Experimental Design for the Optimization of Hydrothermal Synthesis of Samarium Oxide (Sm2O3) Nanoparticles under Supercritical Water Condition

Shahryar Jafari Nejad and Aboali Golzary

***Abstract*—In the present study, synthesis of samarium oxide nanoparticles using supercritical water as a reaction medium in batch type reactor was studied. The crystallographic identity and morphology of the synthesized nanoparticles were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively. The XRD patterns indicate that the well-crystallized samarium oxide nanocrystals can be easily obtained under the current synthetic conditions. The effect of four parameters includes temperature, reaction time; primary concentration of aqueous solution of samarium (III) nitrate and pH of starting solution on reaction efficiency, particle size and the BET surface area were investigated using 24-1 fractional factorial design. Finally, by employing a regression analysis three models based on effect of significant main variables and their binary interactions were proposed which can predict the percentage of reaction efficiency, particle size and BET surface area with acceptable confidence.**

***Index Terms*—Samarium Oxide Nanoparticles, Supercritical Water, Morphology,**

I. Introduction

Recent advances in creating and characterizing size selected atomic clusters in the range 1–100 nm have enabled the first tentative steps in the synthesis of a wide range of new materials from nanoscale particles. Nanometer-sized materials are of greatest interest because they have novel physical and chemical properties that are not characteristic of the atoms or of the bulk counterparts. The large ratio of surface area to volume can contribute to some of the unique properties of nanoparticles [1-4]. For the application of inorganic nanoparticles, hybrid materials of nanoparticles and polymers are of great industrial interest. Control of nanoparticle morphology, perfect dispersion and/or arrangement of nanoparticles in the polymer is essential to achieve functionalization of the hybrid materials: higher mechanical strength (tube, plate), heat conductivity/resistivity (tube/sphere), and gas insulation (plate). Thus, methods to control size, morphology and dispersion in organic molecules need to be developed for nanoparticles.

In the past two decades, there has been an increasing interest in the use of supercritical fluids (SCFs) as an alternative to the use of organic solvents in many industrial applications [5-7].

Among methods to prepare nanoparticles, supercritical hydrothermal synthesis is a unique technique to synthesize metal oxide and hydroxide nanocrystals from aqueous solution of metal salts, in which the size, morphology and crystal structure are controllable [8]. This method relies on high reaction rate of hydrothermal synthesis above the critical temperature of water and lower solubility for the formed metal oxide [9], which causes an extremely high degree of supersaturation of the metal oxide and thus allows nanoparticle formation [7, 10, 11].

Supercritical hydrothermal synthesis process has been extensively explored by Adshiri et al. [12–14], Hakuta et al. [15–18], Li et al. [19], Jafari Nejad et al. [7] in various works to produce nanometric particles of several single and complex metal oxides. They evidenced several parameters of the process that can control dimension and morphology of the produced nanoparticles. Solubility of metallic oxides in supercritical water (SCW), pH of starting solution, the initial concentration of the feed and temperature can play a relevant role in this process.

Rare Earth oxide compounds are basic anhydrides and can therefore react with acids and with strong reducing agents in redox reactions. They are compounds containing at least one oxygen anion and one metallic cation. They are typically insoluble in aqueous solutions (water) and extremely stable making them useful in ceramic structures as simple as producing clay bowls to advanced electronics and in light weight structural components in aerospace and electrochemical applications such as fuel cells in which they exhibit ionic conductivity. Samarium Oxide nanoparticles is a highly insoluble thermally stable Samarium source suitable for glass, optic, ceramic, catalysis [20] applications and infrared absorbing glass to absorb infrared radiation. Also, it is used as a neutron absorber in control rods for nuclear power reactors. The oxide catalyzes dehydration of acyclic primary alcohols to aldehydes and ketones. Another use involves preparation of other samarium salts [21].

There are nnumerous techniques to synthesis samarium particles such as thermal decomposition, by burning the metal in air or oxygen at a temperature above 150 ℃ [21], hydrolysis technique [20]. In this research, we study the production of samarium oxide nanoparticles using supercritical water as a reaction medium in batch type reactor. There are many different conditions affected the synthesis of samarium oxide such as temperature,reaction time, primary concentration of aqueous solution of samarium

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(III) nitrate and pH of starting solution which are studied in this research. To determine the effect of each factor at different levels, a method of experimental design named fractional factorial is applied [7, 22 and 23]. Fractional factorial design enables identification of interactions between factors more accurately and allows determining the effect of one factor among the other factors studied [24]. This paper explains for the first time, how statistically designed experiments are used in identifying the effects of special factors in synthesis of samarium oxide from aqueous solution of samarium (III) nitrate ($Sm(NO_3)_3.6H_2O$) under supercritical water condition.

II. Experimental

A. Materials

Aqueous solutions of samarium nitrate was prepared by dissolving known amount of this salt, Sm $(NO_3)_3.6H_2O$, supplied by Merck in analytical grade in deionized water, to prepare a feed model of desired cation. The pH of the starting aqueous solutions was adjusted to desired values with NaOH and HNO_3 solutions. All other cited chemicals used were of analytical reagent grade.

B. Apparatus

Samarium oxide samples were synthesized by the supercritical water hydrothermal method using the batch type reactor. For the batch type synthesis a pressure-resistant SUS316 vessel with 150 cm^3 volume was used. This reactor was heated using an electrical heater.

C. Procedure

In a typical experiment, 50ml of the aqueous solutions of samarium nitrate with determined concentration and pH was transferred to the reactor vessel. The hydrothermal reaction was performed in the reactor vessel at desired temperature and reaction time. Later, the reactor vessel was quenched with cold water to stop the reaction and products were collected by washing the reactor with deionized water followed by the repeated deionized water washing and centrifugation to remove the unreacted reagent. Then, the samarium oxide nanoparticle dried in oven at 60 ℃ for 24 h. Concentration of Sm^{3+} ion in the solution recovered, analyzed by Inductivity Coupled Plasma Analyzer (ICP) with the precision of ± 0.01 ppm, from which conversion of samarium nitrate (percentage of reaction efficiency) was evaluated. For calibration of the apparatus sample solutions with different concentrations of 0.8 ppm,2 ppm, 4 ppm, 20 ppm, 40 ppm and 80 ppm were prepared and measured everyday using the apparatus.

$$\%\,reaction\,efficiency = \frac{weight\,of\,Sm^{3+}\,in\,starting\,solution - weight\,of\,Sm^{3+}\,in\,recovered\,solution}{weight\,of\,Sm^{3+}\,in\,starting\,solution} \times 100 \quad (1)$$

In the case of processes influenced by multiple variables, statistical experimental design has been shown to be a powerful tool for determining the effects of operational factors and their interactions; this allows process optimization to be conducted effectively. This technique has been used widely in the chemical industry [24].

Four factors, two-level 2^{4-1} fractional factorial method was designed,which means to carry out 8 experiments. Some preliminary experiments were used to plan important variables. The real amount of each parameter is presented in table 1 at low and high levels assigned by (-) and (+), respectively.

TABLE 1: THE REAL AMOUNT OF EACH FACTOR.

Factors	Low level (-)	High level (+)
A: Temperature(℃)	400	470
B: Reaction time (h)	1	2
C: Concentration of salt (M)	0.15	0.25
D: pH of starting solution	3	6

In this research, a 2^{4-1} fractional factorial design was employed to fit a second order polynomial model. The general equation of the second degree polynomial is stated as follows:

$$Y = \beta_0 + \sum_{i=A}^{D} \beta_i X_i + \sum_{i=A}^{D} \sum_{j=A \neq i}^{D} \beta_{ij} X_i X_j + \varepsilon \quad (2)$$

where, Y is the predicted response (%Reaction efficiency, particle size and BET surface area), X_i are the uncoded or coded values of the factors (temperature denoted by A, reaction time denoted by B, concentration denoted by C and pH of the starting solution denoted by D), β_0 is a constant, β_i are the main effect coefficients for each variable and β_{ij} are the interaction effect coefficients. The second order polynomial coefficients were obtained using MINITAB software, and the model was validated for the process conditions used in this study.

D. Characterization

The crystallographic identity of the synthesized nanoparticles was investigated by X-ray diffraction (XRD) measurements. XRD analysis was conducted at room temperature on a Dmax γn X-ray diffractometer (Rigaku) with Cu Kα radiation. XRD analysis was also used to determine crystal size by Scherer's formula:

$$d = \frac{0.9\lambda}{\beta.\cos\theta} \quad (3)$$

where, d is the average crystal size, λ is the X- ray wavelength (0.15406 nm), β is the full-width at half-maximum (FWHM) and θ is the diffraction angle.

The size and shape of the nanoparticles were studied by using a transmission electron microscopy (TEM, JEM-1200 EX II (JEOL, Ltd.)). The surface area of the nanocrystals was determined by the nitrogen adsorption at 77.3 K in a Quantachrome Instruments version 2.2 in accordance with the BET method.

III. Result and Discussion

The effect of four parameters includes temperature,reaction time; primary concentration of aqueous solution of samarium (III) nitrate and pH of starting solution were investigated using an experimental design. The percentage of reaction efficiency, particle size and the BET surface area of the samples are shown in Table.2. The factorial design can cover the main and interaction effects of the parameters within the whole range of selected parameters.

According to the sparsity-of effects principle in factorial design, it is most likely that main (single factor) effects and two-factor interactions are the most significant effects, and the higher order interactions are negligible. In other words, higher order interactions such as three-factor interactions are very rare and considered as the residual which are dispersed randomly.

A. Effect of operating parameters on percentage of reaction efficiency

The effects of the studied parameters and interaction effect between parameters on percentage of reaction efficiency are presented in Figure 1. Analysis of the effect of principal factors showed that these parameters have positive effect on percentage of reaction efficiency. In the considered range of parameters, reaction time and primary concentration of solution are the most significant variables in achieving maximum reaction efficiency. According of positive effect of these parameters increasing in reaction time and primary concentration of solution enhanced the reaction efficiency.

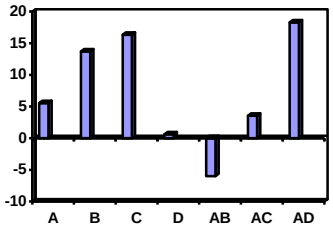

Fig 1: Estimated effects of factors on reaction efficiency using fractional factorial design.

Interaction effect between parameters showed that when the temperature is in high level, increase in reaction time, primary concentration of solution and pH of starting solution has positive effect on percentage of reaction efficiency. But, when the temperature is in low level, increase in reaction time and primary concentration of solution and decrease in pH of starting solution has positive effect on percentage of reaction efficiency. When the reaction time is in high level, increase in primary concentration of solution and pH of starting solution has positive effect on percentage of reaction efficiency and in low level of reaction time, these parameters have negligible effect on reaction efficiency. The interaction effect of concentration-pH showed that in low level of concentration, an increase in pH increases reaction efficiency, but, in high level of concentration, an increase in pH decreases reaction efficiency. The corresponding second-order response model for the % reaction efficiency which is valid for uncoded units is:

$$Y = 266.866 - 0.6504X_A + 88.2529X_B - 278X_C - 75.541X_D - 0.171357X_AX_B + 1.0150X_AX_C + 0.174119X_AX_D \quad (4)$$

An experiment (sample A_9) was performed under certain conditions (Temperature= 500 ℃, reaction time= 1.5 h, primary concentration= 0.35 M and pH= 4) for validation of the model; result showed that obtained reaction efficiency from this experiment (% reaction efficieny= 68.52) is similar to that predicted by the model (% reaction efficiency= 71.926). This model could be considered quite reliable for predicting the reaction efficiency.

B. Morphology and effect of operating parameters on crystallographic analysis

The X-ray diffraction results for the samarium oxide nanocrystals (for example A_3, A_4 and A_5 samples) synthesized by the batch reactor at supercritical water hydrothermal conditions are shown in Figure 2. The XRD patterns match that of the value in the standard card. The XRD patterns indicate that the well-crystallized samarium oxide nanocrystals can be easily obtained under the current synthetic conditions. The strong and sharp diffraction peaks indicate that the as-synthesized samples are well crystalline. Generally, the formation of samarium oxide particles requires a long reaction time with high temperature or postheat treatment. In supercritical water synthesis, samarium oxide nanocrystals formed at relatively low temperature 400-470 ℃ in a single step without an additional heat treatment. This can be attributed to the extremely high hydrolysis reaction rate and the low solvent power of supercritical water that most likely leads to a high degree of supersaturation [7, 25].

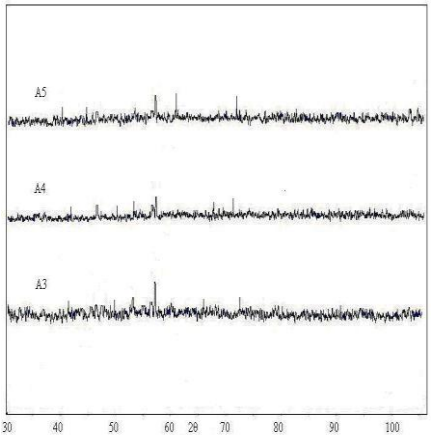

Fig 2: Powder X-ray diffraction patterns for A3, A4 and A5 samples prepared by the batch type reactor under supercritical water condition.

The effects of the studied parameters and interaction effect between parameters on particle size are presented in Figure 3. Analysis of the effect of principal factors showed that in the considered range of parameters, temperature, primary concentration of solution and pH of starting solutions are the most significant variables. According of positive effect of the primary concentration of solution, increasing in this parameter enhances the particle size and negative effects of temperature and pH of starting solutions imply increasing in these parameters decrease the particle size. The reduction of the size of the nanoparticles with increasing temperature was explained by the reduction of the physical coalescence of the nanoparticles [25] or supercritical water provides an excellent reaction medium for the synthesis, since it allows varying the reaction rate and equilibrium by shifting the dielectric constant and solvent density with pressure and temperature. One of the expected benefits is higher reaction rates and lower solubility for metal oxides, which lead to rapid nucleation and smaller particle size of the products [26]. Reaction time has negligible effect on particle size and increase the particle size of samarium oxide slightly. Actually, Short reaction time limits the particle growth. These results are agreed well with the other researches [7, 11, 17, 25 and 27].

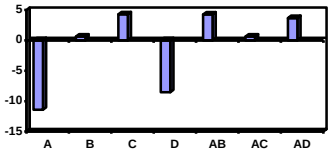

Fig 3: Estimated effects of factors on particle size using fractional factorial design.

Interaction effect between parameters showed that when the temperature is in high level (470 ℃), an increase in reaction time and primary concentration of solutions increases particle size and an increase in pH of starting solutions decreases particle size. But, when the temperature is in low level (400 ℃), an increase in reaction time and pH of starting solutions decreases particle size. But an increase in primary concentration of solutions increases particle size. When the reaction time is in high level, increase in primary concentration of solution increases particle size. But, an increase in pH of starting solution decreases particle size. In low level of reaction time, increase in these parameters decreases particle size. The interaction effect of concentration-pH showed that in low and high level of concentration, an increase in pH decreases particle size. The corresponding second-order response model for the particle size (nm) which is valid for uncoded units is:

$$Y = 302.106 - 0.538X_A - 52.3167X_B - 34.71X_C - 18.024X_D + 0.121714X_AX_B + 0.178X_AX_C + 0.03488X_AX_D \quad (5)$$

An experiment (sample A_9) was performed under certain conditions (Temperature= 500 ℃, reaction time= 1.5 h, primary concentration= 0.35 M and pH= 4) for validation of the model; result showed that obtained particle size from this experiment (particle size= 60.237 nm) is similar to that predicted by the model (particle size = 62.481 nm). This model could be considered quite reliable for predicting the reaction efficiency.

The electron micrographs of the sample A_3 is illustrated in Figure 4. The A_3 sample shown in Figure 4 seems to be having mixture of spherical and cubic morphology with particle size ranging between 40 and 60 nm. Therefore, the TEM data is also in good agreement with XRD data.

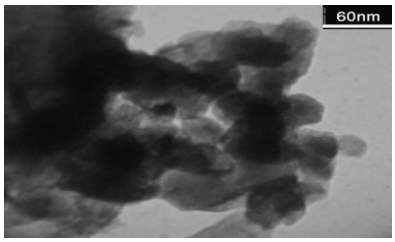

Fig 4: TEM image of samarium oxide nanocrystals synthesized by batch reactor (sample A3)

C. *Effect of operating parameters on BET surface area*

The effects of the studied parameters and interaction effect between parameters on BET surface area are presented in Figure 5. Reaction time and primary concentration of solution have negative effect on BET surface area. According of positive effect of the temperature and pH of starting solutions, increasing in these parameters enhance the BET surface area. Increase in the surface area of samples can be attributed to the reduction of particle size with increasing in temperature and pH of starting solutions. These results are in consistent with XRD and TEM data. The high surface area of the samarium oxides is supposed to be important for the catalytic performance [20].

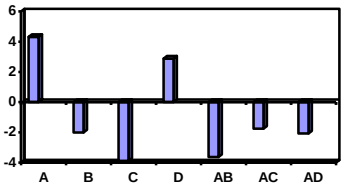

Fig 5: Estimated effects of factors on BET surface area using fractional factorial design.

Interaction effect between parameters showed that when the temperature is in high level (470 ℃), an increase in reaction time and primary concentration of solutions decreases BET surface area and an increase in pH of starting solutions increases BET surface area. But, when the temperature is in low level (400 ℃), an increase in reaction time and pH of starting solutions BET surface area. But an increase in primary concentration of solutions decreases BET surface area. In high and low level of reaction time, an increase in primary concentration of solution decreases BET surface area. But, an increase in pH of starting solution increases BET surface area. The interaction effect of concentration-pH showed that in low level of concentration, an increase in pH increases surface area but in high level has negligible effect on BET surface area. Optimum value for the BET surface area is 32.714 m^2g^{-1} that takes place in 470 K, reaction time of 1 h, primary concentration of 0.15 M and pH of starting solution of 6.

The corresponding second-order response model for the BET surface area (m^2g^{-1}) which is valid for uncoded units is:

$$Y = -145.74 + 0.406X_A + 43.115X_B + 178.93X_C + 9.545X_D - 0.103721X_AX_B - 0.5006X_AX_C - 0.0197X_AX_D \quad (6)$$

An experiment (sample A_9) was performed under certain conditions (Temperature= 500 ℃, reaction time= 1.5 h, primary concentration= 0.35 M and pH= 4) for validation of the model; result showed that obtained particle size from this experiment (BET surface area = 19.937 m^2g^{-1}) is similar to that predicted by the model (BET surface area = 18.045 m^2g^{-1}). This model could be considered quite reliable for predicting the reaction efficiency.

IV. Conclusions

In this study we have successfully demonstrated the synthesis of samarium oxide nanoparticles at supercritical water hydrothermal conditions. The XRD patterns indicate that the well-crystallized samarium oxide nanocrystals can be easily obtained under the current synthetic conditions. The strong and sharp diffraction peaks indicate that the as-synthesized samples are well crystalline. The effect of four parameters includes temperature, reaction time; primary concentration of aqueous solution of samarium (III) nitrate and pH of starting solution on reaction efficiency, particle size and the BET surface area were investigated. Analysis of

the effect of principal factors showed that these parameters have positive effect on percentage of reaction efficiency. Increase in temperature and pH of starting solution can reduce the particle size and enhance the BET surface area. The high surface area of the samarium oxides is supposed to be important for the catalytic performance. The results showed that the optimum value for percentage of reaction efficiency is 64.11 % that takes place in 470 K, reaction time of 2 h, primary concentration of 0.25 M and pH of starting solution of 6 and optimum values for particle size and the BET surface area are 51.611 nm and 32.714 m^2g^{-1}, respectively that take place in 470 K, reaction time of 1 h, primary concentration of 0.15 M and pH of starting solution of 6.

TABLE 2: RESULTS OF 24-1 FRACTIONAL FACTORIAL DESIGN FOR THE REACTION EFFICIENCY, PARTICLE SIZE AND THE BET SURFACE AREA OF THE SAMPLES.

Samples	Temperature	Reaction time	Concentration of solution	pH	%Reaction efficiency	particle size	BET Surface area
	(℃)	(h)	(M)			(nm)	(m^2g^{-1})
A_1	400	1	0.15	3	27.91	76.454	20.131
A_2	400	1	0.25	6	23.03	67.894	22.952
A_3	470	2	0.25	6	64.11	61.395	21.443
A_4	400	2	0.25	3	60.42	76.472	19.625
A_5	470	1	0.15	6	36.49	51.611	32.714
A_6	400	2	0.15	6	29.94	60.614	26.711
A_7	470	2	0.15	3	25.32	61.383	26.271
A_8	470	1	0.25	3	37.51	61.389	26.268

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