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Ceramics International 34 (2008) 269–272
CERAMICS INTERNATIONAL
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# The reaction kinetics of rice husk based cordierite ceramics

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Received 16 July 2006; received in revised form 11 August 2006; accepted 5 September 2006
Available online 13 November 2006

**Abstract**

In this study, rice husk ash (RHA) was used as a silica source for cordierite production. Two different groups of samples were prepared in order to achieve the synthesis of cordierite. In the first group (HS-0), kaolinite, alumina and talc were used as raw materials while in the second group (HS-1), active silica, obtained from rice husk, was added in powder composition instead of kaolinite. The rice husks were subjected to the chemical pretreatment with 2 M HCl, 5% solid at 25 °C before calcinations to increase silica contents of husk ash. The mixtures of raw materials were prepared in $MgO:Al_2O_3:SiO_2$ molar ratio of 2:2:5 and ground in water media. The pressed samples were sintered in air at varying temperatures from 950 °C to 1350 °C and soaked for 1 h. It was found that the higher content of α-cordierite with a lower crystallization temperature could be obtained by using active silica instead of kaolinite in the mixture composition. The activation energy of transition $\mu \rightarrow \alpha$-cordierite was calculated to be 205 kJ/mol for the active silica doped sample.

*Keywords:* D. Cordierite; Chemical treatment; Active silica; Rice husks; Kinetic

## 1. Introduction

Cordierite ($2Al_2O_3 \cdot 5SiO_2 \cdot 2MgO$) is a technically important ceramic that is applied in a great variety of areas due to the well known properties such as low dielectric constant ($\varepsilon = 5$–6), high resistivity ($\rho > 10^{12}\ \Omega$ cm), high thermal and chemical stabilities and very low thermal expansion coefficient ($\alpha = (1\text{–}2) \times 10^{-6}\ ^{\circ}C^{-1}$) [1–3]. In many works on cordierite powder synthesis sol–gel and related techniques are used [4,5]. Douy [4] exploited an elaborate organic gel method (with or without citric acid) for obtaining cordierite powders. The combustion technique for the synthesis of cordierite can also be mentioned. Each of the methods has it's own respective advantages and disadvantages.

In recent years, the processing of low temperature sintering of the cordierite ceramics has attracted attention due to cost reduction. Although dense cordierite ceramics can be obtained from alkoxides at low temperature, the starting materials are very expensive and the fabrication process is complicated. Rather than the alkoxides, the production cost of cordierite can be reduced by using low cost starting materials such as synthetic compounds—oxides, hydroxides and mineral raw materials such as kaolinite and talc. Often some additives—mineralizers and some fluxes such as $B_2O_3$, $Li_2O$, $CeO_2$, etc. are also added to promote the synthesis reactions [6–9] and modify the properties of cordierite ceramic [10,11].

Resources supply and environmental protection are increasingly becoming matters of global concern. It is well known that large amount of rice husk (RH) is left as waste product after the rice production and it has no commercial interest [12]. Their major contents are organic matters such as lignin, cellulose and sugar, which yield carbon when thermally decomposed under inert atmosphere and silica (20–25%), with small amount of trace elements. Recently, RHA has become an important competitive material for preparation of number of silicon compounds such as solar grade silicon [13], silicon carbide [14], silicon nitride [15], zeolite, cements surfactant [16–18] and soft porcelain production [19] due to high surface area, high grade of amorphous form silica and fine particle sizes.

In our previous work, active silica was produced from rice husk ash by leaching method [20]. In the present study, an effort

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doi:10.1016/j.ceramint.2006.09.017

has been made to find out the usage of produced silica as a value additive material in producing ceramic material like cordierite. The effect of active silica on the transformation of μ-cordierite to α-cordierite was discussed in detail.

## 2. Experimental procedures

### 2.1. Material and method

Rice husk, supplied from Kastamonu region of Turkey, was used as a source of silica. Although calcinations parameters are important for the production of high grade RH ash, utilization of this ash as a source of silica is based on the removal of impurities with a low effort. For this reason, the received RHs were firstly pre-treated with HCl under the predetermined optimum conditions before using in cordierite synthesizes. RHs were washed with water to remove the contaminants present then dried in an oven at 100 °C for 24 h. The dried husks were then subjected to the chemical treatment; 2 M HCl, 5% solid at 25 °C before calcinations to increase silica contents of husk ash. After leaching tests, the husk was washed with distilled water and then dried. Acid treated husks were then subjected to the calcinations at 700 °C. A detail of the pre-treatment study can be found in elsewhere [20]. The chemical composition of pre-treated rice husk is shown in Table 1.

In cordierite synthesis part, two different groups of samples were prepared. In the first group, kaolinite, alumina (Seydisehir, Turkey) and talc were used as raw materials for the synthesis of cordierite. In the second group, active silica was added in powder composition instead of kaolinite. Samples were called as HS-0 and HS-1, respectively. The mixtures of raw materials were prepared in an $MgO:Al_2O_3:SiO_2$ molar ratio of 2:2:5 and ground using a planetary ball mill for 4 h in water media. After drying, powder was pressed uniaxially at a pressure of 1.96 MPa to obtain pellets of 13 mm in diameter and 40 mm thickness. Pellets were sintered in air at four different temperatures (950–1350 °C), at rate of 5 °C/min from room temperature up to 1000 °C, and at rate of 2.5 °C/min from 1000 °C to peak temperatures and held for 1 h.

### 2.2. Analytical method

The crystalline phases were identified by using an X-ray diffractometer (Rigaku Co., Tokyo, Japan) from 5° to 60° with scanning speed of 2°/min. The degree of conversion from μ → α-cordierite, $f$, was determined by using the following equation [21]:

$$f = \frac{1}{1 + K^{*}(I_{\mu(1\,0\,1)}/I_{\alpha(1\,1\,0)})} \quad (1)$$

where $I_{\mu(1\ 0\ 1)}$ is the integral intensity corresponding to the (1 0 1) peak of μ-cordierite and $I_{\alpha(1\ 1\ 0)}$ is the integral intensity corresponding to the (1 1 0) peak for α-cordierite, and $K$ is a constant close to 1 [21]. For a better understanding of the crystallization in this system, differential thermal analysis (DTA) was performed on the samples. Differential thermal analyses (DTA) measurements were carried out by using a Linseis Thermowaage L81 model DTA. Samples were heated in air up to 1200 °C at different rates of 5, 10, 15 and 20 °C/min with an alumina reference in order to calculate activation energies of the α-cordierite formation. Assuming that the kinetics of the crystallization process is described by the equation of Kissinger [22], the activation energies are calculated via the using the following equation:

$$\ln\left(\frac{\phi}{T_{\mathrm{p}}^{2}}\right) = \frac{E_{\mathrm{ck}}}{RT_{\mathrm{p}}} + \text{const.} \quad (2)$$

where $\phi$ is the DTA heating rate, $T_{\mathrm{p}}$ the crystallization peak temperature, $E_{\mathrm{ck}}$ the activation energy for crystallization estimated by the Kissinger method, and $R$ is the gas constant.

### 2.3. Characterization

Particle-size distributions of powders were measured by an ultrasonic particle-size analyser (Malvern 2000 Mastersizer Laser Diffraction Particle Size Analyser). Scanning electron microscopy (SEM, Cam ScanS4, Cambridge, UK) was also used for microstructural characterisation.

## 3. Results and discussion

### 3.1. Physical properties

The particle size distribution of samples is given in Fig. 1. It was found that mean grain sizes of HS-0 and HS-1 are 1.3 μm and 1.1 μm, respectively.

### 3.2. XRD analysis

The formation of cordierite and other crystalline phases for samples sintered at different temperatures through 950–1350 °C were determined by XRD analyses (Table 2). It was demonstrated that the formation of cordierite phases is related with the type of starting raw materials. In both samples, no cordierite peaks were detected at 950 °C. The first μ-cordierite peaks were observed by decreasing of $Al_2O_3$ peaks in sample HS-0 at 1150 °C, and α-cordierite phase was formed at 1250 °C. However, for sample HS-1, the main α-cordierite peak ($2\Theta = 10.2°$) was observed at 1150 °C, as 100 °C less than HS-0. This result can be attributed to the physical properties of active silica. Due to the high surface area and ultra fine particles

Table 1
The chemical composition of pre-treated rice husk

| Components | Wt.% |
|---|---|
| $SiO_2$ | 99.50 |
| $Al_2O_3$ | 0.04 |
| $Fe_2O_3$ | 0.04 |
| CaO | 0.09 |
| MgO | 0.08 |
| $K_2O$ | 0.17 |

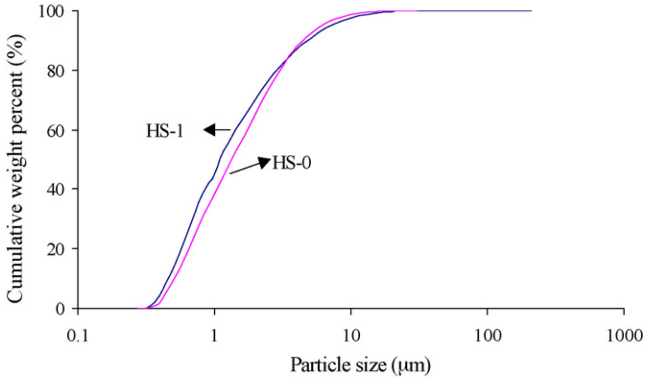

Fig. 1. Particle size distribution of raw material mixtures.

Table 2
Crystalline phases formed in the HS-0 and HS-1 samples sintered at different temperatures

| Samples | 950 °C | 1150 °C | 1250 °C | 1350 °C |
|---|---|---|---|---|
| HS-0 | $A_{(vw)}$–$E_{(s)}$–$MS_{(vs)}$ | $A_{(vvw)}$–$\mu_{(s)}$ | $\alpha_{(vs)}$–$\mu_{(vvw)}$ | α |
| HS-1 | $A_{(vw)}$–$E_{(s)}$–$MS_{(s)}$ | $A_{(vvw)}$–$\mu_{(vvs)}$–$\alpha_{(vvw)}$ | $\alpha_{(vs)}$–$\mu_{(vvw)}$ | α |

E, enstatite; MS, magnesium silicate; A, alumina; α, α-cordierite; μ, μ-cordierite; v, very; w, weak; s, strong.

size, active silica can be reacted easily at low temperature with other raw materials. According to above findings, it can be concluded that using of active silica promote the α → μ-cordierite transformation at lower temperature. Maximum cordierite formation was obtained at 1350 °C for both samples. As a related with the silica source and sintering temperature, the degree of conversion from μ to α-cordierite was calculated according to Eq. (1) and results is shown in Fig. 2. It was found that HS-1 has always higher $f$ value than HS-0. This indicates that addition of active silica instead of kaolinite favours the transition from μ to α-cordierite. During the sintering of cordierite ceramic at high temperatures (1150–1350 °C), active silica reacts easily with other materials compared to kaolinite.

### 3.3. Differential thermal analysis (DTA)

The Kissinger plots according to Eq. (2) are shown in Fig. 3. Based on these data, the activation energies for the formation of α-cordierite are calculated. It can be seen that the HS-0 has an activation energy value of 480 kJ/mol, which is about the same already reported for glassy cordierite powders prepared by melting [23,24]. However, the calculated activation energy for HS-1 (205 kJ/mol) is significantly lower compared to HS-0. This suggest that the samples prepared with active silica should

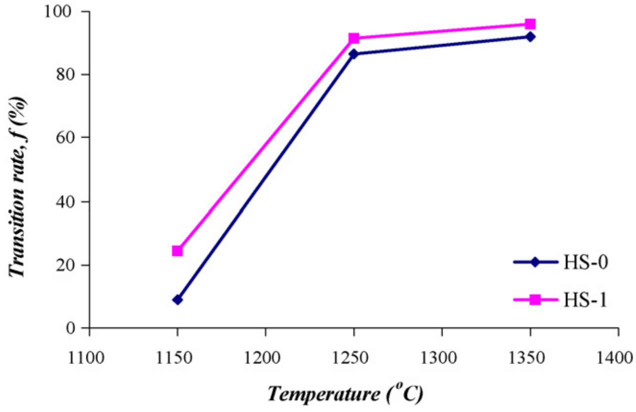

Fig. 2. The degree of conversion of μ → α cordierite vs. sintering temperature.

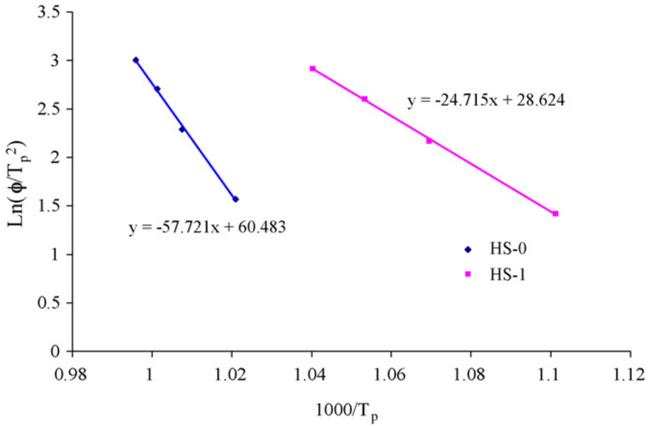

Fig. 3. The Kissinger plots for the HS-0 and HS-1 samples.

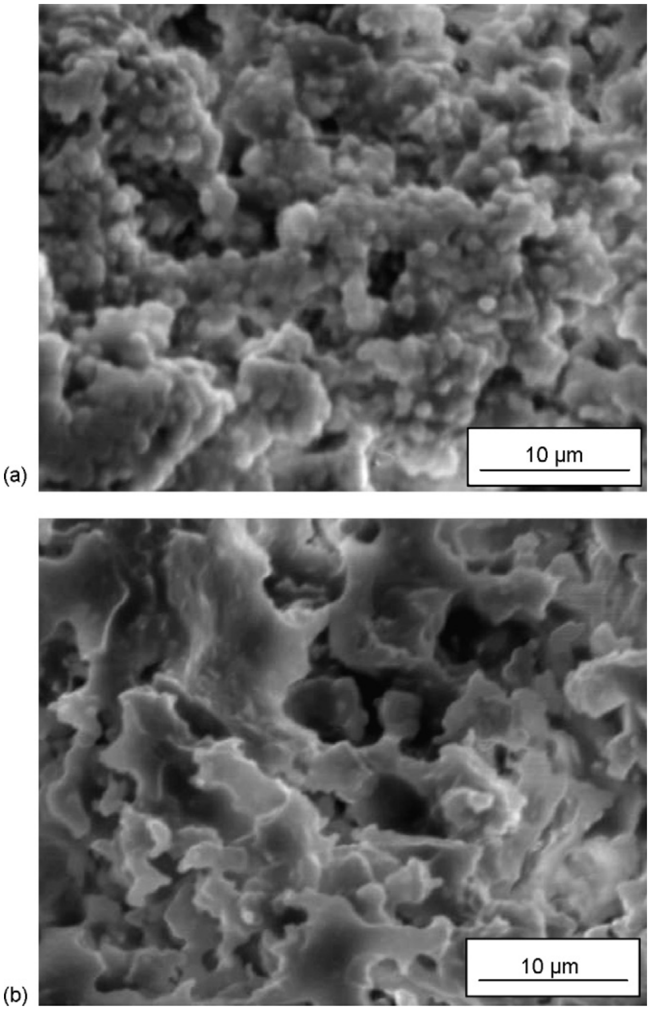

Fig. 4. Representative secondary electron image of the samples sintered at 1350 °C: (a) HS-0 and (b) HS-1.

be more homogeneous and having fine particle size distribution than those obtained by melting. This is an advantage to prevent the occurrence of phase separation observed in cooling step of melting process. Therefore, use of active silica promotes the α-cordierite formation at lower temperatures.

This result shows an agreement with the previous study performed by Kula Kurama et al. [25] in order to find out the influence of active silica as sintering promoters, on the vitrification behavior on soft porcelain. It has been reported that the concurrent presence of porous and amorphous active silica promoted the development of a less viscous liquid phase, which improved the densification kinetics as long as it was operated within defined limits of composition and firing regime. Apart from the fluxing effect of the active silica, considerable fine particle size distribution is also believed to play an important role in enhanced vitrification. This behavior explains the decrease of activation energy by using active silica.

### *3.4. Morphology of sintered products*

Representative SEM photographs of samples, sintered at 1350 °C, are given in Fig. 4. The spherical grains in the microstructure of HS-0 indicate that insufficient liquid phase was obtained whereas planelike grains were not observed for sample HS-1. This result is in agreement with XRD and particle size analyses. By using active silica, as mentioned before, the mean particle size of the mixture was decreased. This leads to proceeding of synthesis reaction more easily for the active silica–talc–alumina system than kaolinite–talc–alumina system and formation of the amorphous phase, dense and pure cordierite.

## 4. Conclusion

The following conclusions can be derived according to test results:

(1) In this study, it was found that RHA can be evaluated as a kaolinite replacement material in the synthesis of cordierite with employing a simple-low cost pre-treatment step including 2 M HCl, leaching at 5% solid, 25 °C. It is believed that such usage helps sustainable manage of raw materials, using the synthesis of cordierite by turning of the waste in to the useable material.

(2) Active silica was found to promote the μ-cordierite to α-cordierite transition at lower temperature because of its high surface area and fluxing properties.

(3) By the employment of RHA as alternative silica source leads to decreasing the activation energy of the crystallization of α-cordierite.

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