite), alongside small traces of spinel and cristobalite (Fig. 3).

Comparing the intensities of the 100% peak of indialite (10.42°) once can conclude that that sample 3 presents a much better crystallized indialite. The intensity ratio between sample 3 ($I_{100} = 2804$) and sample 1 ($I_{100} = 2088$) after annealing at 1300 °C for 1 h (Fig. 3) was 1.34. This observation is consistent with the fact that the peaks of cristobalite and spinel (see the peak intensity from 36.85°, 44.83° and 31.27°) are more intense in the case of sample 1, which suggests the presence of a larger amount of unreacted cristobalite and spinel.

4. Conclusions

Regardless of the selected fuel, α-cordierite could not be prepared directly from the combustion reaction. Mainly this was the result of two factors: the presence of SiO_2, which is inert in terms of redox behavior; the short reaction time and/or the insufficient combustion temperature. As a consequence, the formation of α-cordierite requires additional thermal treatments of the combustion synthesized powders above 1200 °C. In this case, α-cordierite results from the solid state reaction of spinel and cristobalite.

Of particular importance proved to be the way in which the additional thermal treatments were carried out. Thus, it is recommended to crush the very voluminous powder resulting from the combustion process before annealing. In the crushed powder, the formation of α-cordierite starts at 1200 °C, while there was no evidence of α-cordierite in the uncrushed powder—annealed in the same conditions. The absence of cordierite from the uncrushed sample is due to the insufficient contact area between the spinel grains and cristobalite grains, which is caused by the very large volume of combustion synthesized powder.

The best results were obtained when triethylenetetramine was used as fuel, because triethylenetetramine generates an intermediate spinel powder with larger surface area and thus more reactive with respect to SiO_2 grains. At 1300 °C the sample prepared with triethylenetetramine turned virtually into single-phase α-cordierite, whereas in the case of powder obtained by using a combination of urea and monoethanolamine lead to the formation of a mixture of α-cordierite, cristobalite and spinel. The use of fuels which ensure the formation of large surface area spinel powder has positive effects on the formation of α-cordierite.

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