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The effect of ethanol and temperature on the structural properties of mesoporous silica synthesized by sol-gel method

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Abstract

Mesoporous silica nanoparticles are synthesized in the presence of ethanol as a co-solvent and different temperatures by sol-gel process. The spherical mesoporous silica nanoparticles are obtained at 50˚C in presence of 1 ml ethanol. Increasing the reaction temperature with constant amount of ethanol from 30˚C to 50˚C, decreases the particle size scarcely from 84-115 to 86-94 nm and further increasing of temperature from 50˚C to 80˚C, increases the particle size to 160 nm with disordered morphology of mesoporous silica nanoparticles. Presence of ethanol leads to formation of high quality, clear and uniform particles with desirable spherical morphology and larger particles up to 170nm in constant temperature. Furthermore, the structural properties of mesoporous silica nanoparticles are improved by increasing ethanol in the synthesis. According to N2 adsorption-desorption, with 5 ml ethanol, the pore size, pore volume and specific surface area are 3.93 nm, 0.40 Cm3 g^{-1}, and 531 m2 g^{-1}, respectively.

Keywords: mesoporous silica; nanoparticle; sol-gel; ethanol; temperature

1. Introduction

Mesoporous silica nanoparticles (MSNs) have attracted significant attention in variety of fields such as catalysis, bioimaging, biosensors, controlled drug release, and cancer treatment due to their tunable particle size, uniform large pores, and high specific surface area [1,2]. These outstanding properties of mesoporous silica nanoparticles play great role in their applications [3]. The key parameters that influence structural properties of mesoporous silica particles such as particle size, morphology, porosity, are the concentration of TEOS, CTAB, ammonia, water, ethanol and related ratios besides reaction temperature [3-5]. In previous studies significant effect of ethanol as a co-solvent on monodispersity and size of the silica particles, decane/ethanol ratio in pore expanded MSNs, and ethanol/H_2O ratio to control the morphology and porosity structure of MSNs is observed [1, 3, 4, 6]. In addition, Kachbouri et.al. and Zainal et.al. have been studied the effect of temperature on the size of silica particles [3, 7]. Synthesis of spherical mesoporous silica nanoparticles in our study follows the sol-gel process by using

TEOS as a silica precursor in combination with a cationic surfactant such as CTAB as a pore-forming agent and sodium hydroxide (NaOH) as a catalyst in presence of water/ethanol solution. The purpose of this study is to determine the effect of reaction temperature on size, shape, and quality of the synthesized particles in presence of ethanol by sol-gel process. Moreover, the influence of ethanol concentration on internal structure, particle size, and morphology of MSNs has been investigated.

2. Materials and Methods

2.1. Materials

Cetyltrimethylammonium bromide (CTAB, 99 %), tetraethyl Orthosilicate (TEOS, 99%), ethanol (EtOH, 99.9 %) and sodium hydroxide (NaOH, 98.0 %) were purchased from Merck.

2.2. Preparation of mesoporous silica nanoparticles

2.2.1. Procedure

50 ml deionized water, 0.1 g CTAB and desired amount of ethanol (according to Table 1) were added to a flask which was placed in water bath and stirred properly at 760 rpm for 20 min at the set temperature indicated in Table 1. After 20 min, the prepared amount of NaOH (dissolving 0.028 g NaOH in 0.35 ml deionized water) and 0.5 ml TEOS were added dropwise to the solution (0.1 ml/min) and stirred for 2 h. The pH of the solution was about 9 due to the presence of ethanol.

Then, the solution was cooled to room temperature and centrifuged at 7830 rpm for 15 min. Subsequently, the obtained precipitation was washed by ethanol so the pH reduced to 7. Next, the sample was dried in the oven at 60 ˚C for 24 h. In the following, the sample was heat treated in the furnace at 550 ˚C (heating rate: 1˚/min) for 3 h to remove CTAB.

2.2.2. Characterization of spherical mesoporous silica nanoparticles

After the synthesis of mesoporous silica nanoparticles, filed emission scanning electron microscopy (FESEM) and Brunauer–Emmett–Teller (BET) analyses were carried out.

The 6 synthesized samples (by temperature and ethanol variation according to table 1) were analyzed by FESEM (TESCAN model MIRA3, Czech Republic).

Samples 5E-50 and 7E-50 were characterized by Nitrogen adsorption-desorption to evaluate the effect of ethanol on porous structure of MSNs. BET adsorption and BJH adsorption diagrams were also drawn. The analysis was carried out by BELSORP-mini II instrument. The samples were previously degassed at 150◦C for 15 h.

3. Results and discussion

3.1. Effect of temperature

In this regard, synthesis reaction was carried out at 3 different temperatures. Samples 1E-30, 1E-50, and 1E-80 were synthesized with 1 ml ethanol at 30, 50, and 80 ˚C, respectively. FESEM micrographs show that the particle size of synthesized nanoparticles are 84-115 nm, 86-94 nm and 135-160 nm at 30˚C, 50˚C and 80˚C respectively (Table 1). By increasing the temperature from 30 to 50 ˚C at constant material ratio and constant ethanol volumes, slight decrease was observed in the particle size, while by further increasing the temperature to 80˚C particle size increased to 135-160 nm.

Zainal et al. reported that by increasing the temperature from 30 to 70˚C at constant materials ratio, particle size increased in the range of 28 to 113 nm, while Lazareva et al.

found out that by increasing the temperature from 50 to 70˚C at constant reactants ratio, the size of silica particles decreased from 100-150 nm to 30-50 nm [7], [9]. On the other side, Rao et al. concluded that by increasing the temperature from 30 to 70 ˚C in 3 samples in the presence of 8 ml of ethanol, particle size reduced; whereas in the other samples containing 4 and 6 ml ethanol, by increasing the temperature from 30 to 70˚C, particle sized increased [4].

In this research, FESEM micrographs revealed that the particles which were synthesized at 30˚C were non-uniform in size, agglomerated and semispherical, while particles synthesized at 50˚C were more uniform and spherical. However, by increasing temperature to 80˚C, particles became irregular and non-spherical in shape and non-uniform in sized and close together.

It could be concluded that preparing samples at 50˚C gives particles with higher quality in morphology and size.

3.2. Effect of ethanol content on the size and morphology of mesoporous silica nanoparticles

In this experiment, 3 samples of silica nanoparticles were synthesized with different ethanol content at constant deionized water volume (50 ml) and 50˚C. 3E-50, 5E-50 and 7E-50 were synthesized by using 3, 5 and 7 ml ethanol, respectively.

The obtained FESEM micrographs from these samples display that the synthesized nanoparticles have 130-150 nm, 140-160 nm and 150-170 nm size by adding 3, 5 and 7 ml ethanol, respectively. By increasing the ethanol content from 3 to 7 ml at constant temperature of 50˚C, the size of silica particles increases. Furthermore, the more the ethanol content, the more uniform and spherical particles with higher quality were attained. However, particles of 5E-50 and 7E-50 were more uniform and spherical than 3E-50.

Table 1. Synthesis parameters for different samples as well as their particle size

sample	name	parameters		
		T (˚C)	*EtOH(ml)*	*particle size range(nm)*
1	1E-30	30	1	84-115
2	1E-50	50	1	86-94
3	1E-80	80	1	135-160
4	3E-50	50	3	130-150
5	5E-50	50	5	140-160
6	7E-50	50	7	150-170

Rao et al. prepared silica nanoparticles with 4, 6 and 8 ml ethanol at 50 ˚C and reported that by decreasing the ethanol content at constant temperature, particle size reduced from 345 to 128.5 nm in addition to formation of uniform spherical particles in presence of 4 ml ethanol [4]. In another study, Kachbouri et al. reported that by increasing the ethanol content, large spherical silica particles were formed. In other words, when water to ethanol ratio was 0.97:0.3, particle size increases from 60-100 nm to 110-160 nm and by adding more ethanol, particle size increases to 600-730 nm [3]. Rahmani et al. showed that by increasing the ethanol content, morphology of porous silica nanoparticles were significantly changed from semi-spherical to tubular. Additionally, they reported that at water to ethanol ratios of 0.02:1 and 0.1:1, nanoparticles with semi-spherical and tubular morphologies were formed, respectively [6].

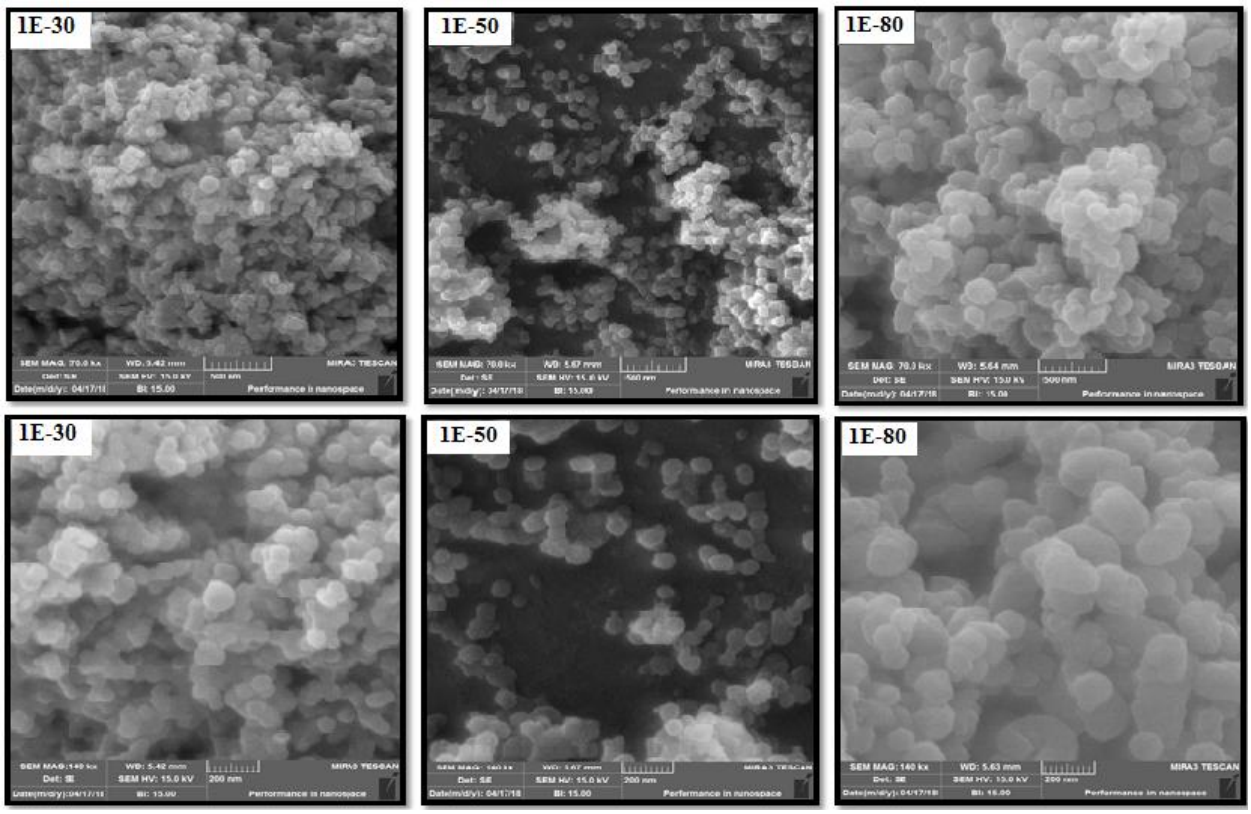


Fig. 1. FESEM images of mesoporous silica nanoparticles prepared at 30 ˚C (1E-30), 50 ˚C (1E-50), and 80 ˚C (1E-80) with 1ml ethanol at low and high magnification.z

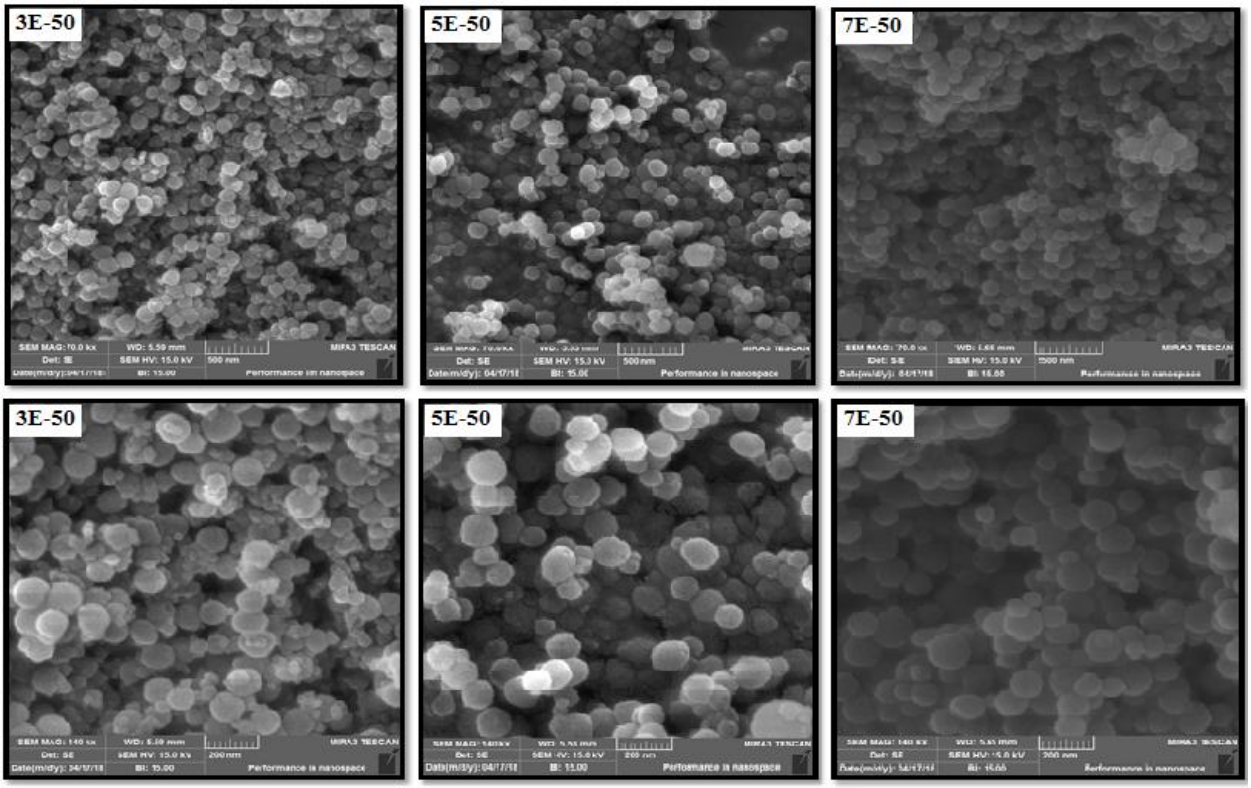


Fig 2. FESEM images of mesoporous silica nanoparticles with varying ethanol amount; 3 ml (3E-50), 5 ml (5E-50) and 7 ml (7E-50) at 50 ˚C at low and high magnification.

3.3. Effect of ethanol content on porous structure of mesoporous silica nanoparticles

As it is shown in Fig. 3-(a) (sample 5E-50) and Fig. 4-(a) (sample 7E-50), nitrogen adsorption and desorption isotherms of synthesized mesoporous silica nanoparticles with 2 different ethanol contents represent type IV isotherm in IUPAC classification. It is evident that pores of nanoparticles synthesized with 5 ml ethanol (Fig. 3-(a) (sample 5E-50)) were well-defined having short distances at the related pressure (P/P0) of 0.4 to 0.7. Furthermore, sample 5E-50, had uniform pores that are close together with narrow pore size distribution.

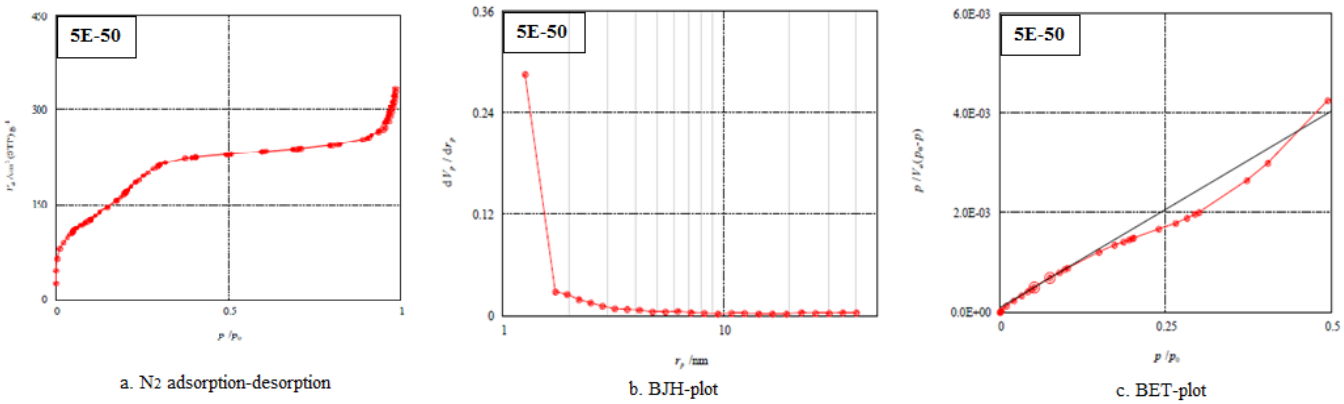
The particles prepared with 5 ml ethanol had specific surface area of 531 m2/g, average pore diameter of 3.93 nm and pore volume of 0.40 cm3/g which was calculated by BET and BJH methods. According to Fig. 3 (sample 5E-50), it can be seen that by increasing the ethanol content to 7 ml (7E-50), the uniformity of adjacent pores and narrow size distribution of the pores were kept; Fig. 4(sample 7E-50) also approves this statement. On the other hand, nitrogen adsorption and desorption of mesoporous silica nanoparticles formed by 7 ml ethanol demonstrates the well-defined pores with short distances in the pressure (P/P0) range of 0.4 to 0.8 (Fig. 4-(a) (sample 7E-50)). Moreover, according to BJH diagrams for the two samples (Fig. 3-(b) and Fig. 4-(b)), the pore volume decreased scarcely from 0.40 to 0.37 cm3 g-1 by increasing the amount of ethanol (Table II).

According to BET diagrams, the specific surface area increased slightly from 531 to 545 m2/g which resulted in increase of adsorption (Fig. 3-(c), Fig. 4-(c) and Table II), whereas the average pore diameter decreased scantly from 3.93 to 3.80 nm by increasing the ethanol content (Fig. 3-(c) and Fig. 4-(c)).

By reviewing other investigations, it can be clearly seen that by increasing the water to ethanol ratio, the specific surface area of mesoporous silica nanoparticles increased and the pore volume reduced [3]. In the present study, specific surface area increased and pore volume decreased only by increasing the ethanol content. On the other side, the pore volume of MSNs synthesized with 5 ml in this study was so much higher than the pore volume of mesoporous synthesized without ethanol by He et al. [10]. In addition, average pore diameter of MSNs at water to ethanol ratio of 0.03:0.97 synthesized by Kachbouri et al. was less than the average pore diameter of synthesized mesoporous nanoparticles with 5 ml ethanol in this investigation [3]

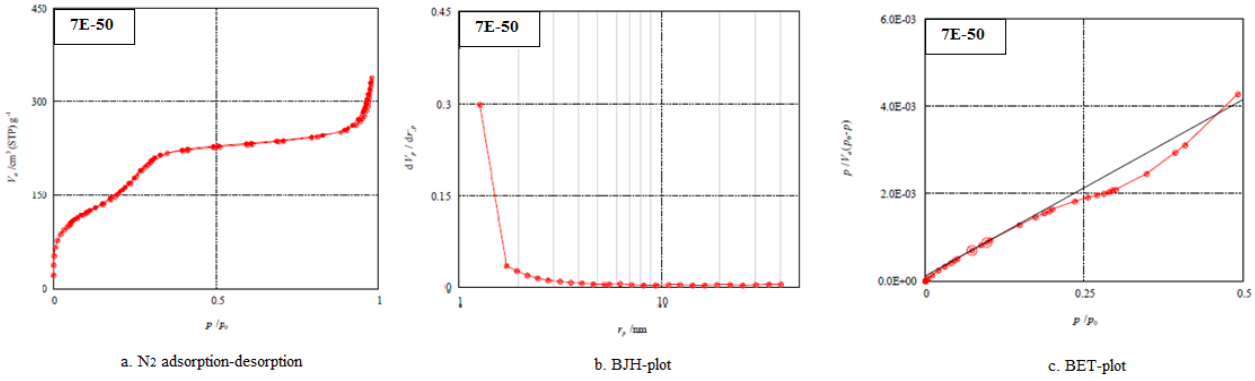
Table 2. The effect of ethanol on porous structure of mesoporous silica nanoparticle

sample	name	parameters		
		Pore volume ***($Cm^3 g^{-1}$)***	***pore size (nm)***	***Specific surface area ($m^2 g^{-1}$)***
5	5E-50	0.40	3.93	531
6	7E-50	0.37	3.80	545



a. N2 adsorption-desorption b. BJH-plot c. BET-plot

Fig 3. N2 adsorption–desorption isotherms (a), BJH-plot (b), and BET-plot (c) of synthesized spherical mesoporous silica nanoparticles with 5 ml of ethanol (5E-50).



a. N2 adsorption-desorption b. BJH-plot c. BET-plot

Fig 4. N2 adsorption–desorption isotherms (a), BJH-plot (b), and BET-plot (c) of synthesized spherical mesoporous silica nanoparticles with 7 ml of ethanol (7E-50).

4. Conclusion

In Summary, mesoporous silica nanoparticles have been successfully synthesized by sol-gel method. By increasing the synthesis temperature from 30 to 50˚C in the presence of 1 ml ethanol, particle size reduced. Besides, by increasing the temperature from 50˚C to 80˚C at the same amount of ethanol, particle size increased. Moreover, silica nanoparticles synthesized at 50˚C had higher quality, more spherical morphology and more uniform particle size than the particles synthesized at other temperatures. FESEM micrographs obtained from samples containing 3ml, 5ml and 7ml ethanol at 50˚C revealed that by increasing the ethanol concentration, the size of mesoporous silica nanoparticles increased. Additionally, increase of ethanol content did not solely affect the morphology of mesoporous silica nanoparticles and only resulted in formation of spherical particles with higher quality and more uniform. Reduction of pore volume and average pore diameter by increasing ethanol from 5 to 7ml provides the optimum ethanol content (5 ml) for preparation of mesoporous

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