



Effect of Solvents on the Synthesis of SrAl₂O₄ Nanoparticles by Reverse Micelle Process

Azita Moheb, Saeid Abedini Khorramie*, Shahram Moradi Dehagi

Department of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, Iran

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Abstract

Three types of solvents with different polarity (cyclohexane, toluene and benzene), a nonionic surfactant Span 40 were used to prepare strontium aluminate (SrAl₂O₄) spinel nanoparticles by a reverse micelle method. The structure of SrAl₂O₄ nanoparticles was characterized by X-ray diffraction (XRD). The morphology and size of the synthesized materials were studied using field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) with using software of IMAGE J. The effect of polarity of solvent on the size and morphology of nanomaterials was studied. It was found that increasing the polarity of solvent affected the average crystallite size of the final product and led to the formation of larger particles. Furthermore, the average particles size was increased from 22 to 37 nm. X-ray diffraction analysis of all the powders was calcined at 1000°C for 2h revealed the formation single phase hexagonal spinel structure. Polarity of solvent is a major factor in controlling the final particles size of SrAl₂O₄ powder.

Keywords: Reverse micelle, Strontium aluminate, Span 40, Nanoparticle, X-ray diffraction.

Introduction

Nanotechnology is the manipulation of materials at the molecular and atomic scale. It is expected that nanotechnology causes a lot of revolutionary changes in the field of life science like diagnostics, bio-materials and drug delivery. This science employs knowledge from the different scientific fields of chemistry, materials science, engineering, chemistry health science and physics. It has many applications in all the field of science. Different types of nanoparticles were used in energy, materials industries, electronic, catalytic and cosmetics [1].

A wide range of organic and inorganic nanomaterials can be synthesized or modified to produce different sizes and shapes with extensive applications in several fields [2-6]. Research has been determined that the physical and chemical properties of nanoparticles can be affected by particle shape and size [7-10]. Therefore, the study of effective factors on particle size and synthesis methods can be the most important topics in the field of nanoparticles synthesis [11-13].

Complex oxides XY_2O_4 with the spinel structure as X and Y represent two different cations with similar ionic sizes make a group of chemically and thermally stable materials, that they are suitable for many applications like ceramics, magnetic, catalysis and optical [14, 15]. Aluminates are better candidates, because of properties such as low surface acidity, high mechanical resistance, high thermal stability and hydrophobicity. These properties make them attractive materials as catalysts [16]. The spinel structure $SrAl_2O_4$ because of long-persisting phosphors had been applied such as luminous watches, exit signs, decorative items, traffic signs, military applications, emergency passageway illumination, lighting equipment and low level lighting [17, 18]. Strontium aluminate can apply as a host for lanthanide ions and exhibits remarkable optical characteristics [17,19]. This material can be applied to preparation new metal compound composites [20]. They exhibit photocatalytic activity because of their photosensitive properties [21,22]. Nanomaterials are used in signposts, billboards, road signs, emergency lighting, interior design and safety indication [23-25].

$SrAl_2O_4$ and another nanoparticles have successfully prepared by many different ways, such as hydrothermal reaction methods [18, 22, 26, 27], via the sol-gel methods [28-33], high temperature solid state reaction [34-36] and co-precipitation methods [37-39]. Among the new techniques for the preparation of nanoparticles, it has been shown that the reverse micelle method has a significant reputation in this field [40-44]. It was reported that method of reverse micelle has an effective control over the particle shape and size, it has a unique benefit to prepare nanoparticles with similar shapes [44,45].

It was reported that the particles size is affected by surfactant and co-surfactant type has been investigated [46-56]. Several studies have shown that reactants concentration in particle size is effective [50-52, 57, 58]. Also, the effect of different solvents has been investigated [46, 59-62]. The

studies have been reported that the size of final particles is changed insignificantly by the addition of electrolyte [63, 64]. Many articles show the final particles size is dependent on the initial water to surfactant molar ratio $W_0 = [H_2O]/[Surfactant]$ [65-75]. Recently, nanoparticles with different chemicals compositions have been synthesized by the reverse micelles [75-77].

In this paper, strontium aluminate nanoparticles were synthesized by microemulsion method and influence of different solvents on the particles size of $SrAl_2O_4$ powder was reported. XRD was used in order to check the crystalline phases of the particles, the morphology and size of particles were characterized using electron microscope (FESEM and TEM).

Experimental

Strontium nitrate anhydrous ($Sr(NO_3)_2$, 99%, Merck), aluminum nitrate nanohydrate ($Al(NO_3)_3 \cdot 9H_2O$, 98.5%, Merck) were used as the precursor of strontium and alumina, respectively. The required amount of strontium nitrate and aluminum nitrate salts (Sr:Al=1:2) was dissolved in de-ionized water to a concentration of 0.1 M. Cyclohexane (99.5%, Merck), toluene (99.0%, Merck) and benzene (99.7%, Merck) was used as an organic solvent.

A solution of reverse microemulsion was prepared by mixing 0.09 M of sorbitan monopalmitate (Span 40, Sigma Aldrich) a nonionic surfactant, 0.93 M of cyclohexane and 0.1 M of mixed aqueous salt solution.

B solution of reverse microemulsion was prepared by mixing 0.09 M of sorbitan monopalmitate (Span 40, Sigma Aldrich) a nonionic surfactant, 0.93 M of benzene and 0.1 M of mixed aqueous salt solution.

C solution of reverse microemulsion was prepared by mixing 0.09 M of sorbitan monopalmitate (Span 40, Sigma Aldrich) a nonionic surfactant, 0.93 M of toluene and 0.1 M of mixed aqueous salt solution. The microemulsion was mixed rapidly, and after 30 min of equilibration 0.2 M of NH_4OH (28%, Merck) was injected into the microemulsion. Then the microemulsion was centrifuged to extract the particles and they were subsequently washed by ethanol to remove any residual surfactant. The powders were dried at 60°C in an oven for 24h, then ground and calcined at 1000°C for 2h. Figure 1 shows the flowchart for the preparation of $SrAl_2O_4$ nanopowders by reverse micelle processing. The phase identification of calcined powders was recorded using X-ray diffractometer (STOE STADI MP) that is shown in Figure 2. The morphology of the calcined powder was observed by FESEM operating at an accelerating voltage of 30 KV (MIRA3 TESCAN) that is shown in Figure 3. The particles size of the calcined powders was analyzed using TEM operating at an accelerating voltage of 200 KV (Philips, CM30) by placing the powder on a copper grid to get the details about the morphology and size of the powders that is shown in Figure 4. The average size of

the particles was estimated from the TEM micrographs using standard software IMAGE J that is shown in Figure 5. The crystallite size of the calcined SrAl_2O_4 powder was calculated from full width at half maximum (FWHM) peak using Scherrer's equation [74].

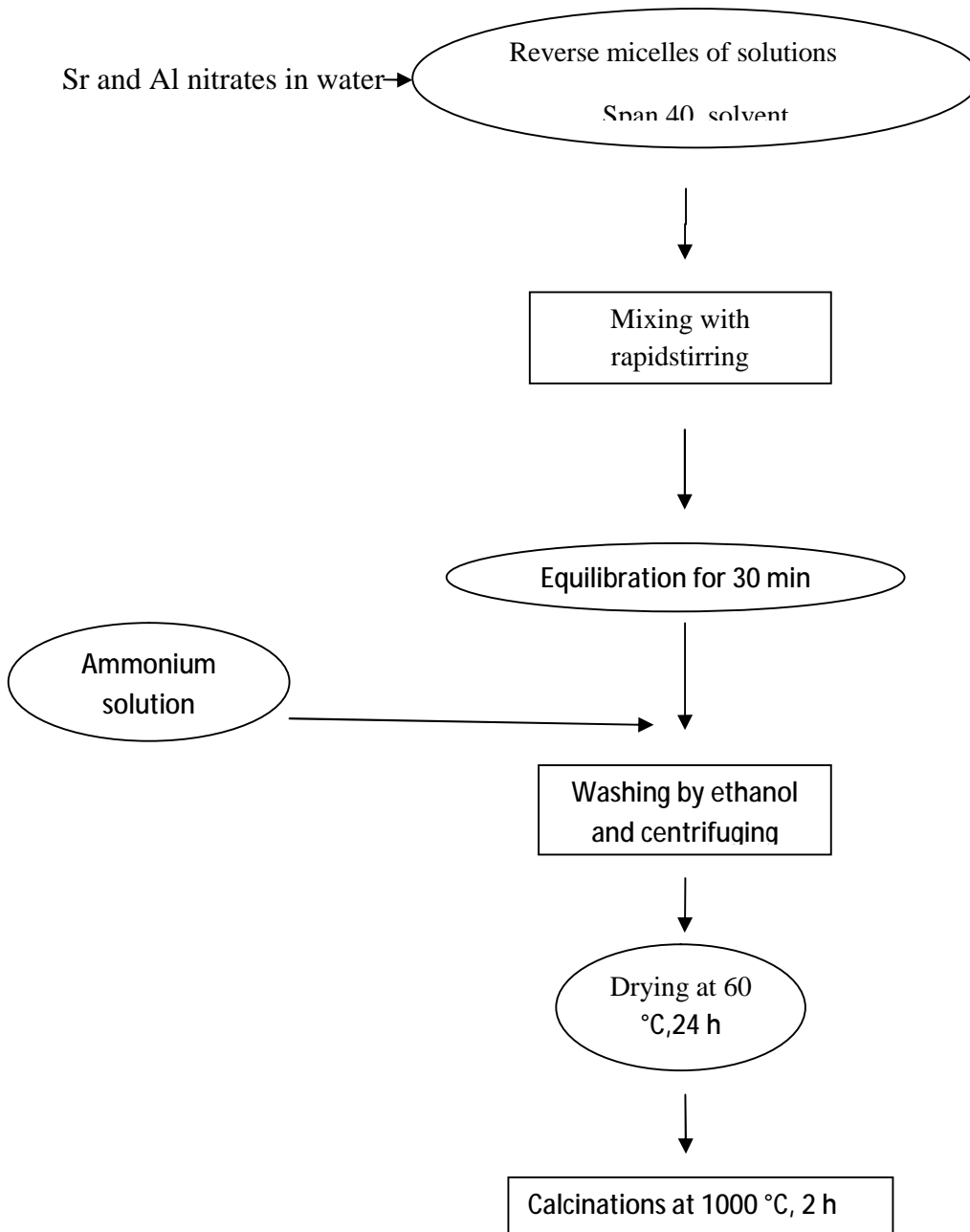


Figure1. Flowchart for the preparation of nanoparticles by reverse micelle processing.

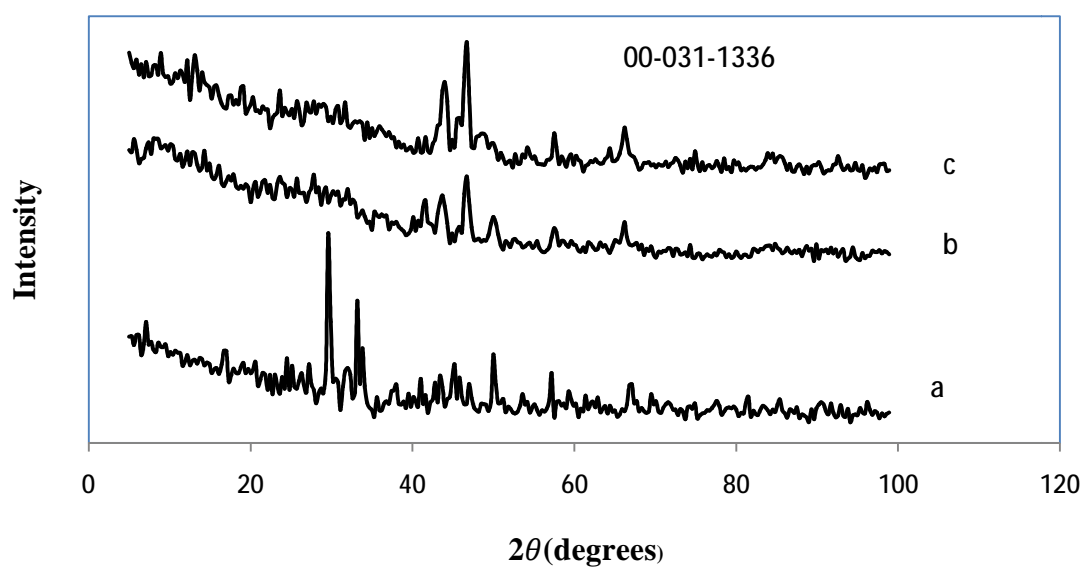


Figure 2. X-ray diffraction patterns of SrAl₂O₄ powder calcined with different solvents, a: cyclohexane, b: benzene and c: toluene.

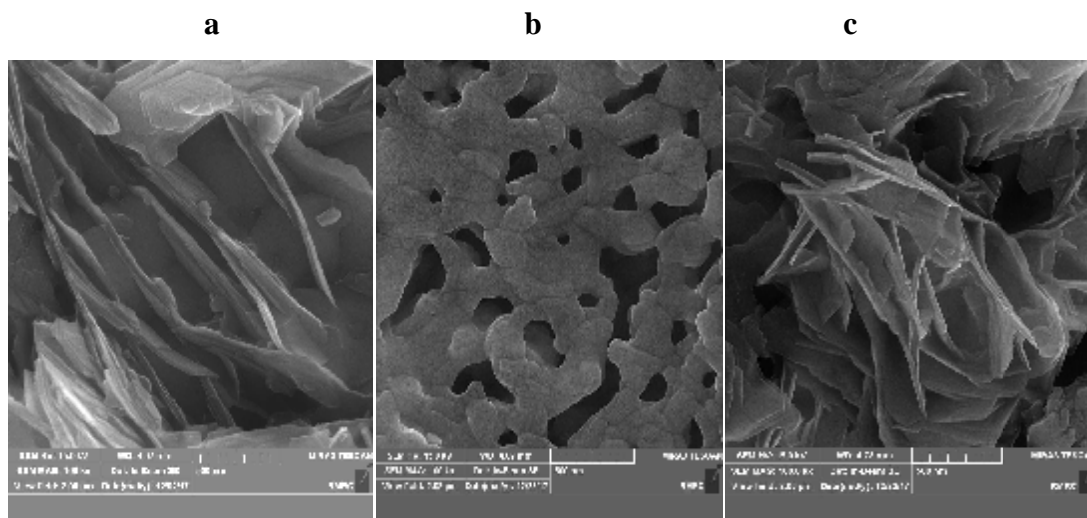


Figure 3. FESEM micrographs of SrAl₂O₄ powder calcined with different solvents, a: cyclohexane, b: benzene and c: toluene.

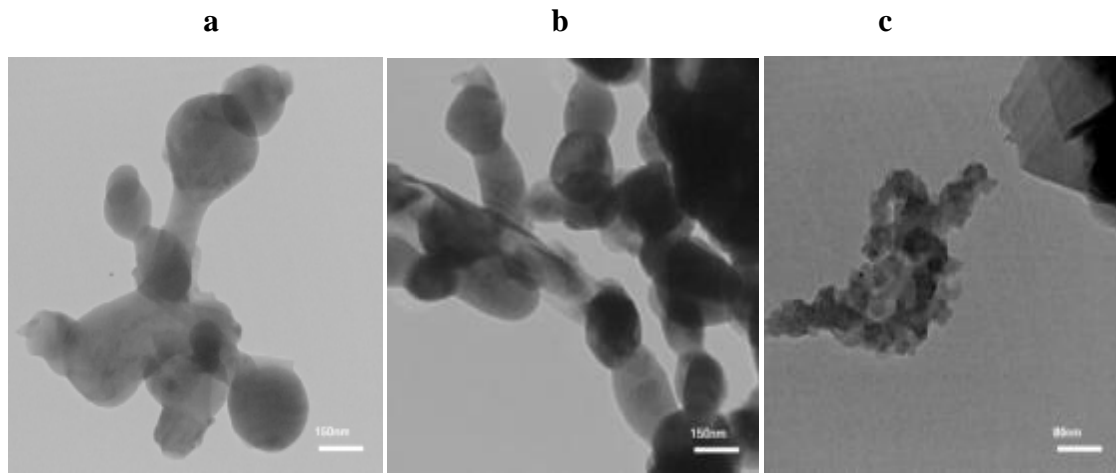


Figure 4. TEM micrographs of SrAl₂O₄ powder calcined with different solvents, a: cyclohexane, b: benzene and c: toluene.

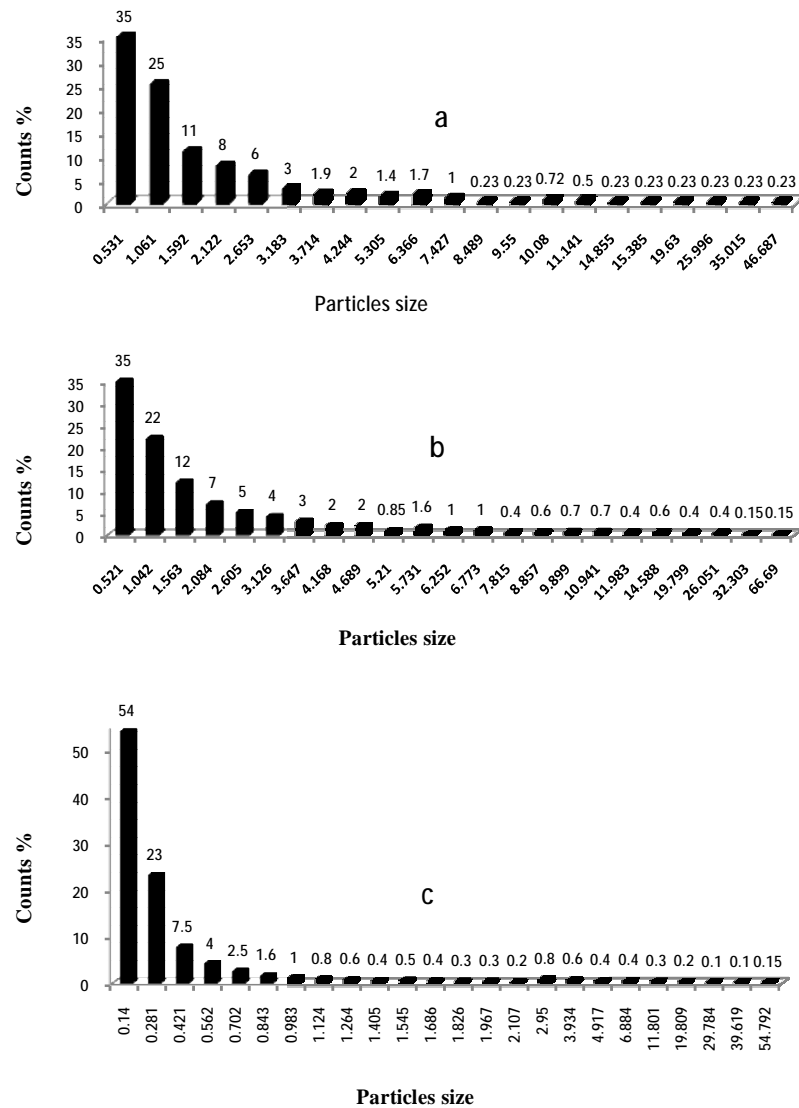


Figure 5. Diagram of particles distribution of SrAl₂O₄ was estimated by using software IMAGE J, a: cyclohexane, b: benzene and c: toluene.

Results and discussions

The XRD patterns of the calcined samples are reported with different solvents at 1000°C for 2h in Figure 1. The detected diffraction peaks are corresponded to the standard patterns of SrAl₂O₄ (ICSD card 00-031-1336). All the samples were found to have a hexagonal crystal structure. According to this analysis, all three patterns show the formation of single phase SrAl₂O₄. No other crystalline phase was found in the calcined samples. Dislocation of peaks (2θ) in XRD with increasing polarity of solvents was increased. The average nanoparticles size is calculated by the following Scherer's equation.

$$D = \frac{k\lambda}{\beta \cos\theta}$$

In the equation, D is the size of the crystallite sample, λ is the wavelength of X-ray source of Cu-K α (1.54 Å), k is the Scherer's constant (0.9), β of FWHM is the width at half its maximum intensity and θ is the half diffraction angle at which the peak is located. The result shows that the size of the synthesized nanoparticles with increasing polarity (dipole moment) of solvent from $u = 0$ Debye (cyclohexane and benzene) to $u = 0.136$ Debye (toluene) was increased from 22 to 37 nm, respectively. Table 1 shows the data of Scherrer's equation and the dislocation value.

Table 1. Scherer's data information for SrAl₂O₄ nanoparticles.

samples	β_{obspeak} (2θ)	position crystallite size (2θ)	type of crystallite (nm)
Cyclohexane	0.370	29.35622	hexagonal
Benzene	0.236	29.25835	hexagonal
Toluene	0.221	28.20637	hexagonal

The surface morphology of samples was reported by FESEM. The FESEM micrographs of SrAl₂O₄ nanopowders in different solvents show that the particles are not uniform in shape. FESEM images show that at cyclohexane, shape of particles are as sheet and are not clung to each other, at benzene shape of them are nearly spherical and the boundary between phases is clear and also density of the particles are more than the other images and also at toluene they are sheet but are clung to each other. In the FESEM images due to the presence of moisture in the environment, agglomeration between nanoparticles is observed.

Figure 4 shows the TEM micrographs and size distribution of nanoparticles. These samples were synthesized with different solvents, surfactant Span 40 and then they were calcined at 1000°C for 2h. All the particles are very fine. TEM images show that the most of SrAl₂O₄ nanoparticles synthesized at cyclohexane and benzene are completely spherical, and at toluene nearly spherical. The average size of the particles estimated from the TEM image using standard software IMAGE J is found to increase with increasing polarity of solvent. The average size of nanoparticles from $u = 0$ Debye (cyclohexane and benzene) to $u = 0.136$ Debye (toluene) are increased, respectively. The nanoparticles size distribution in different solvents is similar to each other that is shown in Figure 5. Increasing of the average size of nanoparticles is agreement with crystallite size data of the targets calculated by Scherer's equation.

Results of experiment show that the polarity of solvent can control the diameter of the nanoparticles in the micro-emulsion.

Conclusion

In the study, SrAl₂O₄ nanoparticles were synthesized in the presence of solvents with different polarity (cyclohexane, benzene, and toluene) and surfactant Span 40 employing the reverse micelle method at 1000°C for 2h. The presence of hexagonal phase was demonstrated and no other crystalline phase was found in the samples. The results of the TEM are agreement with the XRD results. Collectively, it was concluded that the final particle size is influenced by polarity of solvent. The average particle size was increased with increasing of solvent polarity. The presence of moisture in the environment causes agglomeration of nanoparticles. It is expected that these nanoparticles can find applications in different fields such as military devices, emergency passageway, lighting equipment and traffic signs.

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