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Synthesis of cordierite monolithic honeycomb by solid state reaction of precursor oxides

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The synthesis of cordierite monolithic honeycombs by solid state reaction at high temperature of alumina, kaolin, talc and silica has been studied. The synthesized honeycombs have been characterized by DTA and XRD. The crystal composition of the samples have been observed to be very dependent on temperature and time of reaction. Thermal treatment of the monolithic precursors at 1400 °C for 30 minutes allows formation of high purity cordierite with high crystallinity, maintaining the desired monolithic structure of the honeycombs. *© 1999 Kluwer Academic Publishers*

1. Introduction

Cordierite, with the formula $2MgO{\cdot}3Al_2O_3{\cdot}SiO_2$, is a material with high chemical and mechanical durability, low thermal expansivity and low dielectric constant. These characteristics make it an interesting candidate for many industrial applications where good high temperature creep resistence coupled with a high resistence to thermal shock are required [1, 2]. These applications, however, demand high purity cordierite. Because the natural mineral is not abundant or pure enough, cordierite has to be synthesized from raw materials which are readily available and high purity.

Sintering and crystallization of glass powders has been reported as the most conventional way to synthesize cordierite, in which incorporation of suitable fluxing agents can improved the sintering performance by controlling the nucleation process [3–5]. The alternative sol-gel technique from multicomponent metal alkoxide precursors [6, 7] has been used for the preparation of highly homogeneous glasses and ceramics by careful control of the different hydrolysis rates. Based on the knowledge of sol-gel conversions, it is possible to prepare fibers, films or composites that are particularly attractive to the electronic packaging industry.

One of the most extended application of cordierite is as ceramic monolithic honeycomb supports. This structure is increasingly used in many reactor applications, such as petrochemical industry [8, 9], selective reduction of nitrogen oxides [10, 11], selective hydrogenation of alcohols [12], automobile emissions control [13–15] and control of volatile organic compounds [16, 17].

The application of cordierite as monolithic honeycomb requires the synthesis to be made by solid state reaction from a mixture of the precursor oxides. This technique allows to conform the monolithic structure previously to the synthesis without requiring incorporation of any precursor to control the reaction, obtaining a pure cordierite monolithic honeycomb with adequate thermal and mechanical properties for environmental catalysis. However, a serious disadvantage of cordierite compositions prepared by this technique is the narrow firing range. Overfiring results in the deterioration of crystalline cordierite into forsterite and mullite, which appreciably increases the thermal expansion; underfiring fails to develop sufficient crystalline cordierite for low thermal expansion and high resistence shock [18].

The cordierite polymorphism is well known: α-cordierite (hexagonal), β-cordierite (orthorombic) and a metastable μ-cordierite, which evolves to the stable phase α-cordierite at a temperature between 900 and 1000 °C depending on thermal treatment time [6]. The indialite is the name used for the synthesized α-cordierite, with a pseudohexagonal lattice due to the impurities not eliminated in the synthesis process, as occurs with most of the commercial cordierites.

This work was conducted to gain a better understanding of some of the fundamentals involved in the preparation of cordierite monolithic honeycomb substrates. We report on the evolution of the crystalline phases in the cordierite synthesis process with temperature and time, so that this knowledge shall allow us to control the chemical and structural characteristics of the final ceramic monolithic supports to be used as catalytic converters.

2. Experimental

The raw materials were kaolin, talc, silica and alumina, with the composition shown in Table I, determined by X-ray fluorescence.

Based on the SiO_2-MgO-Al_2O_3 diagram [19] the raw materials were mixed in the following proportion: 20.6% alumina, 34.5% kaolin, 40.4% talc, and 4.5%

TABLE I Composition of raw materials (%)

	Al_2O_3	SiO_2	MgO	CaO	Na_2O	K_2O	TiO_2	Fe_2O_3
Caolín	34.69	50.64	0.47	0.30	0.32	2.59	0.12	1.08
Talco	0.31	62.88	31.33	0.13	—	—	0.014	0.49
Sílice	0.39	99.13	0.20	0.15	—	0.07	0.02	0.04
Alumina	99.44	0.21	0.03	—	0.03	—	—	0.02

silica, together with a synthetic methylcellulose polymer which acts as binder in the extrusion process. After homogeneity of the dry raw materials mixture (average particle size = 13 μm), water was added to get an homogeneous, cohesive and easily extrudable paste in a Brabender 350-E mixer.

The paste was extruded in through a circular die of 122 cells/in^2 mounted in the 19/20DN head of the Brabender extruder, at moderate temperature. The obtained cordierite precursor honeycomb was well conformed and with good mechanical resistance to be manipulated in subsequent steps. The samples were dried up to 110 °C under precisely controlled temperature and wetness.

To determine when the solid state reaction takes place, the behaviour of the cordierite precursor honeycomb with temperature was studied by thermal analysis (DTA, Setaram TAG24) in air from 100 to 1500 °C at 40 °C/min.

The identification and evolution of the crystalline phases in the cordierite honeycomb synthesis process was carried out by X-ray diffraction (Phillips PW1710, CuK_α radiation, 2θ range = 5–60°, step scan = 0.015) to samples calcined at different time and temperature.

3. Results and discussion

Fig. 1 shows the DTA diagram of raw oxides physical mixture. It can be seen a first endothermic peak at 550–650 °C, associated with the loss of structural OH corresponding to the transition of kaolin to metakaolin, and also associated to the transition of α-quartz into β-quartz. A second endothermic peak appears at 900–950 °C associated to the transition of talc to protoenstatite, amorphous silica and water vapour. Following is the exothermic peak associated with the decomposition of metakaolin into mullite, α-alumina and α-crystobalite. The last phase transformations of the oxide mixture precursor of cordierite, at 1050–1250 °C, are associated with the crystallization of amorphous silica into crystobalite and the transition of amorphous alumina to α-alumina. Above this temperature the single oxides did not present any transformation except their fusion; however, their mixture presented the exothermic peak at 1300–1425 °C associated with the solid state reaction to form cordierite. Finally, the last endothermic peak at 1450 °C is associated with the fusion of the synthesized cordierite.

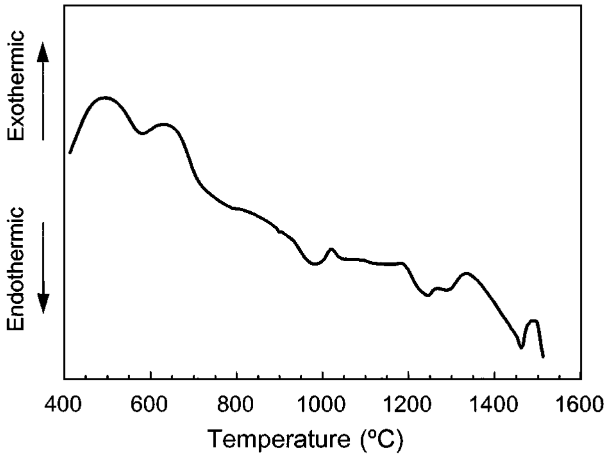

Figure 1 DTA diagram of the cordierite precursor oxides (raw materials) mixture, at a heating rate of 15 °C min^{-1}.

It must be noted the absence in the DTA diagram of any endothermic peak associated with the existence of a metastable phase μ-cordierite and subsequent transition to the stable phase α-cordierite, as described in some other synthesis processes [20–22].

Fig. 2 shows the X-ray diffraction pattern of cordierite precursor honeycomb when submitted for 30 minutes at different temperatures from 850 to 1400 °C, once reached that temperature at 10 °C min^{-1}. Up to 1300 °C it cannot be seen any indication of the lines corresponding to cordierite. Thus, when the sample is treated at 850 °C only quartz and talc (not decomposed yet) appear as crystalline phases. At 1100 °C, the lines corresponding to protoenstatite (from decomposition of talc) appear with quartz. After treatment at 1200 °C the decomposition products of metakaolin to mullite, cristobalite and α-alumina can also be identified.

Above 1300 °C, some lines associated with indialite (the desired cordierite pseudohexagonal polymorph) begin to appear in the X-diffraction pattern (Fig. 2), i.e., the solid state reaction begins to occur as expected from

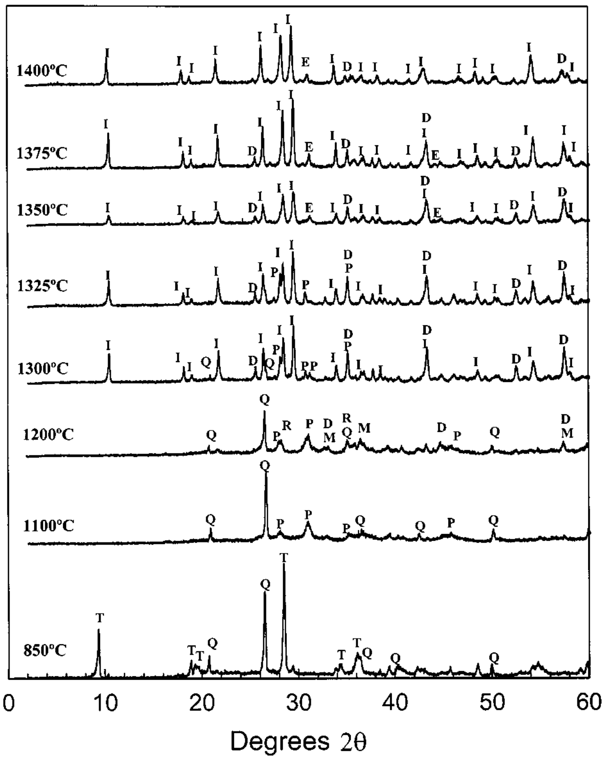

Figure 2 X-ray diffraction patterns of cordierite precursor honeycomb after calcination at differents temperatures. (T: talc, Q: quartz, P: protoenstatite, R: cristobalite, M: mullite, D: corundum, E: spinel and I: hexagonal cordierite or indialite).

the DTA results. Thus, the sample treated at 1300 °C gave with low intensity (low cristallinity) the line of indialite, also appearing the lines associated with the protoenstatite, α-alumina, and small remaining amounts of quartz. With a thermal treatment of the sample up to 1325 °C, the quartz disappeared from the samples but the crystallinity remains low, and this defect in crystallinity is even more pronounced increasing the treatment temperatute up to 1350 °C, whose low intensity diffractogram indicates the presence of amorphous material together with α-alumina and indialite; however, the protoenstatite has disappeared as crystalline phase and small amount of Mg-Al spinel has been generated.

When the solid state reaction is occurring, magnesium liberated from decomposition of protoenstatite forms the Mg-Al spinel with the unreacted free-alumina remaining in the sample. The presence of this spinel has also been discovered in the sol-gel synthesis method as a function of the conditions of hydrolysis of precursors [23]. Treatment at 1375 °C increases the crystallinity of the sample and many lines associated with the indialite were identified, whereas the lines associated with the α-alumina and spinel have been reduced notably. The X-ray diffraction pattern of the sample treated at 1400 °C shows the lines associated with the indialite indicating total crystallinity of this phase, and only small traces of the spinel and α-alumina can be seen.

The presence of the different cordierite polymorphs in the final product is clearly influenced by temperature, but also by the duration of the thermal treatment [24]. Thus, some cordierite monolithic honeycombs have been prepared at the temperature of 1400 °C—total crystallization according to the previous results—for times from 1 to 240 minutes. The X-ray diffraction patterns for these samples are shown in Fig. 3. With the very short time of 1 minute, the spinel and α-alumina lines are observed. These lines decrease with time of exposure (see the diffractogram for times between 10 and 45 min), and after 120 minutes only traces can be observed. However, these conditions (high temperature and long time) deteriorate the honeycomb structure because some semifussion begins to occur in the internal zone of the monolith.

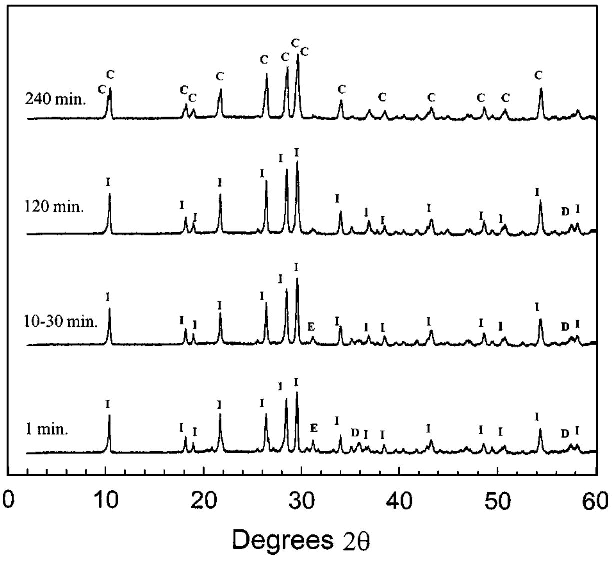

Figure 3 X-ray diffraction patterns of synthesized indialite monolith honeycomb after calcination at 1400 °C for different lasting times.

For longer times, as 240 minutes, the hexagonal line (211) at $2\theta = 29.4°$ is divided into the romboedric lines (241) and (311) (not seen with the resolution of Fig. 3), and it appears the new line (020) together with the (110) at $2\theta = 10.4°$, as it can be seen in Fig. 3 This pattern evidences the transition of indialite, the hexagonal polimorph, into β-cordierite with ortorombic symmetry. This transformation is induced by reordering of Al and Si atoms in the lattice tetraedres, as several distributions are possible between both symmetries [25–27].

4. Conclusions

The synthesis of cordierite monolithic honeycomb to be used as catalytic support has been studied. The monolithic structure was prepared from a mixture of alumina, kaolin talc, silica, and water, using a synthetic methylcelullose polymer as binder. Afterwards, the cordierite was sinthesized by submitting the monolithic precursor to high temperature, occurring the solid state reaction between the raw materials.

From DTA and XRD experiments it has been concluded that the cordierite honeycomb precursor has to be heated up to 1400 °C at 10 °C min^{-1} and maintained at this temperature for 10–30 minutes in order to synthesize the indialite polymorph whith high crystallinity and only small traces of Mg-Al spinel and α-alumina.

To manufacture a cordierite monolithic honeycomb with improved crystallinity the particle size of raw materials should be controlled carefully, so that the solid state reaction can occur atomically in the thin walls of the monolith, allowing the honeycomb structure to be maintained up to large exposure times at 1400 °C. This effect is actually under deeper research.

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