MATERIALS AND METHODS

Chemicals and Instruments

1. Chemicals

1.1 Succinic acid (analytical reagent grade; Mag & Baker LTD Dagenham England)

1.2 Malic acid (reagent grade; Fluka)

1.3 Tataric acid (analytical reagent grade; Fluka)

1.4 Citramalic acid (analytical reagent grade; Fluka)

1.5 Glutaric acid (reagent grade; Fluka)

1.6 Adipic acid (analytical reagent grade; Fluka)

1.7 Mucic acid (reagent grade; Aldrich)

1.8 Tetraethylorthosilicate (analytical reagent grade; Aldrich Chemical company, Inc)

1.9 Amonium hydroxide (reagent grade; J.T. Baker)

1.10 Ethanol (analytical reagent grade; Merck)

2. Apparatus and Instruments

2.1 Vacuum suction apparatus

Vacuum suction apparatus EYELA model Aspirator A-35

2.2 Magnetic stirrer

Magnetic stirrer JENWAY model 1002 stirrer

2.3 Orbital shaker

IKR ® orbital shaker model KS 130 basic.

2.4 Fourier Transform Infrared Spectrophotometer (FTIR)

Solid state infrared spectra of compounds were measured on a Bruker model Equinox 55 Spectrophotometer using potassium bromide disc.

2.5 High temperature electric furnace

High temperature electric furnace was locally made by King Mongkut's University of Technology Thonburi.

2.6 Thermogravimetric and Differential Thermal Analyzer

Thermogravimetric Analyzer model Pekin-Elmer SDT 2960 from Department of Chemical Engineering at Kasetsart University.

2.7 X –ray Diffractometer (XRD)

X-ray diffractometer model miniflex Rigaku/Destop X-ray Diffractometer system at King Mongkut's University of Technology Thonburi.

2.8 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) model JSM 6310 F (JEOL) at National Metal and Materials Technology Center.

2.9 Transmission Electron Microscope (TEM)

Transmission Electron Microscope (TEM) model JEOL JEM-2010 at National Metal and Materials Technology Center.

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Methods

In this study, silica nanomaterials were prepared by template assisted method and the products were characterized by following techniques: Fourier Transform Infrared Spectroscopy, Thermogravimetric and Differential Thermal Analysis, X –ray Diffraction, Scanning Electron Microscopy and Transmission Electron Microscopy.

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

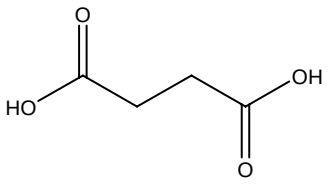
In this study the following parameters which may play a role on the formation of silica nanotubes were studies.

1) Effect of mechanically agitating by means of magnetic stirring.

2) Effect of mechanically agitating by means of shaking.

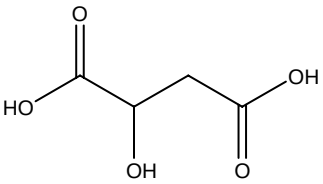
3) Types of organic template. Seven dicarboxylic acids were used as templates. They were succinic, malic, tartaric, citramalic, glutaric, adipic and mucic acids.

C4



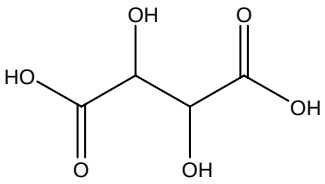
succinic acid

($C_4H_6O_4$)



malic acid

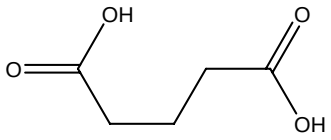
($C_4H_5O_5$)



tartaric acid

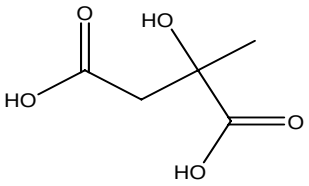
($C_4H_6O_6$)

C5



glutaric acid

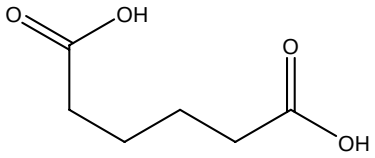
($C_5H_8O_4$)



citramalic acid

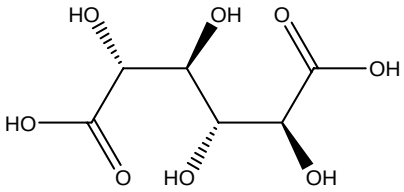
($C_5H_8O_5$)

C6



adipic acid

($C_6H_{10}O_4$)



mucic acid

($C_6H_{12}O_7$)

1.1 Synthesis of silica nanomaterials without template.

Tetraethylorthosilicate (TEOS) 6.0 ml (0.0264 mole) was added to the mixed solution of 0.7 ml of H_2O and 30 ml of ethanol. After stirring for 15 min, 12 ml of NH_4OH (28% aqueous solution) were slowly dropped into the solution within 2 hours. White precipitate was collected, washed with distilled water and dried at 75°C. Finally the product was calcined at 1000 °C for 3 hours.

1.2 **Synthesis of silica nanomaterials with organic template.**

Tetraethylorthosilicate (TEOS) 6.0 ml (0.0264mole) was added to the mixed solution of 0.7 ml of H_2O and 30 ml of ethanol and stirring by magnetic stirrer for 15 min. Then 12 ml of NH_4OH (28% aqueous solution) containing 0.00133 mole of dicarboxylic acid template were slowly dropped into the mixture under magnetic stirring for 2 hours. After that the white precipitate was filtered, washed with distilled water and dried in oven at 75°C. The product was calcined at 1000 °C for 3 hours.

The procedure above was repeated except that the shaker was used instead of magnetic stirrer. The shaking rate was kept constant for all syntheses at 300 rpm. Table 1 lists sample codes for products obtained from various conditions.

Table 1 Sample codes for products.

Condition	Organic acid template	Code*
stirring condition	-	SiW_A
	Succinic acid	SiSu_A
	Malic acid	SiMa_A
	Tataric acid	SiTa_A
	Citramalic acid	SiCi_A
	Glutaric acid	SiGl_A
	Adipic acid	SiAd_A
	Mucic acid	SiMu_A
shaking condition	-	SiW_B
	Succinic acid	SiSu_B
	Malic acid	SiMa_B
	Tataric acid	SiTa_B
	Citramalic acid	SiCi_B
	Glutaric acid	SiGl_B
	Adipic acid	SiAd_B
	Mucic acid	SiMu_B

* Siâ_A and Siâ_B when â represent types of carboxylic acid.
A represent stirring condition.
B represent shaking condition.

2. Characterization of silica nanomaterials.

2.1 Fourier Transform Infrared Spectroscopy (FTIR).

Spectroscopic grade KBr and as-synthesized silica powder were pressed together under pressure (1500 psi) into a pellet. The FTIR spectra were recorded between 400 - 4000 cm^{-1}.

2.2 Thermal Gravimetric Analysis (TGA).

The silica sample was placed in alumina pan which was then placed on the sample holder of thermal gravimetric analyzer. The heating rate was 5 °C /min. Only three uncalcined silica samples which were (1) SiW_B, (2) SiMu_B and (3) SiTa_B were analyzed.

2.3 X-ray Diffraction (XRD).

The silica samples were finely ground in agate mortar. The XRD patterns of three as-synthesized silica samples (SiW_B, SiMu_B and SiTa_B) were recorded from $2\theta = 0 – 70$ degree.

2.4 Scanning Electron Microscopy (SEM).

The silica sample which was coated with gold was placed on a metal stub. The scanning electron micrographs of all as-synthesized silica were obtained.

2.5 Transmission Electron Microscopy technique.

Samples for TEM analysis were prepared by grinding in a mortar and sonicating in ultrasonic bath for 15 min. A few drops of the suspension were added on a grid. After approximately one minute, excess liquid was removed by blowing. The TEM micrograph of SiTa_A, SiTa_B, SiMu_A, SiMu_B, SiSu_B, SiMa_B, SiCi_B, SiAd_B and SiGl_B were obtained.