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Synthesis of organo-functionalized nanosilica via a co-condensation modification using γ-aminopropyltriethoxysilane (APTES)

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Abstract

An easy and swift pathway in preparation of organo-functionalized silica in nanosize range with amine-terminated group via co-condensation method is reported. The process is a self-catalyzed reaction by amine group of organosilane without the addition of ammonia as a catalyst at room temperature. A modified nanosilica with particle size of ~60 nm, highly monodispersed and low aggregation was successfully produced. The use of methanol as a solvent leads to the increase in particle size. CHN, FTIR and NMR analyses revealed the presence of organo-functional group in the bulk and at the surface of the silica particles.

Keywords: Nanosilica; Monodispersed; Modified; Co-condensation

1. Introduction

Silica nanoparticles have been widely used as filler in the preparation of nanocomposites [1–6]. The main disadvantages of incorporation of the fillers into polymers are agglomeration and incompatibilities of silica particles with the organic matrix, which limit their use [7]. It is known that surface modification of silica nanoparticles with coupling agents is an effective way to improve inorganic–organic interfacial compatibility and miscibility with the polymeric matrix, thus enhancing the properties of the composite materials [8]. γ-Aminopropyltriethoxysilane was commonly used as a coupling agent in various applications such as composites, coating, adhesives, protein binder and chromatography [9].

There are three methods for the modification of silica: (a) post-modification (grafting)—subsequent grafting of colloidal nanosilica by using alkoxysilane as a sol–gel precursor and aminoorgano functional alkoxysilane as a modifier, (b) in situ modification (co-condensation method)—simultaneous modification of silica via preparation of colloidal nanosilica using alkoxysilane and modifier and (c) incorporation modification—the incorporation of organic groups as bridging components directly into the pore by the use of organosilica precursors (production of periodic organosilicas) [10].

Most of the literature reported that the application of co-condensation method in the preparation and modification of mesoporous silica by using surfactant or polymeric compound as a template [11–21]. There are a few works on the preparation of nanoparticles via co-condensation method [9,22].

Post-modification is commonly used for modification purpose. However, there are some drawbacks in this method such as reduction of porosity via attaching of organic group to the pore surface and wall, and blocking via diffusion of modifier into the pore for mesoporous silica [10], multiple reaction, time and energy consuming and the use of organic solvent (e.g. toluene) for silica nanoparticles [23,24].

As an alternative approach, we have prepared functionalized silica nanoparticles via co-condensation method by reacting tetraethoxysilane (TEOS) and γ-aminopropyltriethoxysilane (APTES) in ethanol and water. APTES as surface modifier has been utilized to introduce amine group onto silica particles. In addition, APTES also plays the role of a catalyst without the addition of ammonia. The functionalized silica particles were

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characterized by using TEM, SEM/EDX, FTIR, ^{29}Si and ^{13}C CP/MAS Solid NMR.

2. Experimental

2.1. Reagents

Tetraethoxysilane (TEOS, 99%, Fluka), γ-aminopropyltriethoxysilane (APTES, 99%, Aldrich) absolute ethanol (EtOH, 99.5%, Systerm) and distilled water were used without any further purification.

2.2. Procedure

A quantity of 4 mL of TEOS and 1 mL of APTES were first dissolved in 30 mL of absolute ethanol simultaneously under low frequency ultrasound (Bransonic, Model 5510, 42 kHz) at room temperature for 10 min. Then, 1 mL of distilled water was dropped into the mixture at a feed rate of 0.2 mL min^{-1} in an ultrasonic bath for 3 h. The gelled samples were centrifuged and washed with ethanol and distilled water (3 × 7 min, 6000 rpm). Drying was carried out using freeze drying under vacuum for overnight in a freeze dryer (Labconco, Freezon 12). For freeze drying, the samples were frozen and placed under a deep vacuum (1.33×10^{-1} mbar). Under this condition water from the samples was sublimated directly into water vapor, resulting in minimum shrinkage, reduced collisions and low moisture content in the dried samples. Finally, the samples were calcined at 200 °C for 2 h. The standard optimized experimental conditions for the modified silica preparation were tabulated in Table 1.

2.3. Characterizations

Transmission electron microscopy (TEM) images were taken using a Philips CM 12 system. The diameters of 300 particles were measured for the average particle size and the standard deviation. The particle size and distributions were determined using Docu Version 3.2 image analysis software. Elemental analysis was conducted using a CHNS/O analyzer, Perkin-Elmer Series II 2400. Morphology of the samples was also examined using scanning electron microscopy (SEM, Leo Supra 50 VP), equipped with energy dispersive X-ray spectroscopy (EDX) for chemical composition analysis. NMR ^{13}C and ^{29}Si were obtained using a cross-polarization magic angle spinning (CP/MAS) solid state nuclear magnetic resonance (NMR, Bruker AV 400WB). FTIR spectra were recorded using a Perkin-Elmer 2000 FTIR spectrometer. Thermogravimetric analysis (TGA) was carried out on Mettler Toledo TGA/SDTA 851^{e} instrument linked to FTIR (NICOLET 5700) to determine the thermal stability of the modified silica with heating rate of 20 °C min^{-1} under flow of N_2.

Table 1
Optimized experimental parameters for the preparation of modified silica nanoparticles.

Parameters	Optimal value
[TEOS] (mol L^{-1})	0.45
[APTES] (mol L^{-1})	0.12
$R = ([H_2O]/([TEOS] + [APTES])$	25.6
Temperature (°C)	25–50
Reaction time (h)	3.5
Sonication (kHz)	42

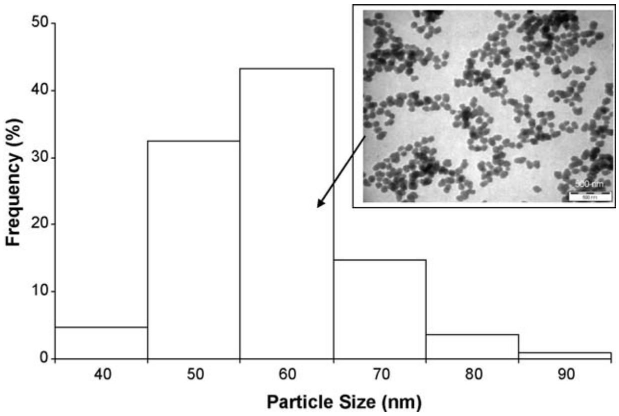

Fig. 1. Particle size distribution modified silica nanoparticles prepared in ethanol (inset TEM image of modified silica).

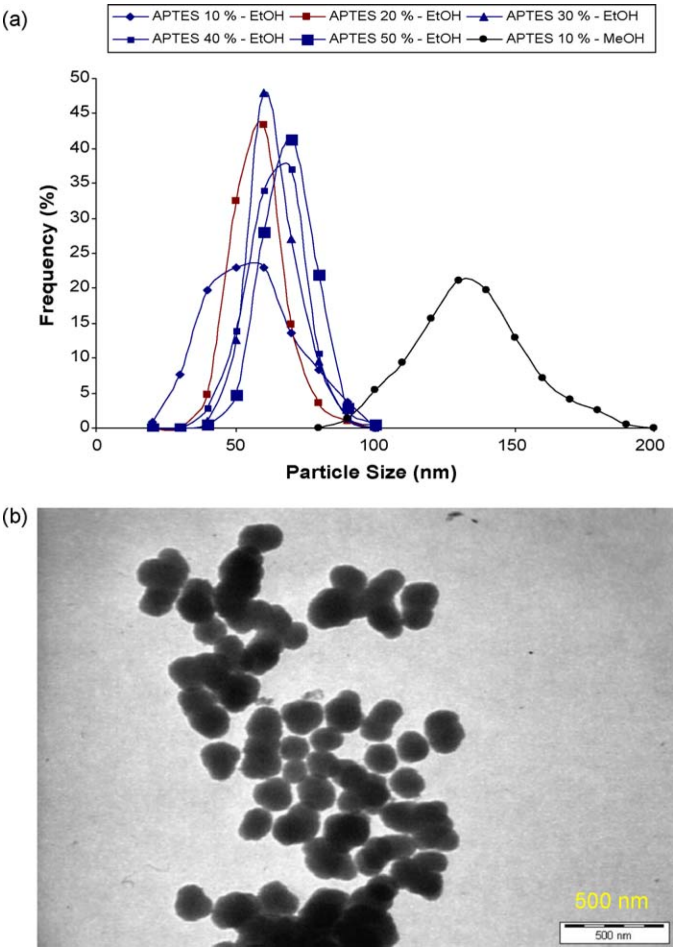

Fig. 2. (a) Particle size distribution (PSD) of modified silica nanoparticles with different amount of APTES and (b) TEM image of modified silica nanoparticles prepared in methanol.

3. Results and discussion

Modification of the silica surface with an organosilane may improve the stability of particles in organic and also aqueous solvent [25]. It is due to the decrease in reactivity and energy level (negatively charging of the surface) of surface resulting from changing in nature of surface (from hydrophilic to hydrophobic) during modification. Therefore, modification of the surface can control the degree of aggregation of primary particles. It can also prevent from any unfavorable aggregation and agglomeration among nanoparticles.

Distilled water added into the reaction vessel as hydrolyzing agent. Due to the low miscibility between orthosilicates and water, a mutual solvent such as ethanol was used [26]. Fig. 1 shows particles size distribution and TEM of the modified nanoparticle prepared by using ethanol as solvent. The results show that the average particle size is 63 ± 8.8 nm with a narrow particle size distribution. The morphology consists of almost spherical nanosize particle, monodisperse with low aggregation. The incomplete spherical shape of particles might be related to the presence of organic groups on the silica by surface modification. The stearic hindrance in the formation of three-dimensional gel network from organically substituted trialkoxysilanes against tetraalkoxysilanes leads to lower the cross-linking density formation on the gel network. On the other hand, under base-catalyzed condition the gel network is predominantly formed from $Si(OEt)_4$ because it reacts faster than $RSi(OEt)_3$ and then condenses onto the network [27]. Thus incomplete three-dimensional gel networking might prevent from the formation of curvature of spherical particles.

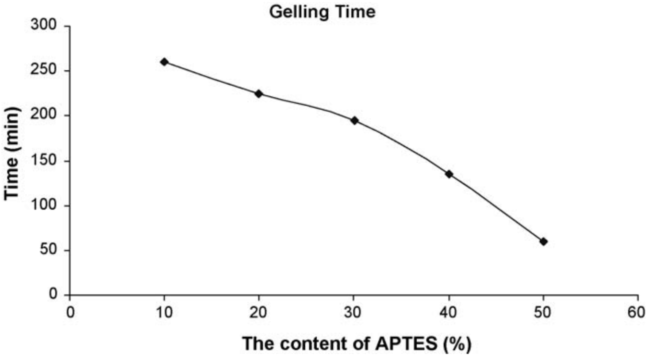

Fig. 3. The effect of gelling time on the addition of APTES.

Fig. 2 shows the effect of addition of APTES on particle size distribution of the silica nanoparticle. The particle size increased with increasing the percentage of APTES (Fig. 2(a)). This is due to the increase in concentration of $-NH_2$ group that leads to the enhancement in the rate of hydrolysis and condensation reaction, which consequently, induces the growth of the particles. Thus, a low loading of NH_2 (APTES 20%) was used to avoid the formation of large particles. The type of solvent also affects the size of silica particles. Particle size depends on the hydrolysis (rate of nucleation) and condensation rates (rate of growth) [28–30]. Therefore, by controlling these two competing reactions, the final particle size and particle size distribution of the powder can be controlled [31]. On the other hand, by increasing viscosity of the medium (or decreasing the diffusion coefficient), smaller sizes are expected owing to the decrease in collision among particles, slowing down the reaction rate. Ethanol has viscosity twice that of methanol. Thus, methanol accelerates the reaction and coalescence of the particles resulting in a larger particle as compared with the ethanol.

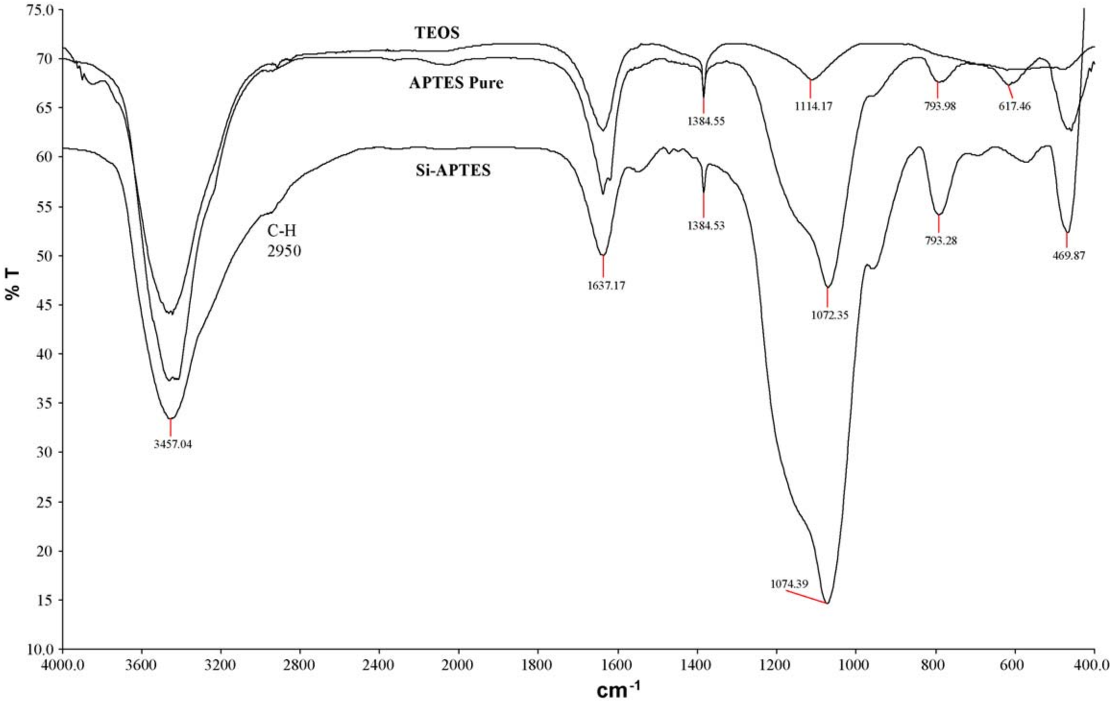

Fig. 4. FTIR spectra of modified silica particles and precursors TEOS and APTES.

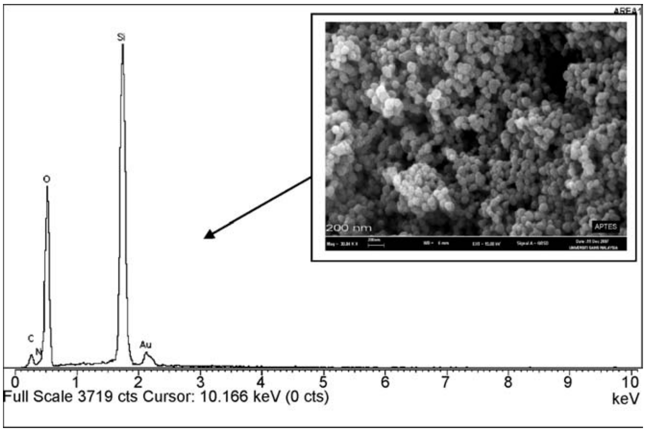

Fig. 5. EDX spectrum of modified silica nanoparticles (inset SEM image of modified silica).

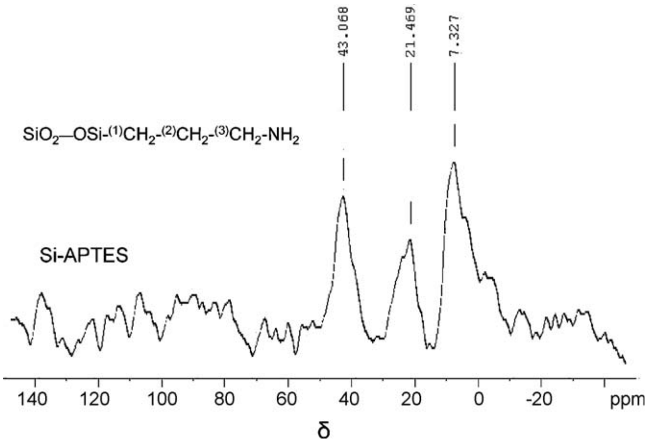

Fig. 7. ^{13}C CP/MAS solid NMR spectrum of modified silica particles.

Fig. 2(b) shows TEM of silica particle prepared in methanol. The results disagreed with those reported by Matsoukas and Gulari's [26] due to the differences in the conditions of Stöber (first-order kinetic) and co-condensation methods employed. Matsoukas and Gulari stated that the larger particle will be produced under slower hydrolysis of TEOS in ethanol, while the lower solubility of organo-functional trialkoxysilane (APTES) in methanol (co-condensation method) compared to ethanol which was expected the larger particle in slower hydrolysis in methanol. The different hydrolysis rate as rate-limiting step between TEOS and APTES might bring about second-order reaction in co-condensation method. So this difference may exhibit different kinetic behavior between conventional sol–gel (Stöber method) and co-condensation methods. The presence of amine group (as a base) in APTES accelerates the rate of hydrolysis as compared with that in TEOS. Thus, the gelling time is reduced with the increasing amount of APTES increased, as shown in Fig. 3.

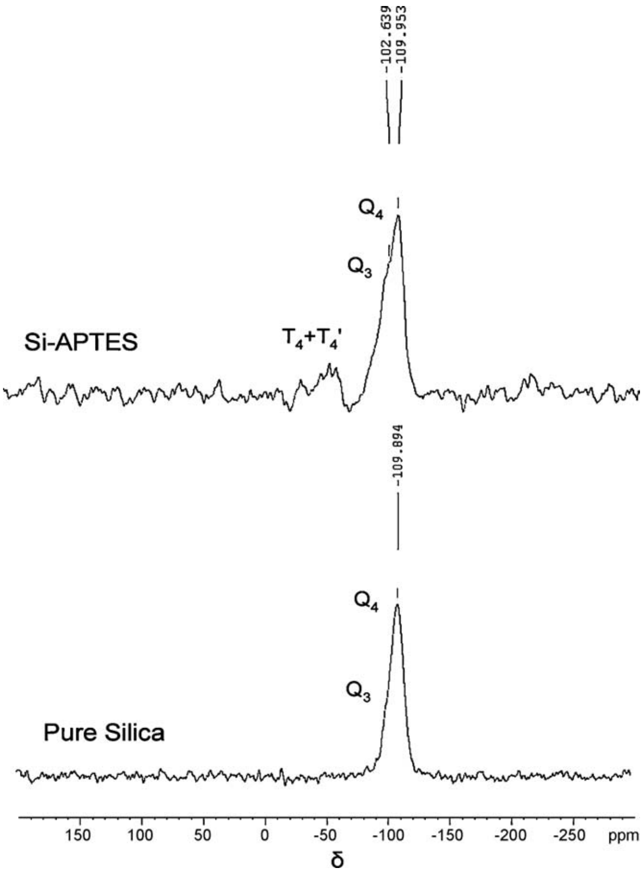

Fig. 6. ^{29}Si CP/MAS solid NMR spectra of modified silica particles.

The functional groups in the samples were identified by the comparison of FTIR data with those reported in the literature [32]. Fig. 4 shows FTIR spectra of the resulting modified silica particles as compared to the starting materials TEOS and APTES. The absorption bands at 3450, 1100, and 950 cm^{-1} correspond to the stretching, asymmetric stretching and bending of silanols groups (Si–OH) on the silica surface, respectively. Intensive bands at 1200–1100 and 467 cm^{-1} represent the asymmetric stretching and bending of siloxane groups (Si–O–Si). Vibrations at 2947 and 1384 cm^{-1} are due to the Si–CH$_2$ stretching and bending mode, respectively. Vibrations at 3500–3400, 1637 and 800 cm^{-1} assigned to the adsorbed water (H–OH, stretching vibration), residual intermolecular water (H–OH, bending) and moisture (H–OH, bending) in the samples. Absorption bands at 3400 and 1616 cm^{-1} represent the stretching and bending vibration of aliphatic amine (N–H) groups. A band at ~3400 cm^{-1} is corresponding to the overlapping of N–H and C–H vibration with siloxane and silanol groups. A weak band in the region of 2850–2950 cm^{-1} is ascribed to symmetric vibration of the C–H groups, indicating the presence of organic substitution in the modified silica [9].

CHN analyzer was used to analyze the presence of amino group in the bulk of modified silica. The results show that 79.5, 18.7, and 22.4 mg g^{-1} of carbon, hydrogen and nitrogen are present in the modified silica, respectively. The nitrogen and carbon are due to the aminopropyl in the organo-funtionalized silica. The presence of nitrogen in the sample again supported by the EDX analysis (16.71% of C, 1.71% of N, 58.75% of O, and 22.81% of Si) as shown in Fig. 5. This demonstrates that co-condensation method can be used as alternative approach for modification of silica. The high content of amino group on the surface and in the bulk of silica increases the hydrophobicity

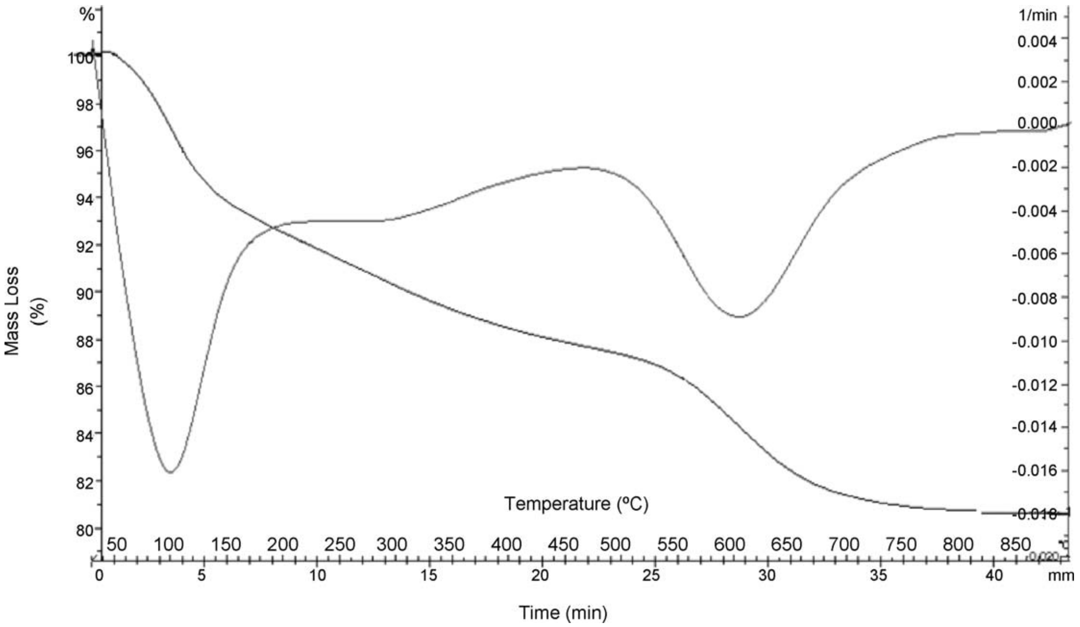

Fig. 8. TGA and DTG thermograms of modified silica nanoparticles via co-condensation method.

and flexibility of silica structure [33]. It enhances the compatibility of organo-modified silica as organic–inorganic filler in nanosize with organic matrix, e.g. polymer.

Fig. 6 shows the ^{29}Si CP/MAS solid NMR spectra. Two intense signals at −109 and −102 ppm are related to siloxane (Si–O–Si) groups (Q_4: fully condensed tetra-functional units) and silanol (Si–OH) groups (Q_3: branching tri-functional units), respectively [34]. The integral ratio of the signal Q_4/Q_3 has been found to be 2.87. −65 to −50 ppm and it corresponds to cross-linked species ($T_4 + T_4' = \mathrm{RSi\ (OSi)_3}$) between siloxane bond. The ^{13}C CP/MAS NMR measurement was performed to determine the existence of organic groups in modified silica nanoparticles (–O–Si–$^{(1)}$CH$_2$–$^{(2)}$CH$_2$–$^{(3)}$CH$_2$–NH$_2$). The results are shown in Fig. 7. The spectrum exhibits three peaks at 7.32 ppm ($^{(1)}$C), 21.46 ppm ($^{(2)}$C), and 43.06 ppm ($^{(3)}$C). The low intensity of the peaks is due to the organic groups in the bulk besides the surface of the particles. Thus, the ^{29}Si and ^{13}C NMR analyses have confirmed the presence of aminopropyl groups on the silica surface. These findings are consistent with the literature on the post-modification of silica using APTES [35].

Thermal stability of the modified silica using TGA/DTG analysis showed two stage mass losses for silica–APTES samples (Fig. 8). The DTG reveals the initial loss at below 220 °C which is related to the adsorbed water on the silica surface, trapped residual ethanol, and partially decomposition of unreacted APTES. The second stage of mass loss is between 220 and 900 °C which represents the degradation of residual starting materials and decomposition of organo-functional group. The results demonstrated that the modified silica is thermally stable above 500 °C.

4. Conclusions

A stable modified nanosilica was synthesized by using a simple and efficient method via co-condensation process. TEM results revealed that an average particle size is ∼60 nm with narrow size distribution and monodispersity. APTES have also played a role as catalyst without the addition of ammonia. Gelling time was decreased with increasing the content of APTES. Methanol promotes the hydrolysis and condensation reactions, resulting in a bigger particle size. CHN and EDX results demonstrated that the presence of amine groups in the modified silica particles. High amount of amino-organic groups in the silica nanoparticles and efficient interaction between surface amino groups and functional groups of organic polymers has provided a prospective opportunity to the efficient preparation of nanocomposites.

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