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A statistical approach to synthesis of functionally modified silica nanoparticles

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ABSTRACT

This study investigates the one-step synthesis of functionalized silica nanoparticles using dichlorodimethylsilane (DDS), and examines the statistical effects of process variables on the synthesized silica particle size. This method simultaneously consisted base-catalyzed hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in the presence of a DDS coupling agent. Fractional factorial design (FFD) is used to identify the most significant variables influencing the synthesis process, as well as the effects of different levels of each parameter on the mean silica particle size. The effects of five parameters (concentration of ammonium hydroxide, TEOS, DDS, ethanol, and reaction temperature) were investigated and the catalyst concentration was considered as the key factor influencing the process. Study of morphology and size of silica nanoparticles using particle size analysis (PSA) and transmission electron microscopy (TEM) showed successfully synthesis of mono dispersed silica nanoparticles with mean particle size of 65 nm. Fourier-transform infrared spectroscopy (FTIR) confirmed after the addition of DDS, $SiCl(CH_3)_2$ functional group took the place of H on the surface of silica nanoparticles, and the nanoparticles found hydrophobic properties.

1. Introduction

A facile and inexpensive method for synthesis of silica nanoparticles is one-step bottom-up method. This method is based on a base-catalyzed hydrolysis of silicon alkoxides in the presence of a silane coupling agent. In the one-step method, silane coupling agents prevent excessive condensation of products during the synthesis process which lead to synthesize of nano-scale particles. Silane agents also change the surface properties of nanoparticles causing to synthesis of hydrophilic and hydrophobic nanoparticles [1–7]. In fact, silane coupling agent is a surface active agent used to establish a link between silica particles and nonpolar environment. Its hydrophilic end is absorbed by silica nanoparticles and the other functional active groups caused to dispersion of particles in the nonpolar solvents. Thus, depending on the surface agent molecular structure, nano silica can be dispersed in both water or organic solvents and reduces the surface tension at the air–water or oil–water interfaces [8,9].

Many types of silane coupling agents, various in chemistry and reactivity, are available. According to the silane functional groups, they can be classified into different classes such as alkyl, amino, epoxy, acrylic and vinyl [10]. So far, varieties of silane coupling agents have been used for one-step synthesis of functionalized silica particles. For example, vinyltriethoxysilane (VTEOS), vinyltrimethoxysilane (VTMS), N-(3-Trimethoxysilylpropyl)pyrrole (TMSPP) and 3-(methacryloyloxy) propyltrimethoxysilane (MPS) were used to this purpose [1–6,11]. In this paper, dichlorodimethylsilane (DDS) is used for the synthesis of functionally modified silica nanoparticles.

One-step synthesis process is performed in the presence of water and a silicon alkoxide such as TEOS. According to Eq. (1), hydrolysis reaction in this system causes to ethyl group, R, replaced with H. Following by the condensation process (Eq. (2)), Si–O–Si network subsequently generated [12]. In this stage, in order to avoid from growing the networks, DDS is added into the solution and prevents from the further condensation process. Based on Eq. (3), on the particles surface, OH group is replaced with chlorodimethylsilane ($SiCl(C_2H_5)_2$) functional group [13], leads to change the nature of the nanoparticles to hydrophobic.

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$$-\overset{|}{\underset{|}{Si}}-OR+HOH\xrightarrow{Hydrolysis}-\overset{|}{\underset{|}{Si}}-OH+ROH \quad (1)$$

$$-\overset{|}{\underset{|}{Si}}-OH+-\overset{|}{\underset{|}{Si}}-OH\xrightarrow{Condensation}-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-+HOH \quad (2)$$

$$SiO2\overset{/}{\underset{\backslash}{-}}OH+Cl-\overset{CH3}{\underset{CH3}{Si}}-Cl\xrightarrow{Functionalization}SiO2\overset{/}{\underset{\backslash}{-}}O-\overset{CH3}{\underset{CH3}{Si}}-Cl+HCl \quad (3)$$

Since the TEOS is not soluble in water, another solvent required in the one-step synthesis process. The solvent should solve TEOS and be soluble in water, so an alcoholic solvent such as ethanol is used. On the other hand, the hydrolysis reaction is done slowly, especially when alcohol added, which makes the system more washy. To speed up the reactions, the catalyst must be used. The basic catalyst such as ammonia is appropriate for this system, because it has low boiling point and can be easily removed from the system [2,4,5,12,14,15].

It is easy to understand that the one-step process for the synthesis of silica nanoparticles have different parameters, which any changes in these parameters may lead to a difference in the characteristics of synthesized nanoparticles. In other words, any alteration in the amount of process parameters (such as chemicals concentrations, reaction temperature, process time and pH), may have complicated and unknown effects on the process. Therefore, to control the method for the synthesis of desired mono disperse nanoparticles, affecting parameters must be carefully evaluated. Design of experiments (DOE) and its statistical analysis, is a suitable strategy to study such complicated processes.

Design of experiments is a collection of mathematical and statistical useful techniques for developing, improving and optimizing the processes. It can be used to evaluate the relative significance of affecting factors even in the presence of complex interactions. DOE selects a diverse and representative set of experiments in which all factors are independent of each other despite being varied simultaneously. The efficiency of experimental design increases as the number of process variables increases. However, this may lead to the increase in number of experiments. In this case, fractional factorial design (FFD) can reduce the number of experimental runs required. In other words, FFD allows testing additional factors without increasing the number of experimental runs; it can save the time and cost of experiments [16–18].

The main objectives of this study are investigation on the one-step synthesis of functionalized silica nanoparticles using dichlorodimethylsilane, determination the most significant variables influencing on the process, and investigation the effects of different levels of each parameter on the mean silica particle size. To the best of our knowledge, the statistic approach presented in this study, has not yet been applied for this process.

2. Experimental

2.1. Materials and synthesis method

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

Two solutions are required for the synthesis of silica nanoparticles; the first one is a solution of water and ammonium hydroxide in ethanol, and the second is the solution of TEOS in ethanol. Both the solutions were prepared in a 100 ml volumetric flask and stirred on the magnetic stirrer (T = 40–60 °C, t = 15 min, r = 400 rpm). After being equal in the temperature of two solutions, the second solution was added to the first one and the resulting solution was vigorously stirred using a magnetic stirrer (T = 40–60 °C, t = 30 min, r = 1000 rpm). At the 5th minute, when solution color is changed to be milky, DDS was suddenly added to the solution and after that no significant change in the solution color was observed.

The solution was centrifuged to discard the supernatant and redispersed in ethanol. The centrifuge process was done at 4000 rpm for 1 h using 10 ml volumetric tubes. The nanoparticles were centrifuged again and dispersed in ethanol. Finally, the powders were dried in an oven at a temperature of 100 °C for 1 h.

2.2. Design of experiments

Various parameters of one-step synthesis method can effect on particle size and morphology of synthesized silica particles. In this section, the influences of different parameters were investigated and the optimal conditions for the synthesis of silica nanoparticles with the minimum size were given. According to literature survey, as well as initially experiment done, five process parameters were chosen for designing the experiments. The variables each one at two levels of low value (−1) and high level (+1), are presented in Table 1.

According to the statistical calculations, to determine the effects of the five parameters, each with two levels, factorial design of experiments of 2^5 (or 32 experiments) must be performed. In order to decrease the number of experiments, fractional factorial design of 2^{5-2}_{III} (with eight experiments) was used in this study. Choosing a fraction in FFD is a process of statistical methods which completely explained in Ref. [16]. The 2^5 factorial design contains four 2^{5-2} factorial design. To select the best fraction, statistical analysis suggested a resolution III design, in which no main effects are aliased with any other main effect, but main effects are aliased with two-factor interactions and some two-factor interactions may be aliased with each other. For a 2^{5-2}_{III} fractional factorial design, factorial effects defining contrast can be written by:

$$I = ABD = ACE = BCDE \quad (4)$$

It means that, D = AB and E = AC are the best generators to design a fraction. Using such generators, designing the experiments is done according to the table of plus and minus signs (Table 2). The selected principal fraction of this table presents the experiments array for the different combinations of the variables. It should be noted that, the eight runs were done randomly and during the experiments, other process parameters were kept fixed to avoid blocking.

Table 1
Variables of the experiments and their different levels.

Parameters	low (−1)	High (+1)
A: EtOH (ml)	25	37.5
B: NH_4OH (aq.) (ml)	1.86	2.79
C: TEOS (ml)	1.98	2.97
D: DDS (ml)	0.55	0.825
E: Temperature (C)	40	60