## RESULTS AND DISCUSSIONS

### 1. Synthesis of silica nanomaterials by sol-gel method.

All products obtained are fine white powder. The yield is about 90-95% . The as-synthesized silica is insoluble in water but soluble in sodium hydroxide.

### 2. Characterization of silica nanomaterials.

#### 2.1 Fourier Transform Infrared Spectroscopy (FTIR)

The comparison of the FTIR spectra between uncalcined and the corresponding calcined silica are shown in Fig 18 and Table 2. A broad

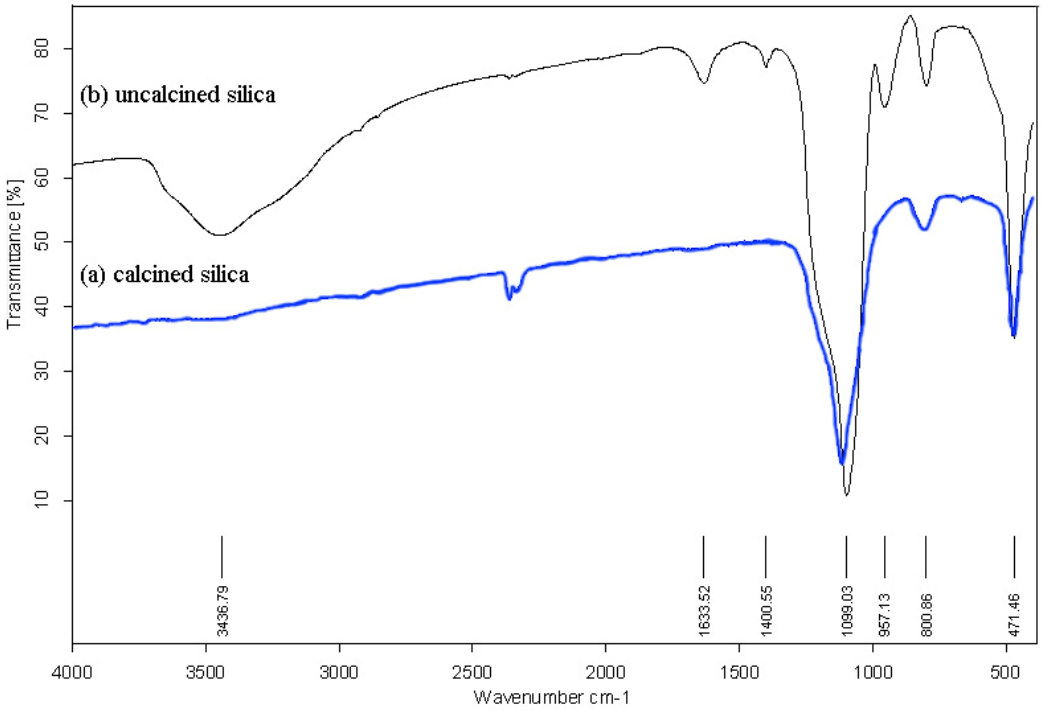


**Figure 18** Comparison the FTIR spectra of silica using tartaric acid template under shaking condition (SiTa_B)

band centering at 3437 $cm^{-1}$ in the spectrum of uncalcined silica demonstrates the presence of hydrogen boned hydroxyl group. In uncalcined silica, there are O-H bonds from water and carboxylic acid which can form intramolecular and intermolecular hydrogen bonding. Consequently, A broad band between 3400 – 3500 $cm^{-1}$ was observed. Other O-H vibration appears at 1630 – 1636 $cm^{-1}$ as a result of bending mode. The vibrational frequencies due to the carboxylic group are observed at 1401 and 957 $cm^{-1}$. The disappearance of peak at 1634, 1401 and 957 $cm^{-1}$ and the reduction in intensity of the broad band at 3437 $cm^{-1}$ in the spectrum of calcined silica indicates that the decomposition of organic acid template and the removal of water took place. The FTIR spectra for silica materials synthesized by stirring and shaking conditions exhibit similar patterns as shown in Figure 19 and 20.

**Table 2** Assignment of the FT-IR band observed in the spectra of uncalcined and calcined silica.

| Silica nanomaterials | FT-IR bands ($cm^{-1}$) | | Assignment |
|---|---|---|---|
| | Observed data | Literature data* | |
| Uncalcined silica | 3000-4000 | 3000-4000 | O-H stretching |
| | 1634 | 1630, 1636 | O-H bending |
| | 1401 | 1410 | C-O stretching of carboxylate |
| | 1099 | 1102, 1191 | Si-O-Si asymmetric stretching |
| | 957 | 950, 953 | Si-OH bond stretching |
| | 801 | 800 | OH bending in silinol |
| | 472 | 462, 464 | Si-O-Si bending mode |
| Calcined silica | 1120 | 1102, 1191 | Si-O-Si asymmetric stretching |
| | 808 | 800 | OH bending in silinol |
| | 472 | 462, 464 | Si-O-Si bending mode |

* source : Jal *et al*. (2004) and references therein.

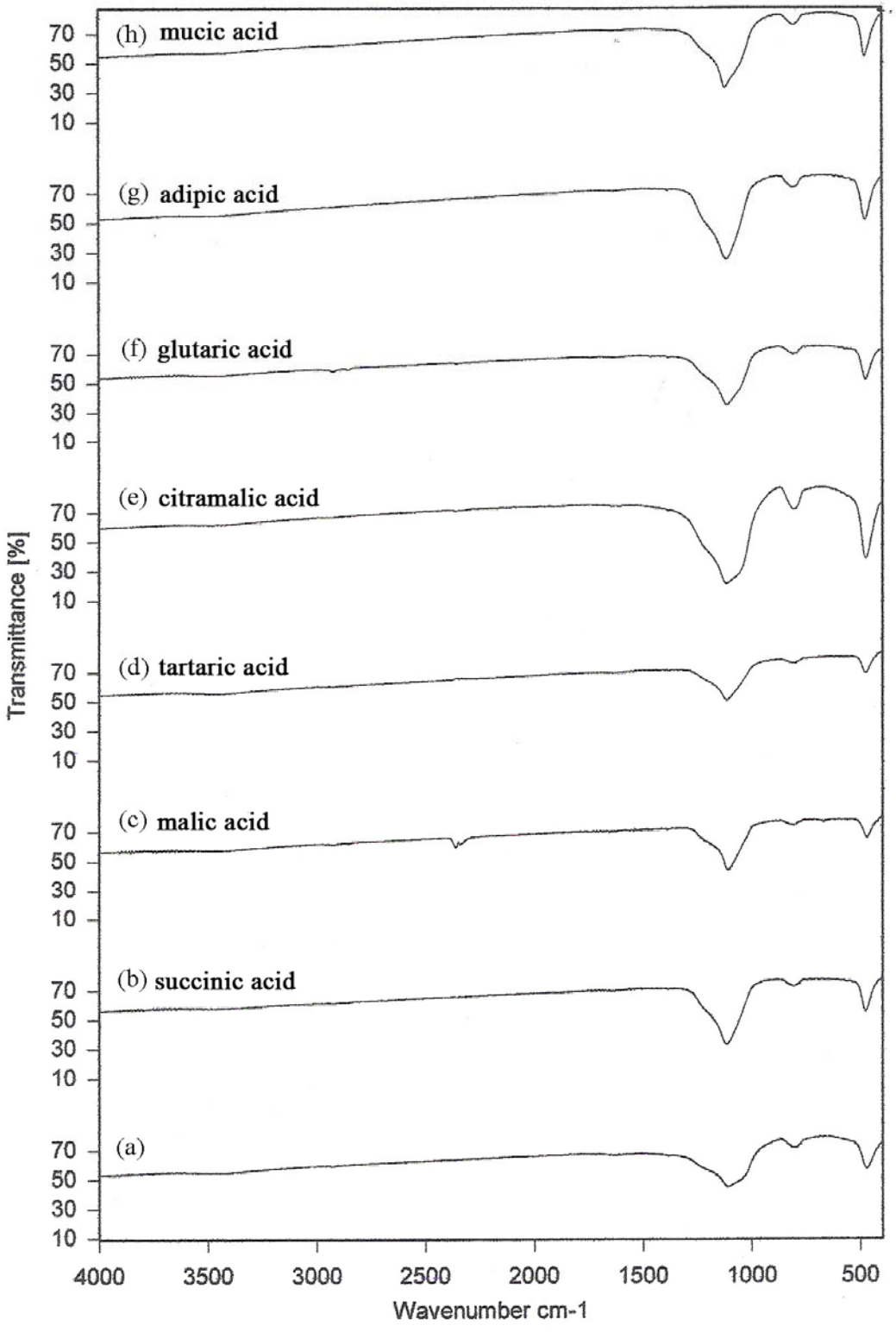


**Figure 19** FTIR spectra of calcined silica agitated by shaking condition. (a) without template and (b)-(h) with template

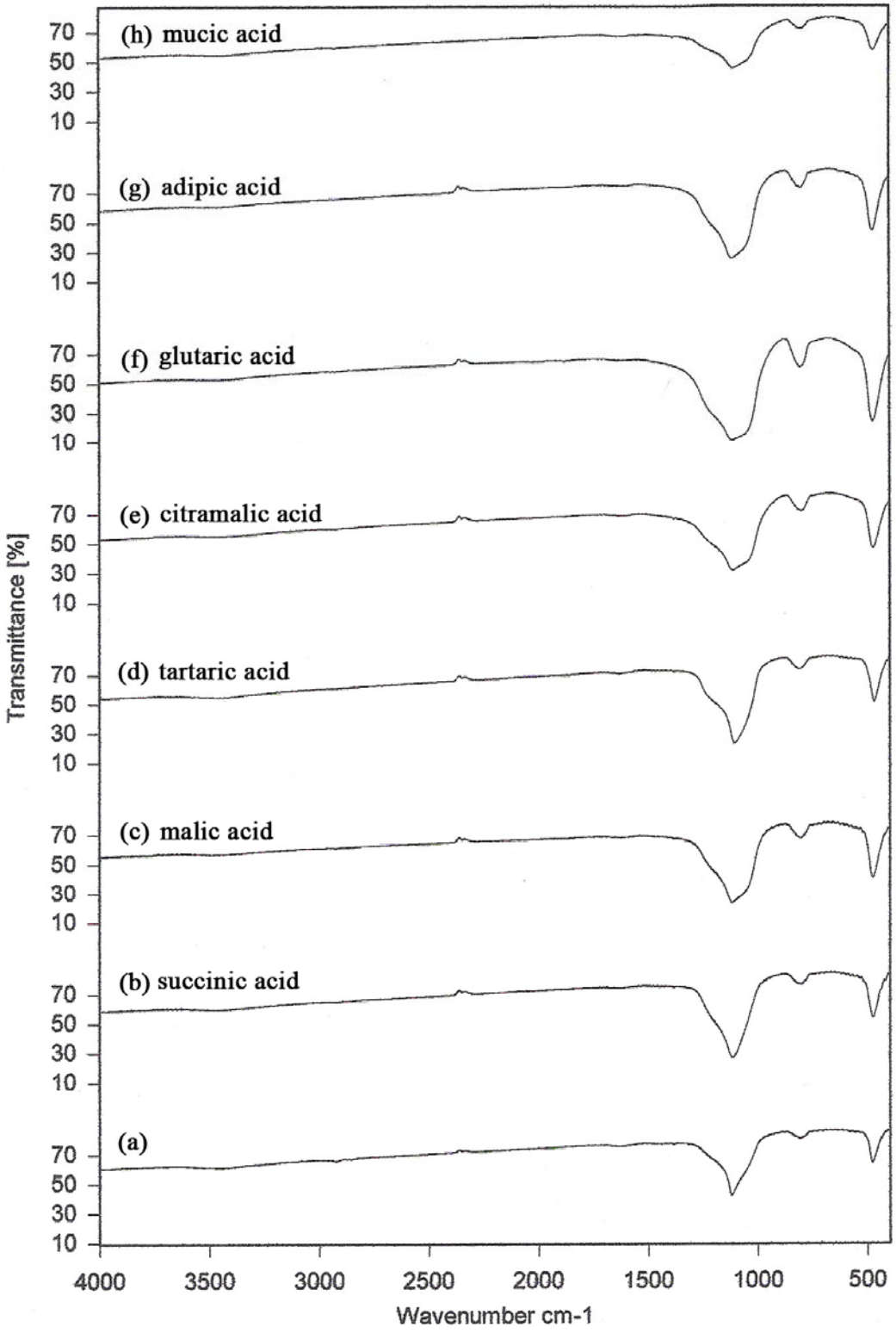


**Figure 20** FT-IR spectra of calcined silica agitated by stirring condition. (a) without template and (b)-(h) with template

The three fundamental vibration bands corresponding to Si-O-Si asymmetric stretching (~ 1,100 $cm^{-1}$), bending (~ 800 $cm^{-1}$) and rocking vibration (~ 470 $cm^{-1}$) for the silica structure were observed.

## 2.2 X-ray diffraction technique (XRD)

The powder XRD patterns of calcined silica materials using tartaric, succinic and mucic acid as template and without template are shown in Figure 21. Only one broad peak at 2θ = 21- 22 degree was observed, indicating that the silica framework is amorphous.

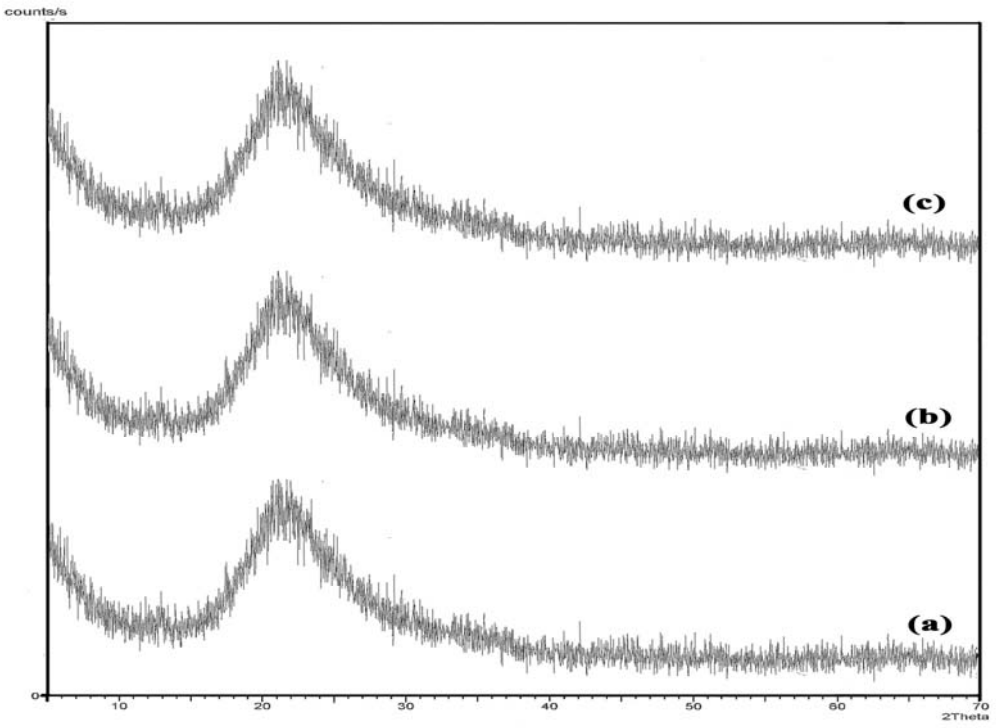


**Figure 21** The powder XRD pattern of calcined silica using (a) without acid, (b) tartaric acid and (c) mucic acid as a template.

## 2.3 Thermal gravimetric analysis (TGA)

The TG-DTA thermogram of three uncalcined silica prepared by using different templates are shown in Fig 22 - 24. During the heating in the temperature range of 50 – 300 °C, two endothermic effects accompanied by solvent ($H_2O$ and $C_2H_5OH$) and $CO_2$ evolution are observed on the DTA curves of templated silica (Fig 23 and 24). The first one observed at 77.0 °C for SiMu_B and 74.4 °C for SiTa_B are ascribed to the release of ethanol. The second one observed at 187.7 °C for SiMu_B and 196.8 °C for SiTa_B can be explained by the release of carbon dioxide from silica sample, which was a result of decomposition of tartaric and mucic acid templates. A broad peak at 390 – 600 °C is due to the dehydroxylation of hydroxide layer on silica surface. DTA curve of untemplate silica (SiW_B) increases slowly after the first endothermic peak, indicating no decomposition of organic acid (Fig 22).

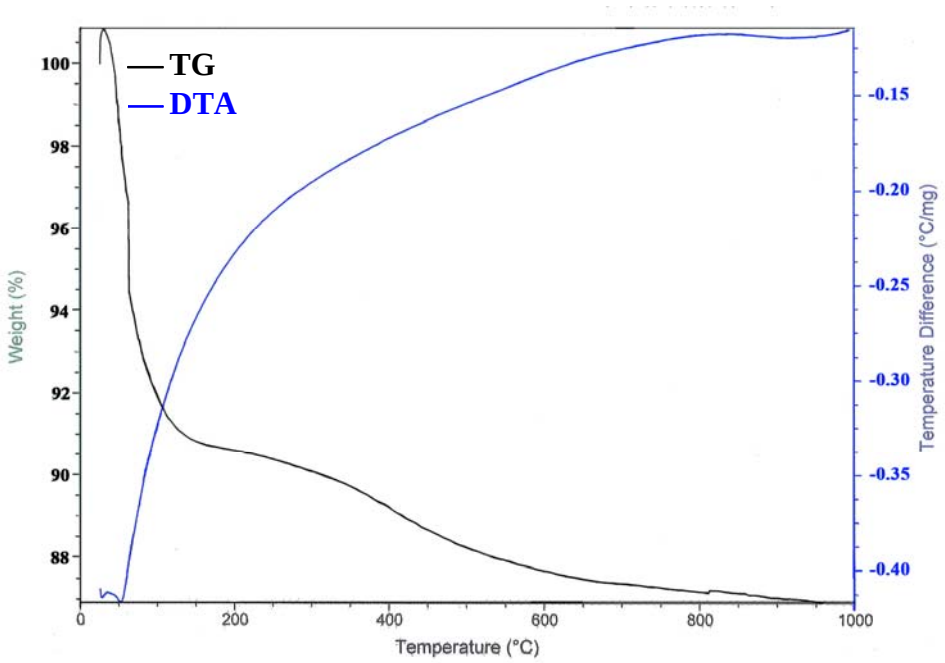


**Figure 22** TG-DTA thermogram of uncalcined silica materials without template (SiW_B).

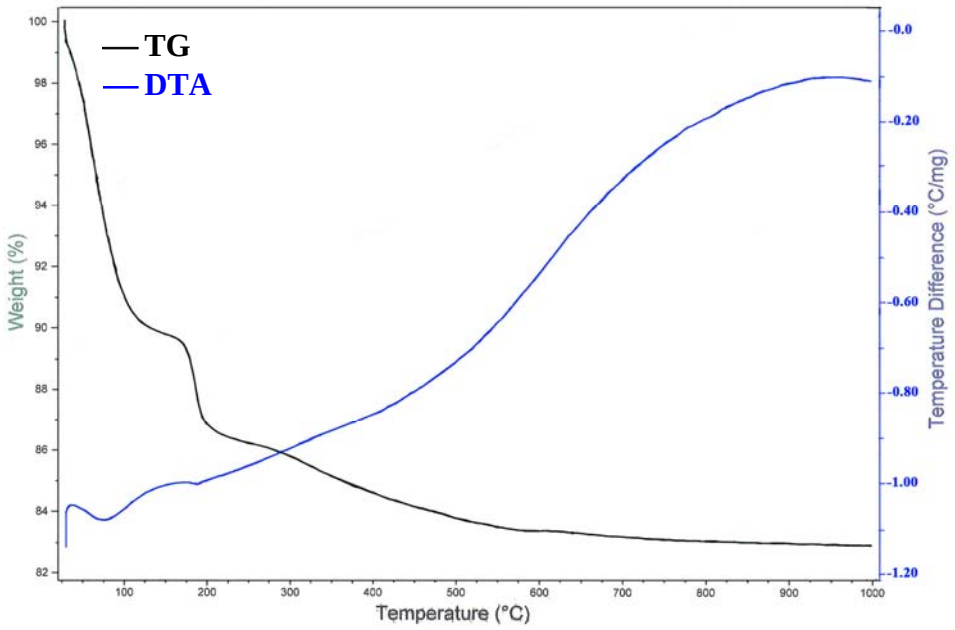


**Figure 23** TG-DTA thermogram of uncalcined silica materials with mucic acid template (SiMu_B).

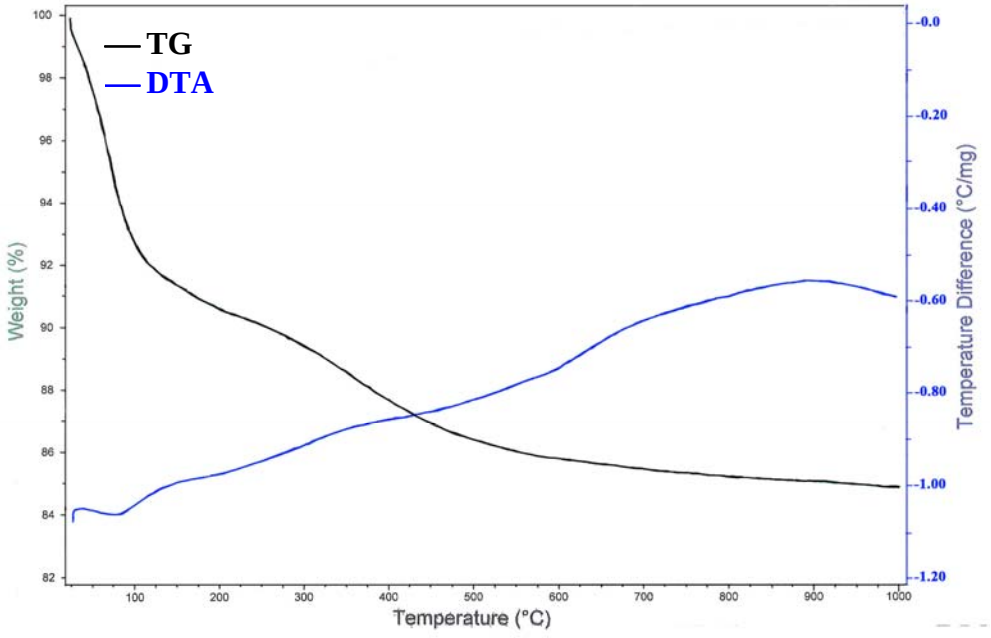


**Figure 24** TG-DTA thermogram of uncalcined silica materials with succinic acid template (SiTa_B).

TGA thermograms show three steps of weight loss from synthesized silica materials. The weight loss between 50 – 125 °C is due to the solvent evaporation. The second step of weight loss at 125 – 250 °C is a result of the decomposition of organic acid template and the last step at 250 – 600 °C indicates the dehydroxylation in silica.

After calcinations at 1000 °C, the TGA thermogram exhibits no weight loss for all temperatures. The horizontal straight line thermogram reveals the stability of silica material (Fig. 25).

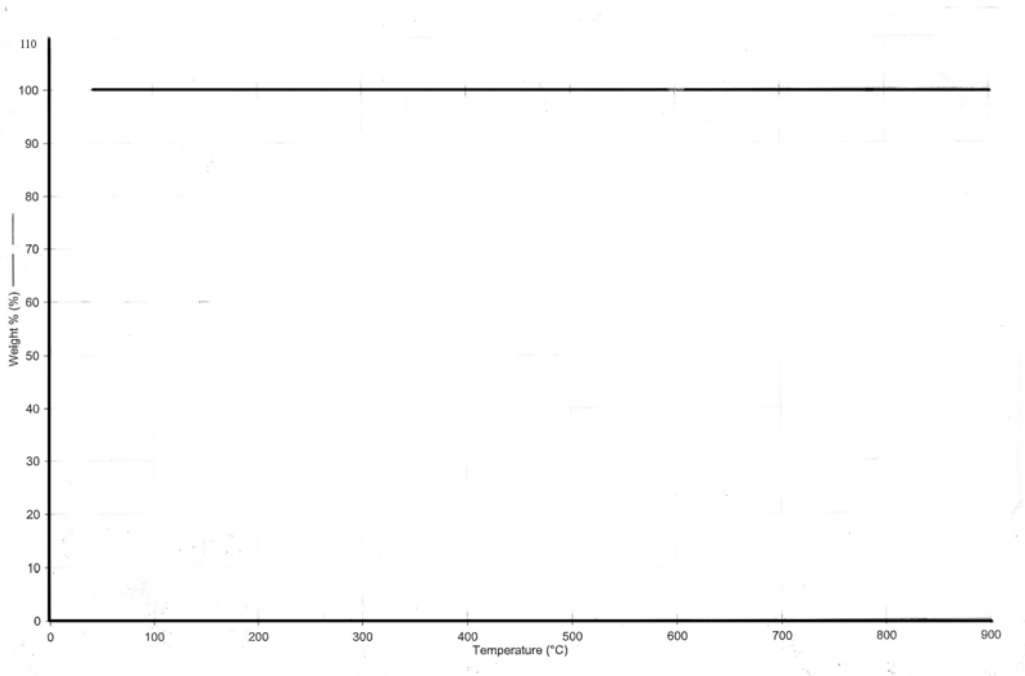


**Figure 25** TGA thermogram of calcined silica materials (SiTa_B).

### 2.4 Scanning electron microscope (SEM).

After calcinations the morphologies and microstructures of sixteen silica products prepared from organic acid templates under stirring and shaking conditions were shown in Fig 26 - 27. Three types of morphologies were found

from SEM images, i.e., sphere, plate and tube (Table 3). All reaction products were spherical particles and aggregates except SiTa_B, SiMu_A and SiMu_B which contained small amounts of non-uniformed cylindrical tubes.

**Table 3** Three types of morphology found in SEM image.

| sample | shape and size of silica | | | |
|---|---|---|---|---|
| | sphere diameter (nm) | plate length (nm) | tube | |
| | | | outer diameter (nm) | length (μm) |
| Stirring method | | | | |
| SiW_A | 210 – 250 | - | - | - |
| SiSu_A | 120 – 300 | - | - | - |
| SiMa_A | 70 – 120 | - | - | - |
| SiTa_A | 190 – 250 | - | - | - |
| SiCi_A | 190 – 280 | - | - | - |
| SiGl_A | 800 – 1100 | 1700 – 2200 | - | - |
| SiAd_A | 800 – 1200 | 1600 – 2200 | - | - |
| SiMu_A | 700 - 1000 | - | 400 - 550 | 3 – 3.4 |
| Shaking method | | | | |
| SiW_B | 690 – 750 | - | - | - |
| SiSu_B | 230 – 310 | 520 -720 | - | - |
| SiMa_B | 280 – 630 | - | - | - |
| SiTa_B | 310 – 580 | - | 190 | 1.2 – 1.5 |
| SiCi_B | 220 – 390 | - | - | - |
| SiGl_B | 210 – 300 | - | - | - |
| SiAd_B | 210 – 350 | - | - | - |
| SiMu_B | 500 - 600 | - | 200 | 2.5 – 2.6 |

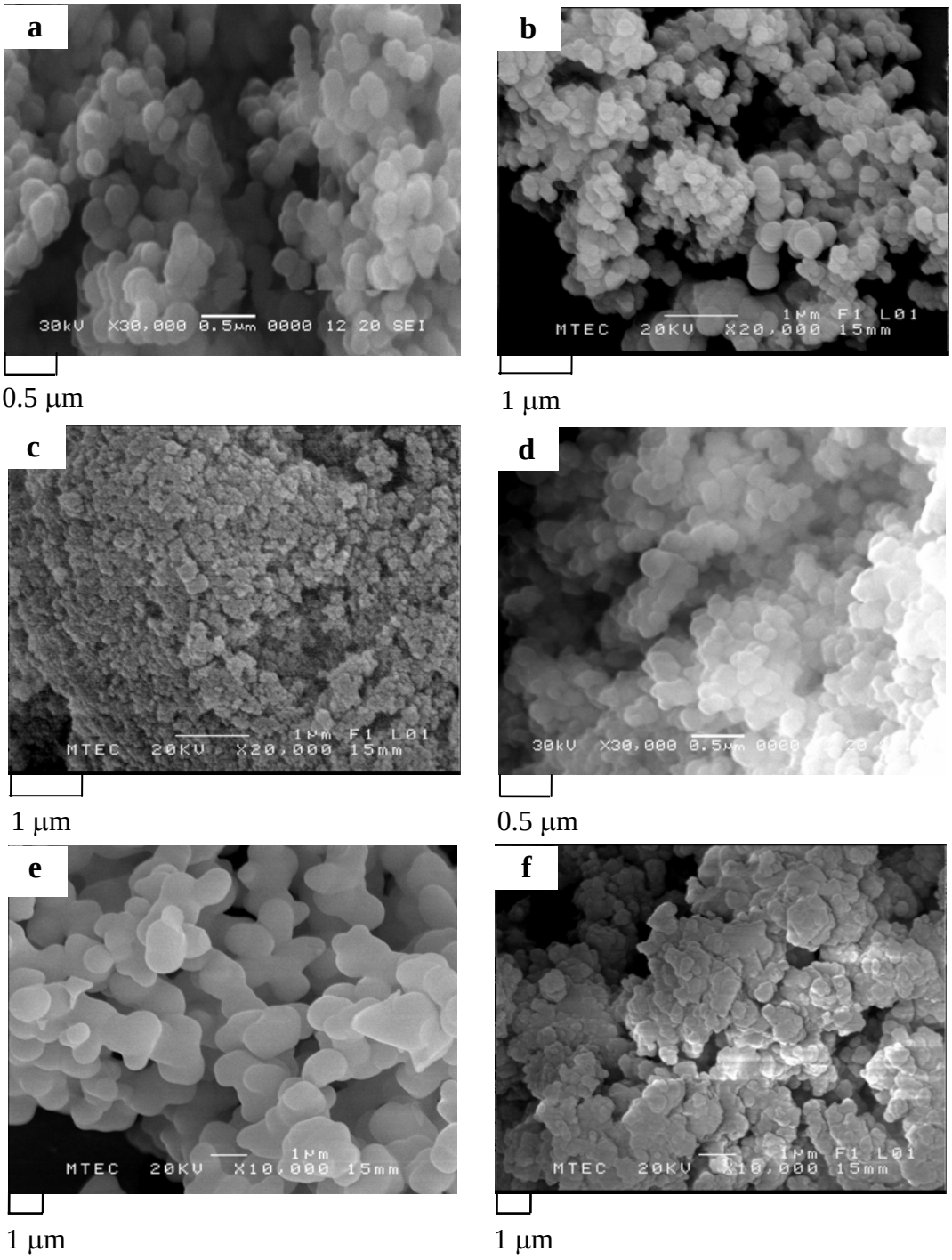


**Figure 26** SEM images of silica materials from stirring method using organic acid templates (a) SiW_A 30,000X, (b) SiSu_A 20,000X, (c) SiMa_A 20,000X, (d) SiTa_A 30,000X, (e) SiGl_A 10,000X and (f) SiCi_A 10,000X.

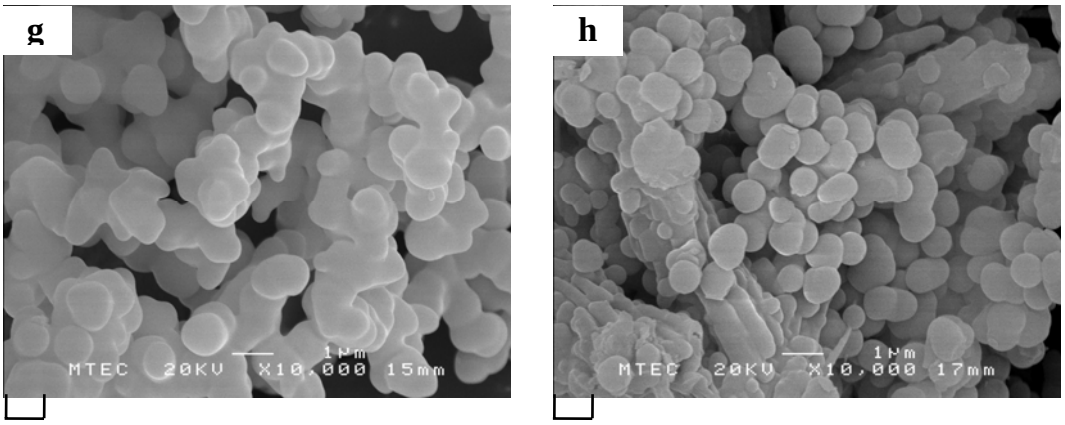


**Figure 26** SEM images of silica materials from stirring method using organic acid templates. (g) SiAd_A 10,000X and (h) SiMu_A 10,000X. (continue)

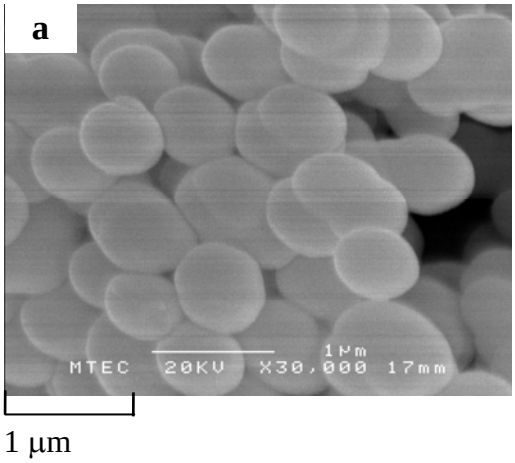


**Figure 27** SEM images of silica materials from shaking method using organic acid templates. (a) SiW 30,000X.

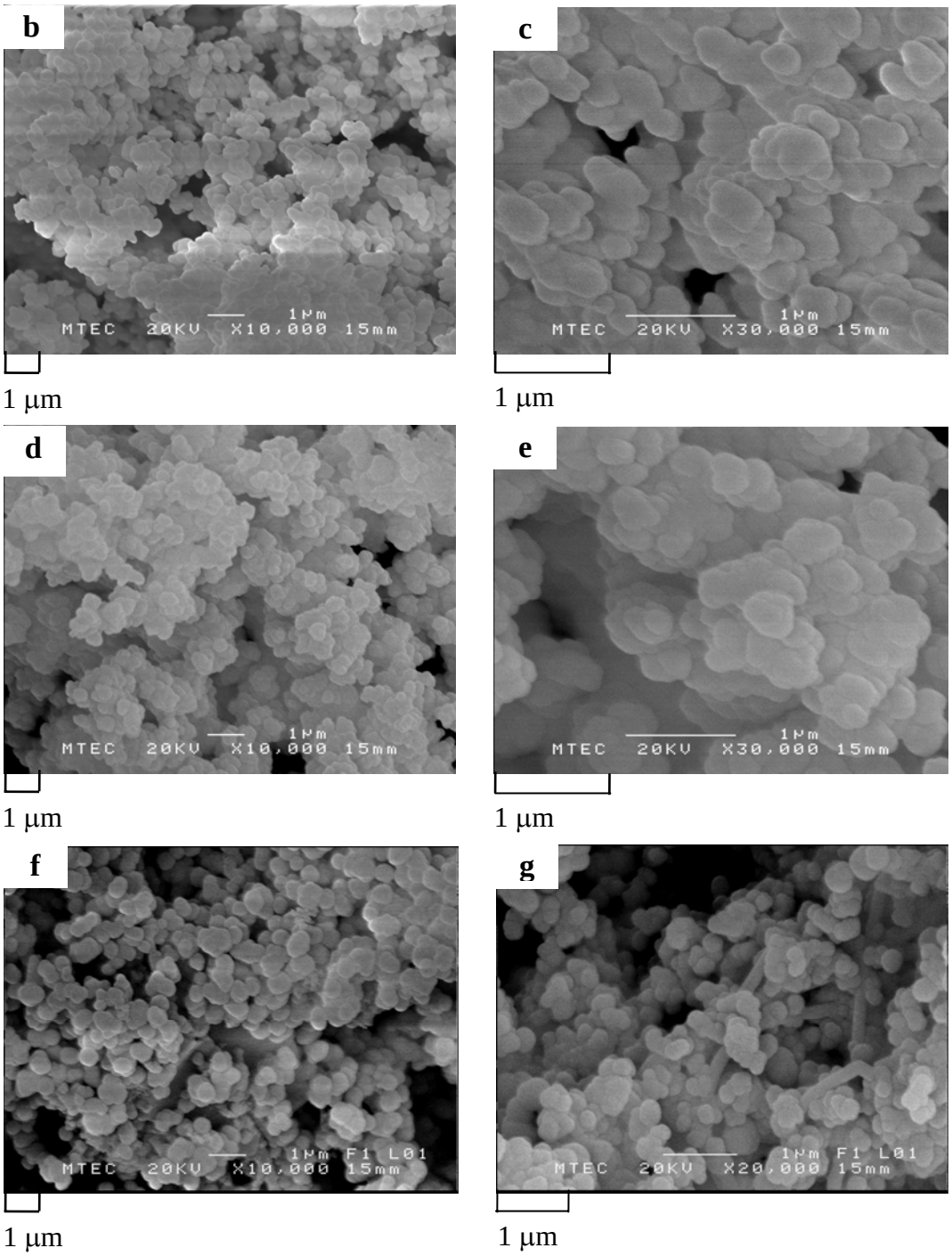


**Figure 27** SEM images of silica materials from shaking method using organic acid templates. (b and c) succinic acid 10,000X and 30,000X, (d and e) malic acid 10,000X and 30,000X, (f and g) tartaric acid 10,000X and 20,000X. (continue)

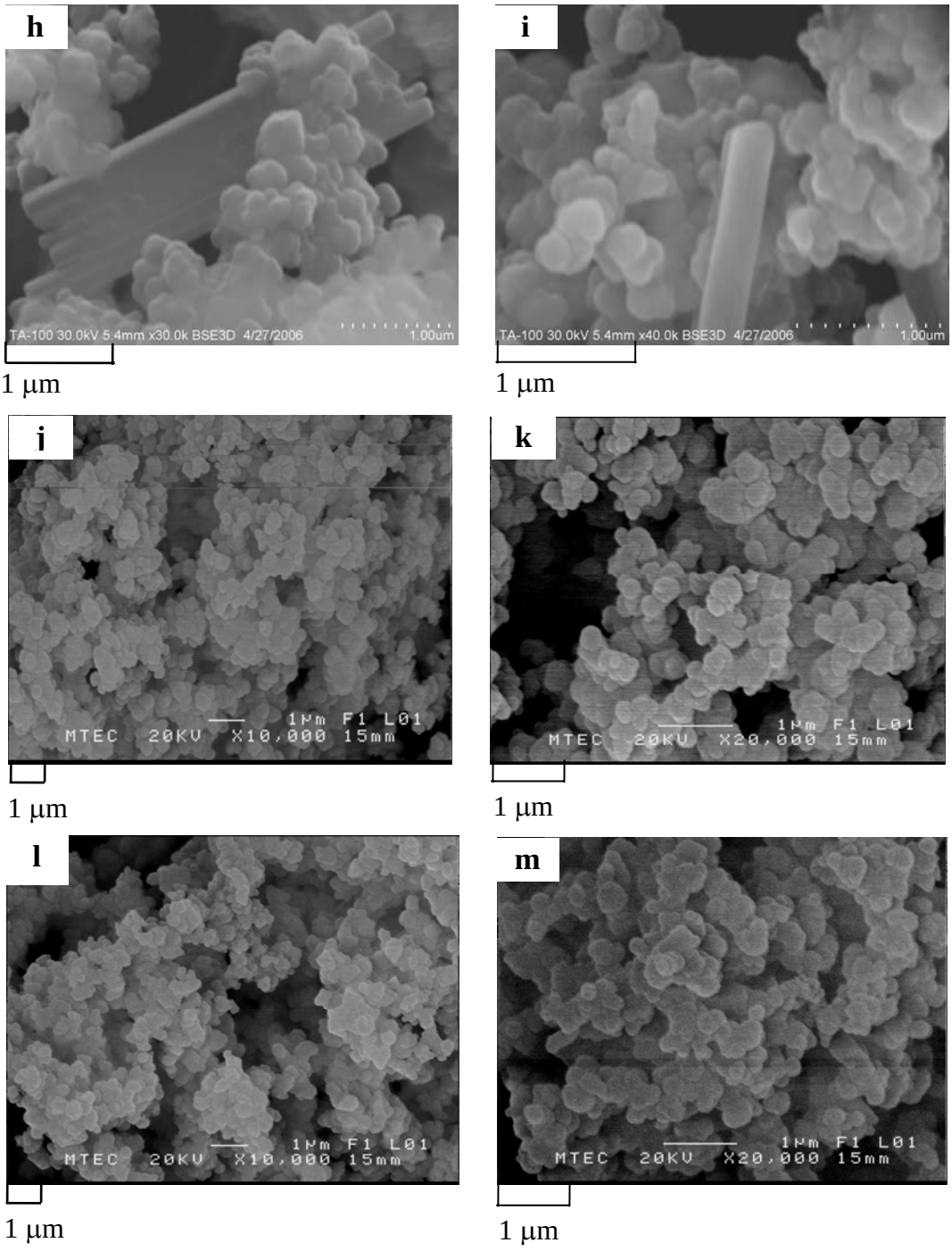


**Figure 27** SEM images of silica materials from shaking method using organic acid templates. (h and i) FE-SEM images of silica from tartaric acid 30,000X and 40,000X, (j and k) glutaric acid 10,000X and 20,000X, (l and m) citramalic acid 10,000X and 20,000X. (continue)

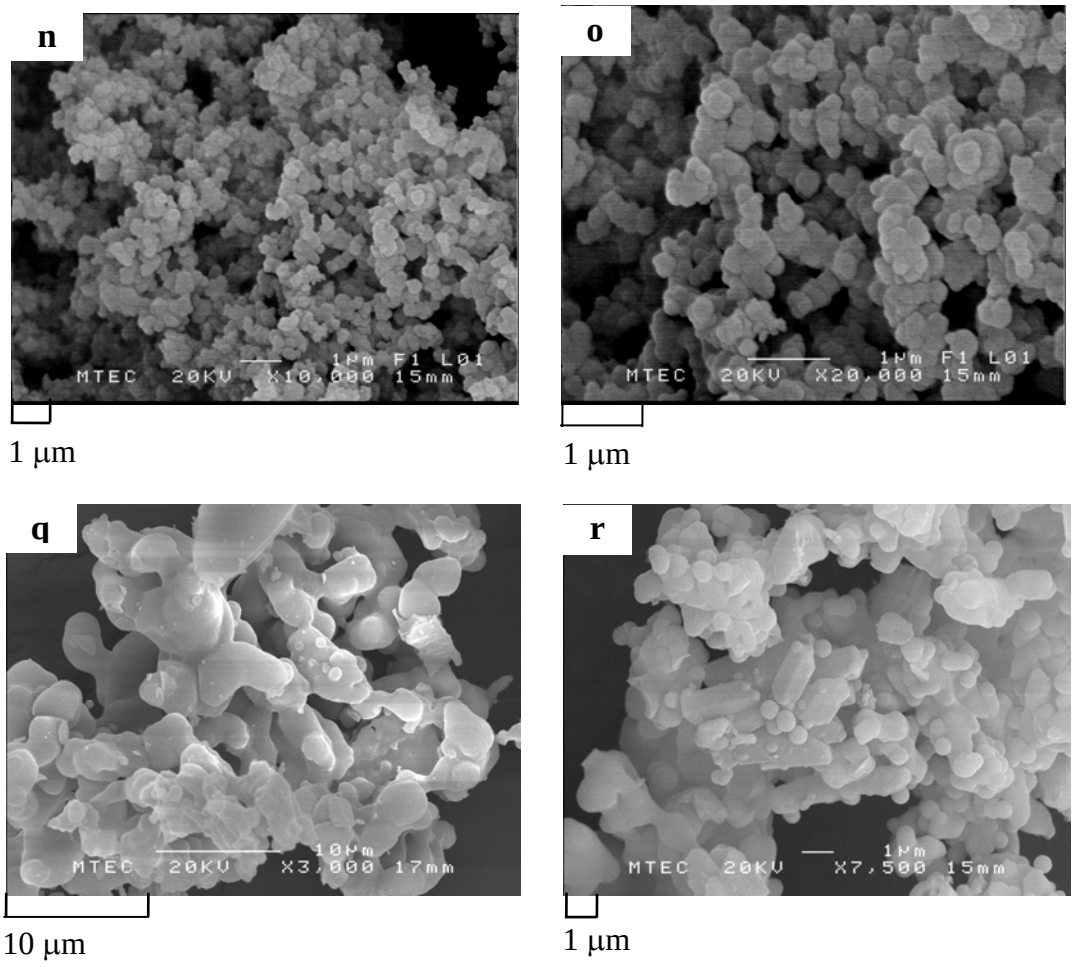


**Figure 27** SEM images of silica materials from shaking method using organic acid templates. (n and o) adipic acid 10,000X and 20,000X, (q and r) mucic acid 10,000X and 20,000X. (continue)

### 2.5 Transmission Electron Microscopy (TEM)

TEM pictures were taken after calcinations of the silica powder from sol-gel process. Morphologies of the synthesized product are investigated by transmission electron microscope (TEM). Three morphologies are typically observed, which are sphere, plate and tube. Nevertheless, there are only two organic acid templates, which are tartaric and mucic acids can produce silica

tubes. These tubes are found with at least one end open and the opposite close as a curve end.

### 2.5.1 TEM images of the calcined silica nanotube which prepared under stirring condition.

TEM image of silica nanotubes using tartaric acid as a template reveals, that the silica nanotubes obtained are not uniform (Fig 28). These nanotubes have lengths of 4.3 μm and the outer diameters of 10-50 nm. The single wall thickness is about 10 nm. Most of them have a smooth morphology, each tube having longitude uniformity in diameter along the tube axis. Figure 29 shows the TEM images of silica nanotubes which were prepared from mucic acid template. The tube has an outer diameter of 500-600 nm, inner diameter of 100 – 120 nm.

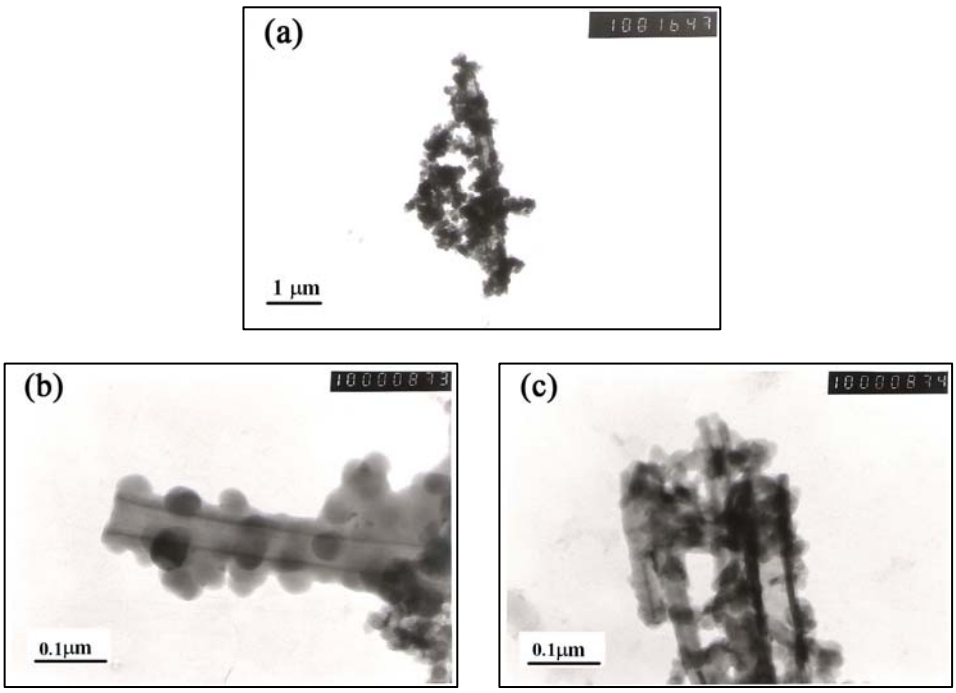


**Figure 28** TEM images of silica nanotubes that using tartaric acid as a template under stirring method (a) 16,500X and (b and c) 150,000X.

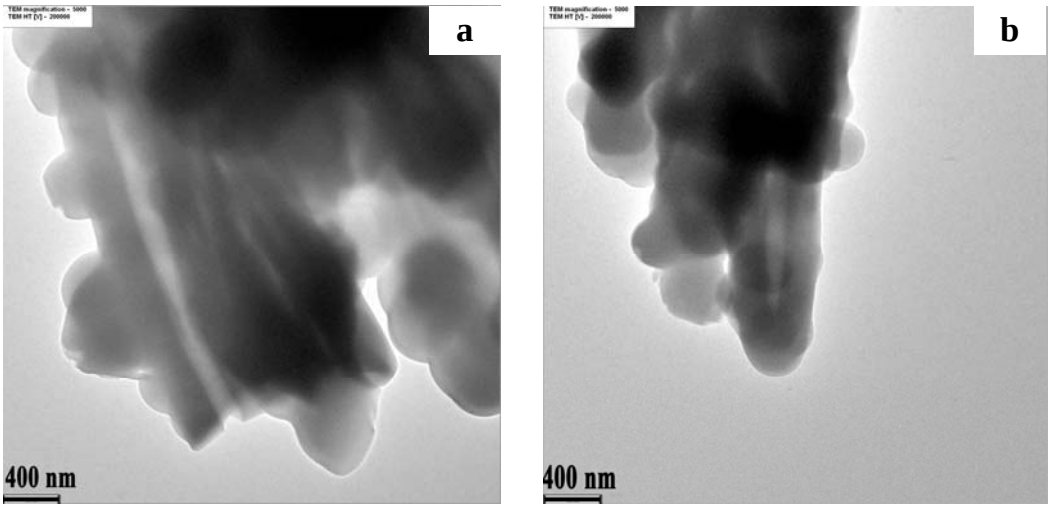


**Figure 29** TEM images of silica nanotubes using mucic acid as a template under stirring condition (a) 4,000X and (b) 5,000X

### 2.5.2 TEM images of the calcined silica nanotube which prepared under shaking condition.

From TEM images the silica products obtained by shaking condition containe more tubular structures than those obtained by stirring. When tartaric acid is used as template, the tubular silica are not uniform. The inner diameters, outer diameters and lengths observed are 8-80 nm, 100-250 nm and >1000 nm, respectively. All tubes observed are single wall (Fig 30). For mucic acid template, the inner diameters, outer diameters and lengths are 270-570 nm, 640-1200 nm and > 1300 nm, respectively (Fig 31).

The TEM images of silica materials which are produced by using the other organic templates, i.e., succinic acid and glutaric acid shows no hollow spheres (Fig 32). The diameter of silica materials in all products from shaking condition are listed in Table 4.

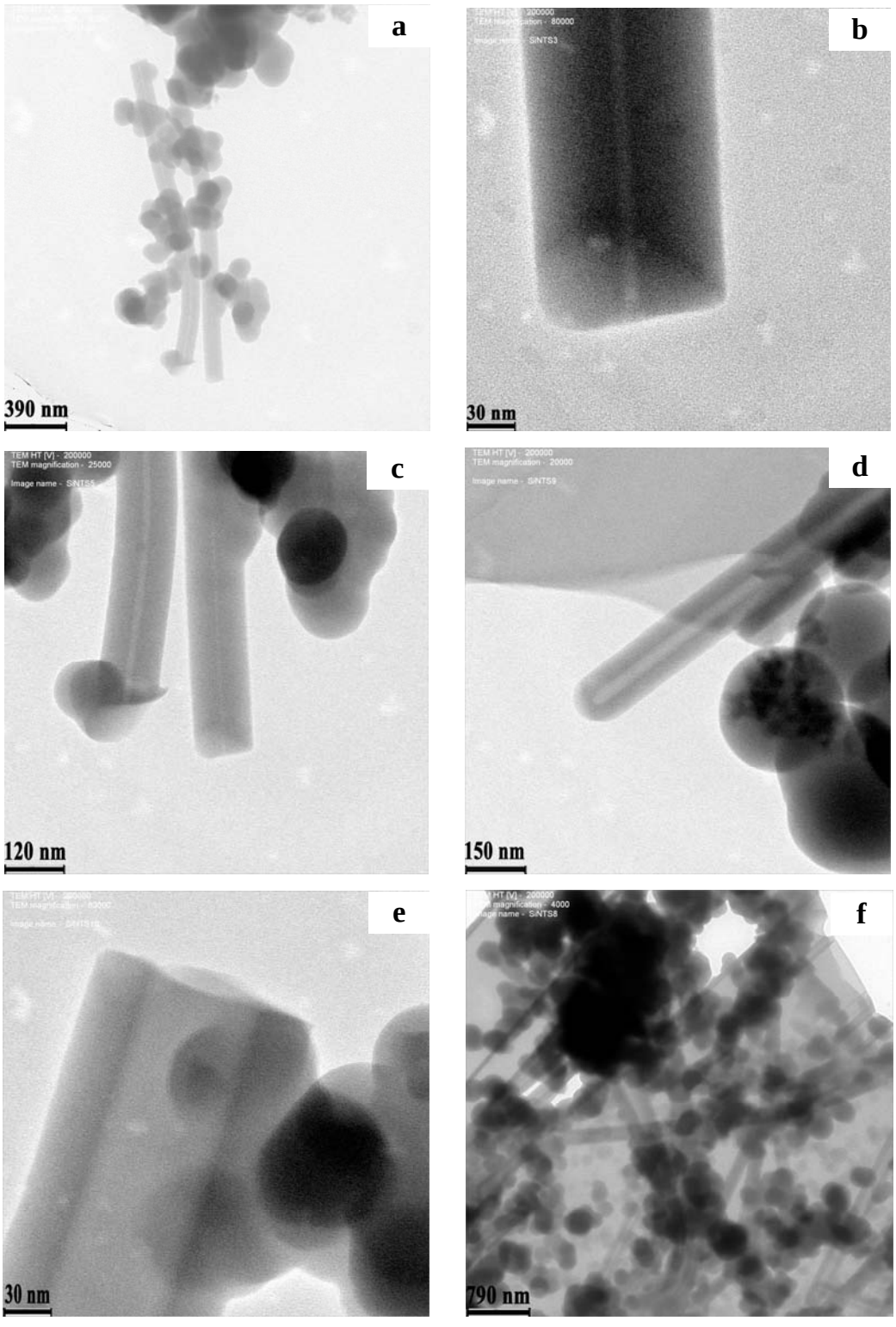


**Figure 30** TEM images of silica nanotubes using tartaric acid as a template under shaking condition (a) 8,000X, (b and e) 80,000X, (c) 25,000X, (d) 20,000X and (f) 4,000X

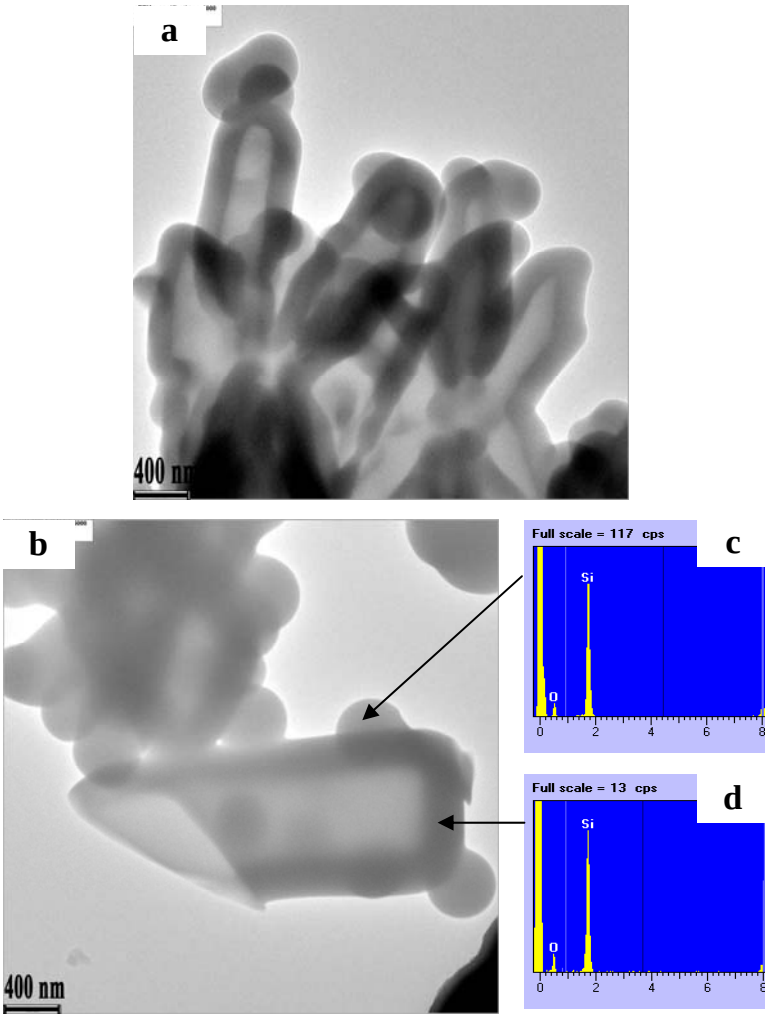


**Figure 31** TEM images of silica nanotubes using mucic acid as a template under shaking condition (a) 4,000X, (b) 5,000X and (c and d) show EDS spectra of sphere and wall of silica products.

**Table 4** The diameter of silica materials in all products under shaking condition were observed from TEM images.

| sample code | shape and size of silica | | | |
|---|---|---|---|---|
| | | tube | | |
| | sphere diameter (nm) | inner diameter (nm) | outer diameter (nm) | length (μm) |
| SiW_B | 80 – 200 | - | - | - |
| SiSu_B | 150 – 250 | - | - | - |
| SiMa_B | 100 – 220 | - | - | - |
| SiTa_B | 310 – 580 | 8 – 80 | 100 – 250 | 1.2 – 1.5 |
| SiCi_B | 100 – 150 | - | - | - |
| SiGl_B | 210 – 300 | - | - | - |
| SiAd_B | 50 – 100 | - | - | - |
| SiMu_B | 500 - 600 | 265 – 585 | 640 – 1200 | 1.3 – 2.8 |

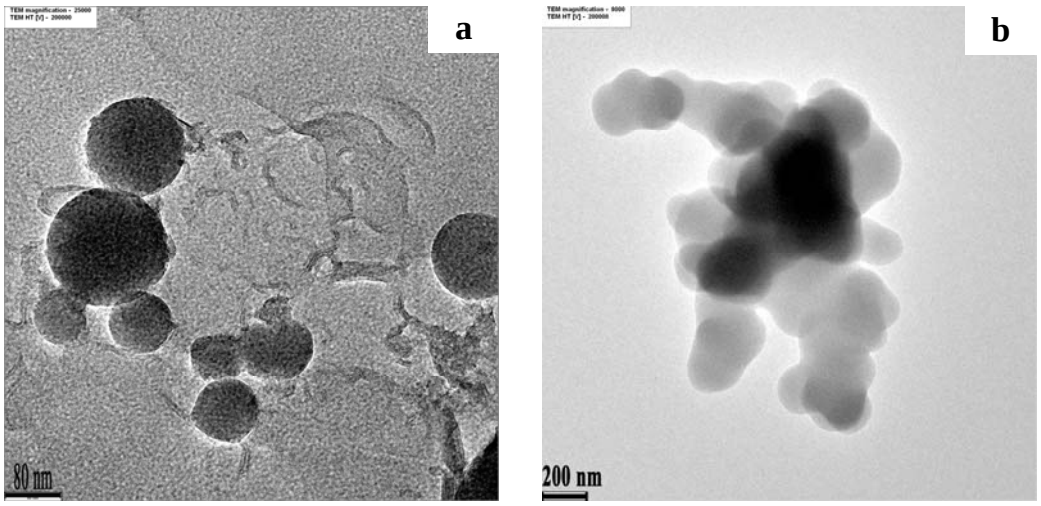


**Figure 32** TEM images of silica materials using acid template under shaking condition (a) SiW_B 25,000X and (b) SiSu_B 8,000X

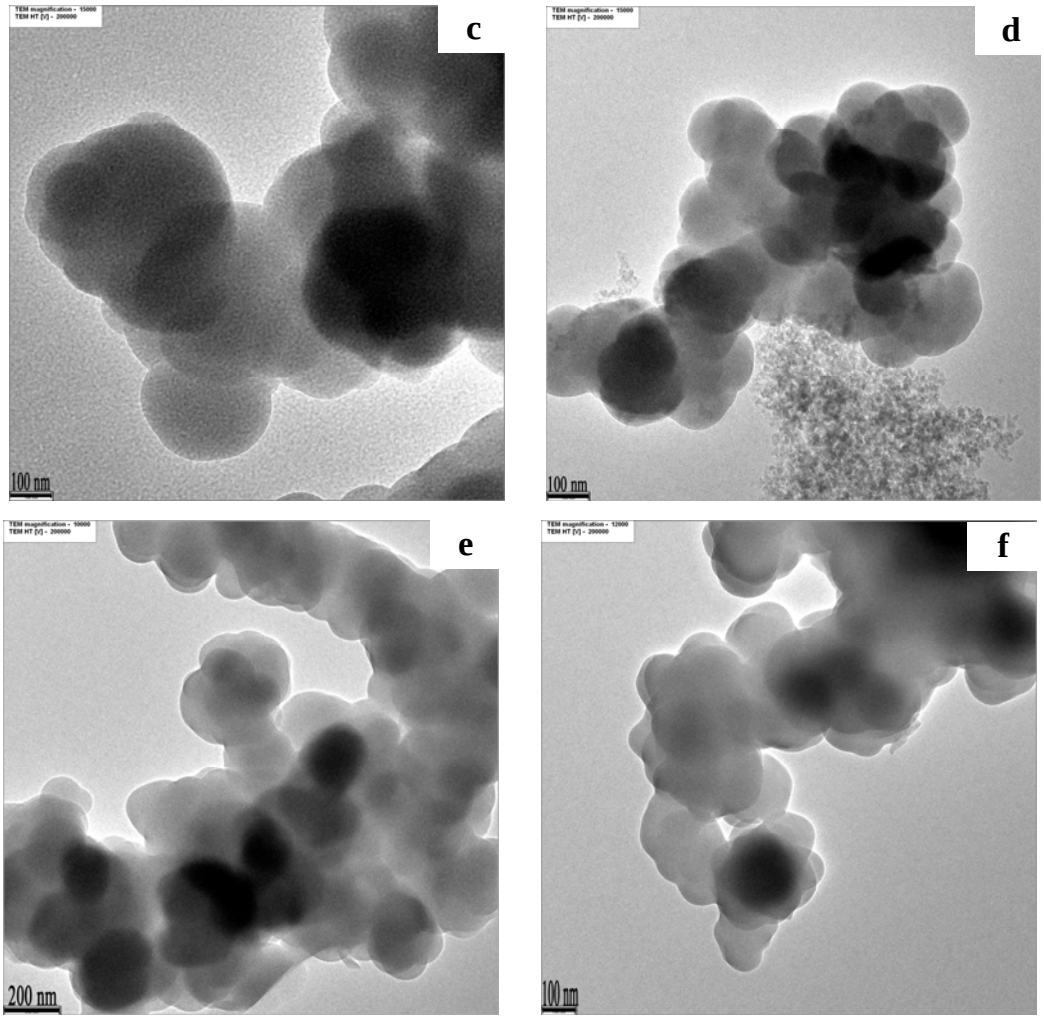


**Figure 32** TEM images of silica materials using acid template under shaking condition (c) SiMa_B 15,000X, (d) SiGl_B 15,000X, (e) SiCi_B 10,000X and (f) SiAd_B 12,000X. (continue)

## 3. Proposed mechanism for silica nanotubes formation.

From this study it can be concluded that only polyhydroxyldicarboxylic acids, which have hydroxyl groups at every methylene carbon atoms, can act as templates for the formation of silica nanotubes. This means only tartaric and mucic acids can be used as templates. For non-template process only uniform spherical shapes were observed. The proposed mechanism may start with the

formation of rod-like materials of acid template molecules by a slow aggregation process through the intermolecular hydrogen bonding between themselves (Fig 33). If the acids have several or no hydroxyl groups at methylene carbon atoms, the stable rod-like templates do not form. When an acid solution in the presence of ammonia is added to TEOS alcoholic solution, the interaction of the template with TEOS takes place. TEOS are hydrolyzed onto the surface of the cylindrical organic acid templates. The hydroxyl groups in acid and in hydrolyzed TEOS form hydrogen bonds with each other. After

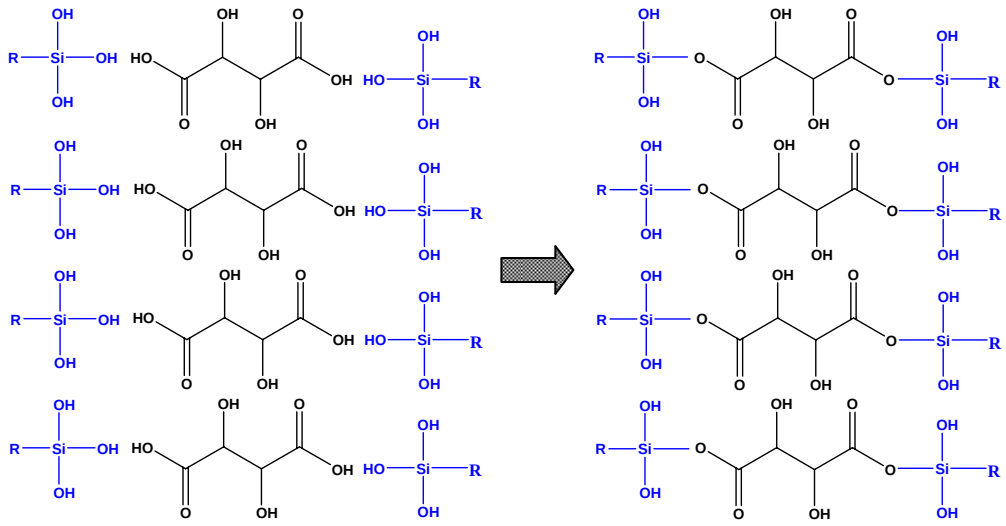

**Figure 33** Proposed mechanism for silica nanotubes formation using tartaric acid as template.

condensation/hydrolysis of the TEOS are complete, the silica are formed on the surface of templates. In this study the ammonia solution was mixed with acids before adding to TEOS thus the efficiency of forming rod-like template should be low because the acids react with base forming their salts. Consequently only few interactions between TEOS and organic templates occur. Simultaneously the condensation and hydrolysis of the TEOS without templates take place. After calcinations the products obtained are both spherical and tubular silica.