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Effect of catalyst concentration and time of reaction on shape and morphology of synthesized mesoporous silica nanoparticles through Stöber method

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Abstract: In this study, mesoporous silica nanoparticles were synthesized based on the Stöber method. Effects of some processing parameters including reaction duration and catalyst concentration on the shape and morphology of synthesized nanoparticles were investigated. It was found that 50% decreasing in amount of catalyst (ammonia) leads to the production of smaller spherical silica nanoparticles approximately up to 61 %. By changing the time of the reaction no remarkable difference was observed among the sols.

Keywords: Sol-gel method, Silica nanoparticles, Stöber method, Ammonia, Time of reaction.

Introduction

Recently "porous metallic oxide nano materials" have attracted great attention in the field of optical and electrical applications, medical science, protection coatings, solar energy applications etc. Such porous materials are usually synthesized by using "sol – gel" process. The major advantage of this method is saving up the energy consumption because the nanoparticles could be synthesized at room temperature. Sol - gel method is based on the transition from a liquid (so – called Nanosol colloidal solution) into a solid state (normally a milky powder material) [1].

Nanosols are colloidal solutions of nanometer sized metal oxide particles in aqueous or organic solvents. Due to the very high surface area of such small particles the nanosols are metastable, thus, for example, during a coating process the particles will aggregate due to the evaporation of the solvent, easily forming a three-dimensional network. Sol - gel process can be basically divided into three steps: formation of the nanosol by hydrolysis of the precursor material and subsequent condensation reactions, the coating process, then drying or curing [2]. Any kind of reactive material with the ability to participate at the gel formation can be used as precursor. Based on published surveys the use of matal alkoxides is more beneficial [1]. Hydrolysis of the alkoxy derivatives of metals or semi-metals would transform them into the corresponding hydroxides. These hydroxides are mostly unstable in higher concentrations and therefore tend to undergo subsequent condensation reactions. The condensation reactions lead to the formation of particles with sizes in the nanometer range. Frequently used precursors are, for example, tetraethoxysilane $Si(OC_2H_5)_4$ (TEOS), titanium(IV)isopropoxide $Ti(OC_3H_7)_4$ or $Al(OC_4H_9)_3$. The product of the reaction described is the so-called nanosol, which is a liquid dispersion of low viscosity (usually in the range of 1 to 6 mPas) containing nanosized particles. This nanosol can be easily applied to numerous substrates, forming dense layers after the evaporation of the solvent [2]. The main steps for preparing sol-gel derived coatings are depicted in Figure **1**.

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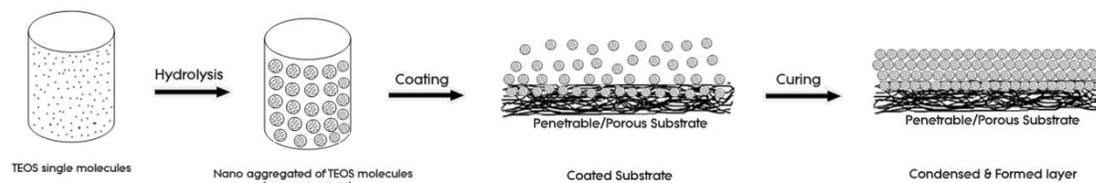
Figure 1: Main steps for the preparation of nanosol coatings (sol-gel process), here shown for a silica coating.

Before 1960s, there was no specific route to the synthesis of colloidal suspensions of metal oxides in form of hydrosols or aerosols, consisting of homogeneous particles of uniform shape and size. In 1968, Stöber proposed a simply method for the synthesis of monodisperse silica nanoparticles by means of hydrolysis of a precursor under alkaline condition [3]. Using ammonia as catalyst, spherical and monodisperse silica nanoparticles can be produced.

There are many published surveys in the field of synthesizing colloidal silica nanoparticles based on the original Stöber method [3-20]. The role of reactants on the final size of obtained silica nanoparticles have been proved in some investigations [3, 4, 7-11, 13, 18, 19].

According to many potential applications of silica nanoparticles and especially their ability to alter the morphology of various substrates [22 - 27] to consider the literature survey there are few studies focused on the possible effects of reactants on the shape and capability of morphology changing of silica networks. In this paper, it was focused on the effect of processing parameters including temperature, catalyst concentration and reaction duration on the morphology and distribution of silica nanoparticles.

Results and discussion

The SEM micrographs with average particle size (in the range of 24 to 388 nm) of synthesized SiO2 nanoparticles and TEM image of Sample No.4 are shown in Figure **2**, Table **1** and Figure **3** respectively.

Table 1: Avarage of particle size of different synthesized nano silica by sol gel process (obtained from SEM micrographs).

sol sample no.	Mean particle size (nm)
1	388
2	24
3	48
4	78
5	77

The possible reactions that are totally occurred in "sol – gel" process can be classified into 6 ones [1]:

$$\equiv Si - OR + HOH \longrightarrow \equiv Si - OH + ROH \qquad (1)$$

$$\equiv Si - OH + \equiv Si - OH \longrightarrow \equiv Si - O - Si \equiv + HOH \qquad (2)$$

$$\equiv Si - OH + \equiv Si - OR \longrightarrow \equiv Si - O - Si \equiv + ROH \qquad (3)$$

$$(OR)_3 - Si - OH + HO - Si - (OR)_3 \longrightarrow [(OR)_3 - Si - O - Si - (OR)_3] + H - O - H \qquad (4)$$

$$(OR)_3 - Si - OR + HO - Si - (OR)_3 \longrightarrow [(OR)_3 - Si - O - Si - (OR)_3] + R - OH \qquad (5)$$

$$Si(OR)_4 + 4H_2O \longrightarrow Si(OH)_4 + 4R - OH \qquad (6)$$
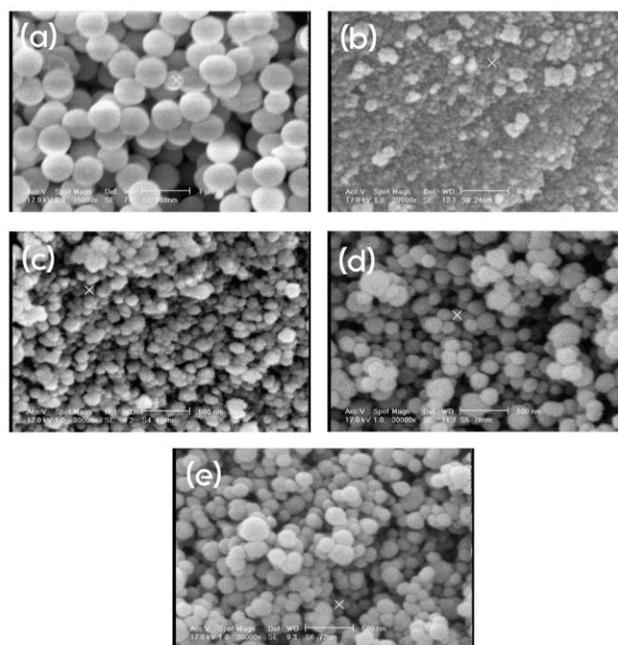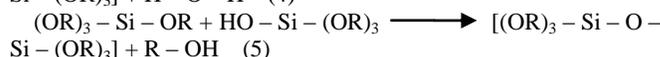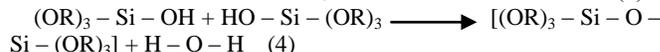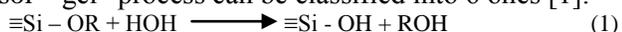
Figure 2: SEM micrographs of synthesized sols: (a) sol 1 (b) sol 2 (c) sol 3 (d) sol 4 (e) sol 5.
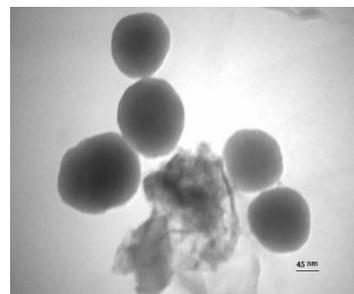
Figure 3: TEM micrograph of sol 4.

In the first step, precursor is hydrolyzed to form silicic acid in hydroxide form (Equation (1)). Because of its instability, silicic acid may undergo the condensation reaction. In this stage two possible

"Water or Alcoholic condensation reactions" would come to pass (Equations 2&3). After about 10 min the opalescence of the solution is increased. After this initial phase, the solution regularly is changed to white turbid color. Equations (4&5) are attributed to the partial hydrolysis of the precursor. These reactions are strongly dependent to the molar ratio of the reactants. The hydrolysis reaction is completed by gaining the stoichiometric molar ratio of water:Si(OR)4 to the four (Equation (6)) [1].

It is claimed that in the sol–gel process the microstructure of the synthesized nanoparticles are usually affected by the hydrolysis and condensation reactions. These two parameters are controlled by adjusting the PH of the solution. Under acidic condition, condensation reactions start after completion of the hydrolysis of the precursor. In this circumstance the synthesized nanoparticles have microporous (pore size <2 nm) structure. On the contrary by using an alkaline media as the catalyst, condensation reactions are faster than hydrolysis so that the final synthesized nanoparticles have mesoporous (2nm < pore size < 50 nm) structure [1]. The BET result indicated that specific surface area of nanoparticles was about 27.897 m^2/g.

In this study "Ammonia" was used as an alkaline catalyst. According to Stöber et al [3], and Matsoukas and gulari [7], with increasing the amount of catalyst the particle size would increase. Vice versa the decreased size also is reported [8]. In this study, increase in the amount of ammonia leads to increase in the size of silica nanoparticles. Comparing sols 1 with 2 and also sols 3 with 4, it is clear that decreasing in the amount of catalyst would reduce the particle size of the synthesized sols up to 61%. It is reported that the size of silica nanoparticles is controlled by the relative contribution from nucleation and growth [19]. As mentioned in advance, during sol-gel process the first step is to hydrolysis of the precursor. The consequence is to form intermediate complex as the result of the reaction between ethoxy groups of precursor with the water molecules. In the next step two possible condensation reactions, "Alcoholic" or "Aqueous" would be happened. These reactions will cause forming dioxide silicon compounds in the bulk of nanoparticles network [19]. Growth rate has significant effect on synthesized nanoparticles size; low growth rate so would decrease it and high growth rate would increase the size of nanoparticles.

The most important role of ammonia is to control the morphological shape and size of nanosilica particles. As Stöber reported, in the absence of ammonia, the

irregular shapes of the silica nanoparticles flocculated were formed with uneven distribution [3].The hydrolysis is a very slow process, thus acid or alkaline catalysts are used to speed up the process. According to Stöber method, ammonia promotes the rate of hydrolysis and condensation reactions (resulting in faster kinetics) [8], so that less ammonia concentration would cause slower kinetics and reduced size of nanoparticles. Figure **4** confirms this.
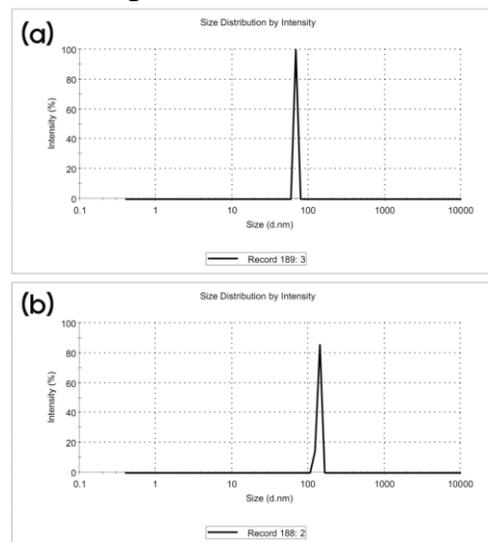
Figure 4: Particle size distribution graphs for: (a) Sol no.3 (b) Sol no.4.

It was observed that the stirring times had no significant effect on the structure of nanoparticles, and the nanoparticles represented the same mean value in method 5, compared to method 4.

By analysis of X-ray diffraction, the crystalline structure was observed. It is reported that the characteristic peak corresponding to the silica crystalline structure is appeared at $2\theta = 22°$ in the XRD diagram [28]. According to Figure **5**, the characteristic crystalline peaks are realized at $2\theta = 8.1°$ and $22°$. However, the crystalline peaks are not sharp. As the sol-gel process is performed under moderate temperature, well-ordered crystal lattice (tetrahedral structure) could not be continuous over a large range. Thus in some regions the atoms form a continuous random network (long range order would not be present anymore in these regions). Based on the XRD results, synthesized nanoparticles showed both of crystalline and amorphous regions.
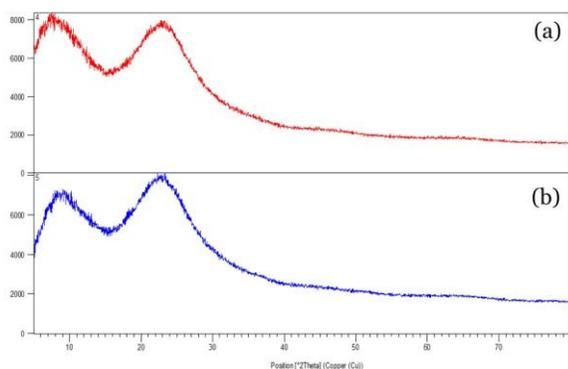
Figure 5: XRD diagrams of: (a) sol 4 (b) sol 5.

Conclusion

In this study it was proved that varying reaction parameters in sol- gel process can alter the size and shape of synthesized silica nanoparticles. The most predominate factor among reagents, is the growth rate of affected by the concentration of catalyst. It can alter the size of nanoparticle in the range of 61%. So, different colloidal nanoparticles can be obtained which can show different surface properties when are fabricated on a surface. As the process was performed at low temperatures both of crystalline and amorphous regions were obtained.

Experimental

Materials:

Tetraethylorthosilicate (TEOS), Hydroxide Ammonium (NH_4OH 25%) and Ethanol (C_2H_5OH 98%) were purchased from Merck Company (Germany).
Methods:

Synthesis of SiO₂ by sol-gel method: SiO_2 nano-particles were prepared via the sol-gel process based on the method proposed by Stöber (1968) for the synthesis of SiO_2 nano-particles from TEOS precursor in the presence of alkaline catalysis [3]. Five sols were synthesized using the Stöber method by three different procedures (Table **2**).

Characterization:

Powder samples were sputter-coated with gold to a thickness of approximately 200 A° for 120 S and their morphology were observed by a scanning electron microscopy (SEM) (XL30,Philips, Royal Philips Electronics, Amsterdam, Netherlands) at 17 keV. The SiO_2 nano structures were also observed with the transmission electron microscope (TEM) (EM 10C, Zeiss, Oberkochen, Germany). The size of silica nanoparticles was measured with a particle size analyzer (Malvern Instruments, Malvern, Worcestershire, UK). To identify the crystalline phase and structure of synthesized nanoparticles, XRD patterns were collected by means of a X-ray diffractometer, equipped with a Ni-filtered CuKα radiation X-ray source (30 kV and 30 mA) (X'Pert Pro MPD, PANalytical, Almelo, Netherlands). Specific surface area of silica nanoparticles was determined from N2 adsorption/desorption isotherms by a Surface area analyzer (Belsorp mini II, Bel Japan, Tokyo, Japan). All samples were outgassed for 1 hour at 300°C and 0.1 Pa prior to measurement. Specific surface area was calculated by the BET method and reported in m^2/g.

Table 2: Different procedure for preparing five basic different sols.

Sol sample	Preparation methods	Reference
1	50 ml ethanol, 7.5ml ammonium hydroxide 25% and 3 ml TEOS were mixed at room temperature for 24 hours	Based on [4]
2	50 ml ethanol, 5ml ammonium hydroxide 25% were stirred for 30 minutes at 60° C and then 3ml TEOS was added drop by drop. Then it was mixed at room temperature for 24 hours	Based on [5]
3	25ml ethanol, 0.5ml Ammonium hydroxide and 3.6ml distilled water and 11.5ml TEOS was mixed at room temperature for 24 hours	Based on [6]
4	25ml ethanol, 1 ml ammonium hydroxide, and 3.6 ml distilled water and 11.5ml TEOS were mixed for 24 hours at room temperature	Based on [6]
5	25ml ethanol, 1 ml ammonium hydroxide, and 3.6 ml distilled water and 11.5ml TEOS were mixed for 2 hours at room temperature (sol 5 had the same condition as sol 4, except that sol 5 was stirred for 2 hours)	Based on [6]

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