LOW TEMPERATURE MOLTEN SALT SYNTHESIS OF NANO CRYSTALLINE $MgAl_2O_4$ POWDER

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Abstract: *$MgAl_2O_4$ (MA) nano powder was synthesized via molten salt technique, by heating stochiometric composition of MgO and nano boehmite. The reactant and potassium chloride, as the reaction media, were fired at 800-1000 °C at different dwell times (0.5-5 h) in the ambient atmosphere. After washing and filtration, the spinel nano powder was characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) techniques. It was demonstrated that the formation temperature decreased to 850 °C. The nano spinel particles revealed an average size of 30 nm with a narrow size distribution. The mechanism of $MgAl_2O_4$ formation was found to be a template type where the morphology and size of product were similar to those of alumina formed from boehmite decomposition. Prolonging the reaction time from 0.5 to 3 h, the reaction was further completed and crystallinity was improved. However, the increase of temperature was more effective in this regard.*

Keywords: *spinel nano powder; molten salt method; boehmite*

1. INTRODUCTION

Magnesium aluminate, $MgAl_2O_4$ (MA), is an important candidate as a refractory raw material because of its superior physical and chemical properties such as high melting point (2135 °C), low thermal conductivity, high strength at room and elevated temperatures and good corrosion resistance [1]. This material has potential to be used as catalyst support in petrochemical industries for alkane dehydrogenation [2-3], methane oxidation [4] and catalyst support [5].

Solid-state synthesis is the conventional rout to produce the $MgAl_2O_4$ spinel from reaction between MgO and Al_2O_3 as primary materials. This reaction occurs by diffusion of Al^{3+} toward MgO and Mg^{2+} toward Al_2O_3, forming an spinel layer which acts as a barrier layer against the diffusion agents [1, 6 - 7]. Therefore, the formation of spinel by solid-state reaction requires high temperature (~1400 °C) and long time firing conditions. Other synthesis techniques like sol-gel of metal alkoxides, co-precipitation and combustion synthesis have also been applied for synthesis of MA spinel [8-10]. However, these routs suffer from complexity, unfriendly environment, reproducibility and expensive precursors.

Molten salt synthesis (MSS) has many advantages such as cost effectiveness, easy setup, low temperature synthesis and controllable size of products. The MSS process has been widely used for synthesis of single and multi oxide powders such as PZT-PZN-PSM, $CoWO_4$ and SnO_2 [11-13]. Zhang et al. have used Al_2O_3 and MgO as raw materials to synthesize spinel powder by MSS method at different salt media such as KCl, NaCl and LiCl. They have shown that complete formation of spinel phase occurred at 1150 °C in KCl and NaCl [14-15]. In this way, the formation of spinel took place by template formation mechanism and final spinel product adopts the morphology of alumina used as a precursor. This shows that the alumina behaves as a template while MgO dissolves in molten media and Mg^{2+} diffuse to alumina surface and form the spinel phase. Although the formation of spinel by MSS process has been reported but there is no report of using nano boehmite as precursor.

In this research, we synthesized a nano structured spinel by taking nano boehmite as a precursor for alumina source. The aim was to produce nano spinel at low temperature by

molten salt method and optimizing the processing parameters such as synthesis temperature, time and salt to oxide weight ratio.

2. EXPERIMENTAL PROCEDURE

High purity MgO (Merck, Germany), nano boehmite (Sasol, Germany), and KCl (Merck, Germany) were used as primary raw materials. In order to prepare the samples, an equimolar composition of MgO and nano boehmite precursors were dispersed in double ionized water using magnetic stirrer and probe ultrasonication. Then, MgO dispersion added to obtained dispersed nano boehmite suspension and followed by stirring and heating to remove the media dispersion. Finally, the mixture was dried at 120 °C for 10 h. The dried and pulverized powder was finally mixed with KCl salt in salt to oxide weight ratio of 3:1. The mixture was heated in alumina crucible covered with an alumina lid for 0.5-3 h at temperatures ranging from 800 to 1000 °C. After cooling to room temperature, the solidified mass was washed and filtered in hot double ionized water several times to remove the salts. The obtained powder was then dried at 120 °C for 10 h. Phase analysis and microstructural studies were performed on the obtained powder using XRD and SEM. The crystalline structure of the powders was investigated by X-ray diffraction (Philips pw3710) with Cu Kα radiation. The average crystallite size of the powder was estimated from the Scherrer equation from XRD patterns. The surface area of powders and powder morphologies were observed using N_2 adsorption–desorption isotherms in a surface analyzer equipment at 77 K and a scanning electron microscope (SEM, Vega II Tescan), respectively.

3. RESULTS AND DISCUSSION

In order to find the proper temperature range of the reaction, DSC/TGA analysis was carried out. The result is plotted in figure 1 which shows the DSC/TGA curve for mixture of AlOOH and MgO in KCl salt heated with a rate of 10 °C.min-1. In DSC curve from 100 °C to 205 °C, there are two endothermic peaks a and b associated with the slow weight loss in TGA curve. These are attributed to moisture removal from the sample and escape of surface chemicals, namely dispersants, from particles. The weight loss accompanied with an endothermic peak c at about 345 °C is associated to transformation of AlOOH to α-Al_2O_3. The endothermic peak d

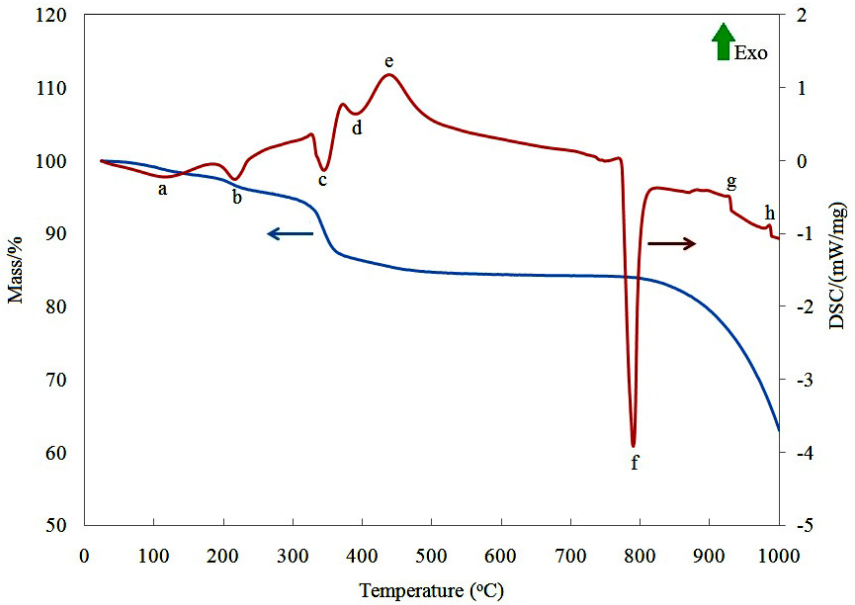

Fig. 1. DSC/TGA curve of sample heated up to 1000 oC with a rate of 10 oC/min.

(385 °C) and exothermic peak e (423 °C) events belong to hydroxide dissociation and transformation of amorphous MgO to crystalline structure respectively [16]. It is clear that treatment of MgO in water causes the formation of $Mg(OH)_2$ during the primary mixing. The (f) endothermic peak at 780 °C is correlated to KCl salt melting and, finally, the small exothermic peaks at 850-900 °C (g and h) may be related to the primary and secondary spinel formation respectively. However, to judge on formation of spinel the XRD data should support this finding. This experiment shows the sample heated to 800 °C should virtually contain molten KCl along with MgO and Al_2O_3 components.

Figure 2 shows the XRD patterns of the samples heated at 800, 850, and 1000 °C for 3 h with 3/1 salt to oxide ratio. It demonstrates that the sample fired at 800 °C contains unreacted Al_2O_3 and MgO phases. However, increase of temperature to 850 °C results in complete formation of spinel. At 1000 °C, the product consists of a well crystallized $MgAl_2O_4$ monophase.

Figure 3 shows XRD patterns of $MgAl_2O_4$ powders obtained by firing of nano boehmite-magnesia-KCl mixture powder at 850 °C at different soaking periods with 3/1 salt to oxide ratio. It is clear from the patterns that the spinel peaks begin to appear at 850 °C when fired for only 0.5 h. By increasing the soaking time to 1 h, the alumina peaks disappear while the MgO is still detectable. As mentioned before, magnesia also exists along with the sample. The Alumina phase, however, hardly could be detected. Comparison of XRD patterns in figure 2 and 3 indicates that temperature is more influential than time in formation of spinel in MSS process. Existing of MgO and disappearance of Al_2O_3 in the sample fired at 850 °C for 0.5 and 1 h may be explained as follows. The Mg^{2+} ions migrate into the alumina particles and form spinel on the basis of a template mechanism. As the layer of spinel on alumina particles thickness the migration of Mg^{2+} ions require higher temperature or longer time to reach to core alumina. The alumina has the possibility of being solved in spinel and form alumina rich spinel. Therefore, alumina could not be detected. The other possibility is since little remained alumina cores covered by spinel are difficult to be detected by X-ray diffraction.

In addition, comparison of present results with previous report [14] clarifies that using boehmite instead of alumina as precursor lowers the synthesis temperature to about 300 °C. This happens because conversion of nano boehmite into γ-Al_2O_3 introduces fine and reactive alumina particles which react with MgO much faster than α-Al_2O_3. The nano γ-Al_2O_3 resulted from nano boehmite decomposition also well dispersed throughout the KCl salt media. This dispersion of nano particles encourages the formation of spinel at significantly lower

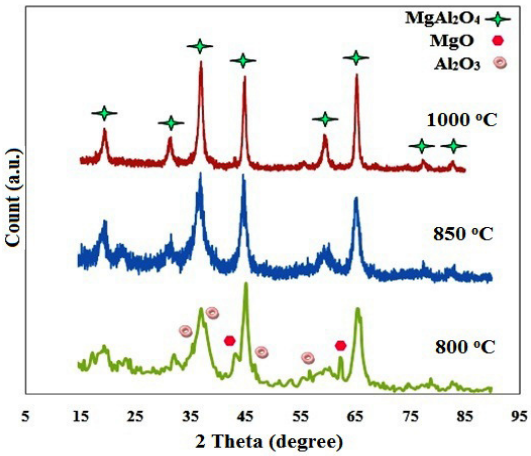

Fig. 2. XRD patterns of the samples heated at different temperatures for 3h with 3/1 salt to oxide ratio.

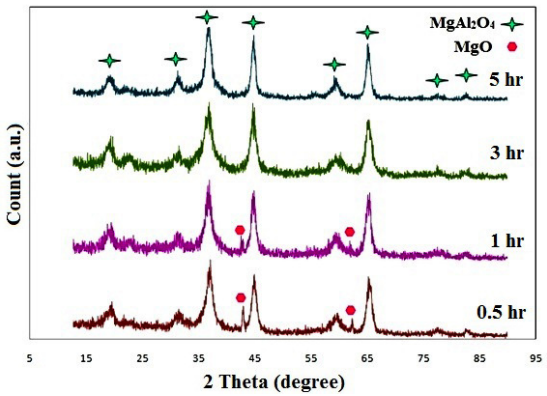

Fig. 3. XRD patterns of the samples heated at 850 °C for different times with 3/1 salt to oxide ratio.

temperatures compared to solid state reaction. Therefore, this is not surprising that reaction under present conditions initiates at about 850 °C where the solid state reaction usually happens at above 1300 °C.

In addition to the heating temperature and the soaking time, the salt/oxide weight ratio also affected the molten salt synthesis procedure. XRD patterns of the powders with different salt/oxide ratios heated for 1 h at 850 °C, are shown in figure 4. For the powder obtained at 850 °C for 1 h with salt to oxide weight ratio of 3:1, $MgAl_2O_4$ was the main phase with a small amount of MgO. Further increase of salt to oxide weight ratio to 5:1 accelerated the reaction and caused a single phase formation. At higher ratios (e.g. 7:1) no significant change can be observed. It seems that by increasing the amount of salt the viscosity of media (mixture of salt and oxides) decreases and this facilitates the diffusion of MgO towards Al_2O_3 species. There is also another parameter which may play a role in synthesis. In fact as the TG curves show, some of KCl evaporates from the system at temperatures above the melting point and leaves less salt to help diffusion process.

Crystallite size and surface area of the synthesized powders as a function of the temperature and the time are presented in Table 1. The crystallite sizes differ from 10-15 nm depending on the temperature, time, and salt to oxide weight ratios. The surface area also varies between 100-140 m^2/gr.

Molten salt synthesis procedure of MA involves, (1) diffusion of dissolved MgO (in the form of Mg^{2+}) onto γ-Al_2O_3 particle surfaces, (2) diffusion of MgO (probably in the form of Mg^{2+}) to the unreacted γ-Al_2O_3 core through the formed continuous $MgAl_2O_4$ spinel layer, and (3) reaction between diffused MgO and unreacted γ-Al_2O_3. Therefore, it can be suggested that the formation mechanism of spinel is "template formation mechanism" and γ-Al_2O_3 plays the role of

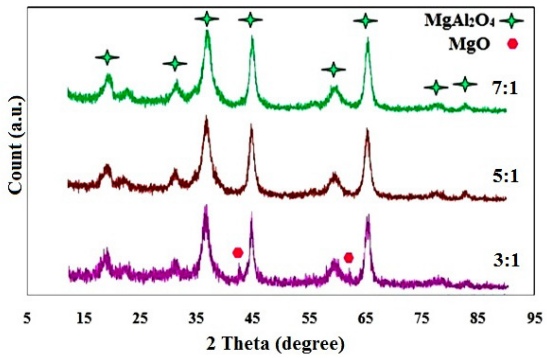

Fig. 4. XRD patterns of the samples heated at 850 °C for 1 hour at different salt to oxide weight ratios.

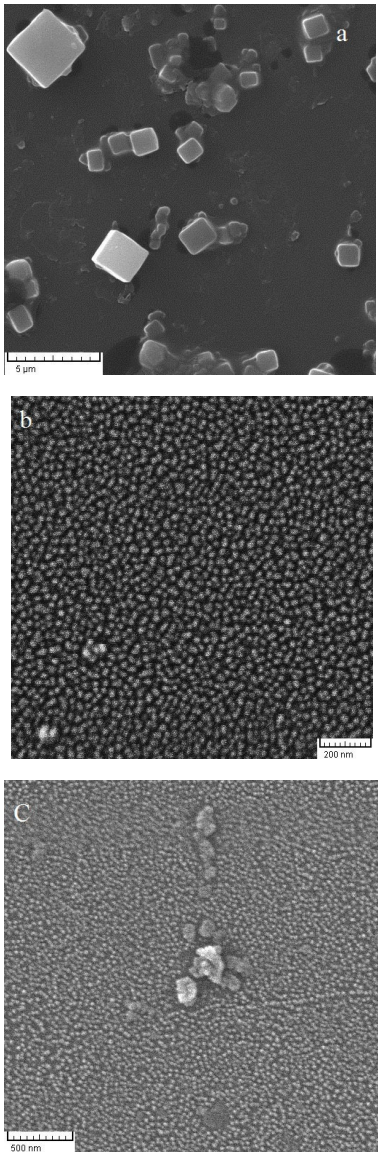

Fig. 5. SEM micrographs of starting materials as well as prepared $MgAl_2O_4$ powder by molten salt method at 850 °C for 3h. (a) magnesia, (b) γ-alumina from boehmite precursor, and (c) synthesized spinel.

Table 1. Phase composition, crystallite size and surface area of of the synthesized powders at different temperatures and dwell times.

Temperature (°C)	Time (h)	Salt/Oxide weight ratio	Phase composition	Crystallite Size d_{XRD}(nm)	Surface Area $S_{BET}(m^2/g)$	Particle Size d_{BET} (nm)
800	3	3/1	Al_2O_3-MgO-$MgAl_2O_4$	---	---	---
850	3	3/1	$MgAl_2O_4$	10.7	133	12.6
1000	3	3/1	$MgAl_2O_4$	14.5	103	16.3
850	0.5	3/1	MgO-$MgAl_2O_4$	---	---	---
850	1	3/1	MgO-$MgAl_2O_4$	8.5	140	12.0
850	5	3/1	$MgAl_2O_4$	11.6	126	13.3

template for the synthesized MA. Thus, the synthesized spinel powder should retain the size and morphology of the γ-Al_2O_3. In order to prove this justification, we carried out tests at 850 °C for 3h where MgO and nano boehmite were separately processed and the results were compared to fired mixture of MgO plus nano boehmite under the same conditions. Figure 5 shows the SEM observation of these samples. Magnesia crystallizes in the form of cubic particles after washing out the salt (figure 5a). Nano size γ-Al_2O_3 particles are presented in figure 5b show spherical shape with an average size of 30 nm. In figure 5c, the nano spinel particles synthesized by MSS process is shown. It is obvious that the size and morphology of spinel is very similar to those of γ-Al_2O_3. This finding indicates that formation of spinel is via a template process where the synthesized spinel adopts the shape of γ-Al_2O_3.

4. CONCLUSIONS

1. Synthesis of nano $MgAl_2O_4$ spinel was carried out by MSS process by heating stochiometric amounts of magnesia and boehmite in a KCl salt. Nano size spinel powder can be produced by conducting the process at 850 °C for 3h.
2. Although the formation of nano $MgAl_2O_4$ spinel initiates at 800 °C, completion of synthesis requires higher temperature or longer heating time. The temperature is more influential than time.
3. The mechanism of synthesis is a template type where the spinel product adopts the morphology and size of γ-Al_2O_3 formed from decomposition of the primary boehmite.

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