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Original Research Paper

Dichlorodimethylsilane mediated one-step synthesis of hydrophilic and hydrophobic silica nanoparticles

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ABSTRACT

Hydrophilic and hydrophobic silica nanoparticles were synthesized by a cheap, simple and low temperature one-step method. The method involves a catalytic reaction between ammonium hydroxide, tetraethyl orthosilicate (TEOS) and dichlorodimethylsilane (DDS) in an ethanol solvent. The effects of different parameters such as chemical concentration and reaction temperature were investigated on size of the synthesized silica particles. Characterizations of hydrophilic and hydrophobic particles were performed using dynamic light scattering (DLS), X-ray diffraction analysis (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). According to the results, by reducing the amount of ammonium hydroxide, ethanol and temperature, the size of hydrophilic silica particles can be reduced to 129 ± 10.4 nm. Other sides, addition of DDS agent caused to silica particles found hydrophobic property and size of the particles reduced to about 65 ± 6.5 nm.

1. Introduction

Silica nanoparticles have an outstanding position in scientific research, because of their various industrial applications, such as pigments and coating [1], rubber [2], cement and concrete [3], catalysts [4], pharmacy, electronic, thermal insulators and humidity sensors [5,6].

Among different methods which have been used to synthesis silica nanoparticles, sol-gel method has more advantages because of its low temperature process, simplicity, high-quality product and compositional designing [7–9]. The sol-gel process compromises hydrolysis and condensation of metal alkoxides ($Si(OR)_4$) such as tetraethyl orthosilicate (TEOS) or inorganic salts such as sodium silicate (Na_2SiO_3) in the presence of mineral acids (e.g., HCl) or bases (e.g., NH_3) as the catalyst [10]. The silica particles produced by the sol-gel method are hydrophilic inherently, which make them insoluble and unsuitable in oily media. To overcome this limitation and synthesizing hydrophobic nanoparticles, surface functionalization of silica particles with silane coupling agents has been introduced [11–13]. Therefore, the method for the synthesis of hydrophobic silica particles involves two steps of sol-gel synthesis of silica particles and their surface functionalization.

Recently, a novel one-step method has been introduced for synthesis of finer hydrophobic silica particles. The method consists of a base-catalytic reaction between silicon alkoxide and a catalyst in the presence of a silane coupling agent [14]. One-step method is more versatile in comparison to the pervious method; it is easier, faster and provides the possibility of synthesizing nano-sized silica particles [14–16].

Marini et al. [14] used vinyltriethoxysilane (VTEOS) as the silane coupling agent for synthesis of functionally modified silica nanoparticles. Final particles were in core-shell structure with a carbon-rich phase in the shell and silicon-rich phase in the core. In that study, TEOS/VTEOS molar ratio of 90/10 and, reaction temperature of 40 °C using ethanol as the solvent yielded the desired core-shell structure after 30 min reaction. Pourabbas and Pilati [16] investigated one-step synthesis and surface modification of silica particles with the pyrrole-bearing trialkoxysilane compounds. The final polypyrrole-grafted silica nanoparticles had mean diameter of about 220 nm and 50 wt.% of grafted polypyrrole with respect to the total weight of polypyrrole formed on the surface of the cores. In other study, vinyl and acrylate modified silica particles were synthesized through one-step method by using vinyltrimethoxysilane (VTMS) and 3-(methacryloyloxy)

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propyltrimethoxysilane (MPS). Spherical silica particles with average diameter ranging from 50 to 700 nm were synthesized, and it was found that the modifier silane can reduce the size of the silica nanoparticles due to the non-hydrolysable substitution in its chemical structure [15].

In this paper, application of dichlorodimethylsilane (DDS) as a silane coupling agent is studied for surface modification of silica particles. Effects of different parameters such as concentration of ammonium hydroxide, TEOS, DDS, ethanol, as well as reaction temperature on the size of the particles have been investigated and conditions for synthesis of hydrophilic and hydrophobic silica nanoparticles presented.

2. Materials and methods

Ethanol (C_2H_5OH, 99.5%), tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$, 99%), dichlorodimethylsilane (DDS, $Si(CH_3)_2Cl_2$, 99%) and ammonium hydroxide (NH_4OH, 25%) all from Merck Co. as well as distilled water were purchased as raw materials.

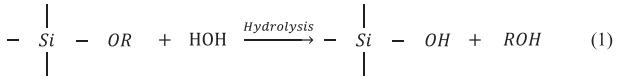
The first solution was prepared by mixing distilled water, ammonium hydroxide and ethanol and stirred for 15 min using a magnetic stirrer. The second solution also prepared by mixing TEOS and ethanol in a 100 ml volumetric flask. Two solutions were mixed when their temperature became equal and the resulting solution was kept at the desired temperature for 30 min. During this process, the silica nanoparticles begun to sediment and the solution became milky color. It should be noted that, after finishing the above steps, the resulting silica particles have hydrophilic behavior. In order to attain the hydrophobic properties of the obtained material, DDS was added to the solution to the desired value in the fifth minute when solution started to become milky color. Finally, silica particles were collected by centrifugation at 4000 rpm for 1 h and then washed with water and ethanol for two times. Then the final products were dried at 100 °C for 1 h.

Table 1 presented the design of experiments used throughout this study. Variable parameters of experiments are concentration of ammonium hydroxide, TEOS, DDS, ethanol, and the reaction temperature.

Size distribution of synthesized silica particles was measured using dynamic light scattering (DLS, Fritsch A22) and standard deviation (SD) and mean size of particles in each experiment reported. Phase identification of silica particles was performed with a Philips X' Pert diffractometer using Cu K_α radiation (λ = 0.15406 nm). Also, investigation of morphology of silica nanoparticles is performed by transmission electron microscopy (TEM, Philips CM120) and scanning electron microscopy (SEM, VEGA/TESCAN) equipped with energy dispersion spectroscopy (EDS). Also surface chemical characteristic of the silica nanoparticles was studied by fourier transform infrared spectroscopy (FTIR, AVATAR 370). In addition, in order to investigation of thermal behavior of synthesized silica nanoparticles, thermogravimetric analysis (TGA) was performed by the STA 503 instrument with a heating rate of 10 °C/min from 25 to 1000 °C under air atmosphere.

3. Results and discussion

Proposed one-step synthesis process was performed in the H_2O-TEOS system, while ethanol and ammonium hydroxide were used as the solvent and basic catalyst, respectively. The main reactions in such system involve hydrolysis and condensation. According to Eq. (1), hydrolysis reaction causes the ethyl group, R, replaced with H. Subsequently and following the condensation process (Eq. (2)), Si—O—Si network generated.



(1)

(2)

Hydrolysis and condensation reactions act as the nucleation and growth mechanisms during the synthesis process. Therefore, different process parameters which influence on such reactions kinetics can control the size of silica particles.

Mean size of the particles as well as their standard deviation measured by DLS and the results were reported in Table 1. According to the array of experiments in this table, different experimental runs can be used to investigate the effects of individual parameters on the particle size.

The effect of NH_4OH concentration was studied under the experiments No. 1–4. Fig. 1 shows the variation of silica mean particle size at different concentrations of ammonium hydroxide. Generally, the particle size increases with increasing the ammonium hydroxide concentration. It can be explained by the catalyst role of ammonium hydroxide which speeds up the hydrolysis and condensation reactions. It seems that higher ammonium hydroxide concentrations are more effective on the condensation reaction kinetic so leading to the growth of silica particles. However, lower catalyst concentrations may increase the hydrolysis rate and higher nucleation causes to formation of smaller particle size. Same observation of other researchers confirm the fact that ammonium hydroxide concentration is one of the important parameters in controlling the size, shape and size distribution of particles [7,15,17].

The effect of ethanol concentration on the particle size is given in Fig. 2. These effects were investigated in two states of with and without DDS addition. First, it was observed that DDS can reduce the size of synthesized silica particles. On the other hand, ethanol concentration has two different effects on the size of the silica particles. While hydrophilic particles (without DDS) size increases

Table 1
Array of designed experiments and corresponding standard deviation and mean size of particles synthesized in each experiment.

Run	NH_4OH (mmol)	C_2H_5OH (ml)	Temp (°C)	TEOS (mmol)	DDS (mmol)	Particle size (nm)	
						Mean	SD
1	24.15	25	40	8.86	0	149	10.6
3	72.45	25	40	8.86	0	263	20.7
5	48.3	12.5	40	8.86	0	129	10.4
7	48.3	25	50	8.86	0	176	13.4
9	48.3	25	40	4.43	0	136	8.6
11	48.3	25	40	8.86	4.53	85	4.4
13	48.3	25	40	8.86	6.8	462	31.8

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