CHAPTER III
EXPERIMENTAL SECTION

3.1 Materials

Octadecyltrichlorosilane (ODS) was received from Sigma. (Heptadecafluoro-1,1,2,2-tetrahydrodecyl) dimethyl-Chlorosilane (HFD) was obtained from Gelest Inc. Precipitated silica (Hi-Sil® 233) obtained from PPG-Siam Silica Co., Ltd. has a reported BET surface area of 138 m^2/g. Potassium bromide, phenol 99.5%, methyl alcohol 99.9%, and trichloroethylene (TCE) 99.5% were obtained from Carlo Erba Reagenti Company. Acetonitrile 99.8% and pyridine were received from Merck Company. Toluene was supplied by Baker Company. Sodium hydroxide, potassium dihydrogen phosphate, potassium hydrogen phthalate, and hydrochloric acid were used for adjusting the pH. Ozone was produced using an ozone generator OG20 manufactured by Verfahrenstechnik Universal GmbH Company. All solutions were prepared with distilled water.

3.2 Methods

3.2.1 Chemically bonded monolayer of hydrocarbon on silica

The procedure to construct the chemical bonding of octadecyltrichlorosilane (ODS) (Thakulsukanant et al., 1997) is given as follows:

1. Mix ODS and 6 g of silica with 180 ml of toluene in 500 ml round bottle flask equipped with a condenser.

2. Reflux the mixture for 12 hr, then add 25 ml of methanol and reflux again for 3 hr.

3. Filter the mixture through a membrane filter and wash the solid with 400 ml of distilled water (to remove HCl salt) followed by 400 ml of toluene (to remove excess reagent).

4. Wash the solid with toluene by means of a soxhlet extractor for a day and then dry it at 80 ^{o}C for 12 hr.

5. Measure the spectra of the ODS treated silica on a Bio-Rad FTS-45A infrared spectrometer using the diffuse reflectance technique.

6. Analyze the carbon percentage of ODS treated silica by elemental analyzer, Perkin-Elmer, and also calculate the bonded ODS per gram of silica (μmoles/g) using the following expression derived by Berendsen et al., 1980.

$$N\ (\mu moles/g) = \frac{10^6 P_C}{1200 n_C - P_C (M-1)} \qquad (3.1)$$

where P_C is the measured carbon percentage;
M is the molecular weight of the bonded molecule;
n_C is the number of carbon atoms in the bonded silane molecule.

In eq (3.1) the factor $P_C(M-1)$ corrects for the weight increase of the silica.

3.2.2 Chemically bonded monolayer of fluorocarbon on silica

The method to chemically bond the (Heptadecafluoro-1,1,2,2-tetrahydrodecyl) dimethyl-chlorosilane (HFD) which is the monochlorosilane reagent on the silica surface (Berendsen et al., 1978) is described below:

1. Activate the silica at 200°C at vacuum pressure of 1.5 torr for 12 hr.
2. Mix HFD, 100 ml of toluene, 2.5 ml of pyridine, 4 g of activated silica in 250 ml round bottle flask equipped with condenser.
3. Reflux the mixture 87 hr at 100°C. This reaction is carried out in a dry nitrogen atmosphere.
4. Wash the bonded phase with dry toluene (to remove excess reagent), dry methanol, methanol/water 1:1, water (to remove the pyridine-HCl salt), methanol and ether consecutively.
5. Dry it at 150°C in vacuum oven for 12 hr.
6. Measure the spectra of the HFD treated silica on a Bio-Rad FTS-45A infrared spectrometer using the diffuse reflectance technique.
7. Analyze the carbon percentage of HFD silica by elemental analyzer and also calculate the bonded HFD per gram of silica using eq. (3.1).

3.2.3 Adsolubilization measurements

Phenol and trichloroethylene (TCE) were used to study the adsolubilization on monolayers. Phenol was used as a polar organic solute and TCE was used as a nonpolar organic solute. The experimental procedure is given as follows:

1. Prepare 185 ppm of phenol solution.
2. Mix 15 ml of phenol solution and 0.7 g treated silica in a 22 ml teflon-lined septa cap vial, then shake it at 30°C for 2 hr.

3. Withdraw the aqueous phase from a vial to filter it.

4. Measure the phenol concentration by using a Hewlett Packard Series 1050 HPLC with Hewlett Packard column spherisorb ODS2 5 μm, 125 mm* 4 mm and a UV detector 1050 series.

5. Calculate the concentration of phenol in admicelles by subtracting that in the aqueous phase from the total concentration.

6. Repeat steps 2-5 by varying surface coverage and type of treated silica.

The TCE adsolubilization study was conducted in the same manner as phenol. The initial concentration of TCE was 680 ppm. The concentration of TCE was analyzed using Perkin Elmer Gas Chromatography with the flame ionization detector.

3.2.4 Stability measurements

The effects of agitation speed, agitation time, pH, and temperature on the stability of monolayers were studied in this part. For example, the procedure utilized for studying the effect of agitation speed can be described as follows:

1. Mix 0.1 g of treated silica with 50 ml of distilled water in a 250 ml beaker.

2. Place it in a temperature controlled bath (DT Hetotherm) set a 25°C and agitate it using a mechanical stirrer (Janke & Kunkel IKA® Labortecnik) with speed No.1 for 30 minutes.

3. Filter the solution and dry the solid in an oven at 80°C for overnight.

4. Measure the carbon percentage of the solid by elemental analyzer. The stability was then determined by a comparison of the carbon percentage obtained before and after a stability test (C/Co).

5. Repeat steps 1-4 with varying agitation speeds.

For other effects studied the experiments were conducted in similar manners by varying the parameter of interest while keeping others constant.

The stability of treated silica under ozone conditions was studied by the following procedure.

1. Mix 0.15 g of treated silica with 100 ml of distilled water in a 500 ml wide neck reaction flask.

2. Ozone was fed into the solution at a flow rate of 15 l/hr while stirring the solution at 500 rpm with the solution temperature constant at 30°C. The experimental apparatus for ozone oxidation is shown in Figure 3.1.

3. Filter the solution and dry the solid in an oven at 80°C for 12 hr.

4. Measure the carbon percentage of the solid by elemental analysis. The stability was then determined by a comparison of the carbon percentage obtained before and after a stability test (C/Co).

5. Repeat steps 1-4 with varying the concentrations of ozone and pH of the solution.

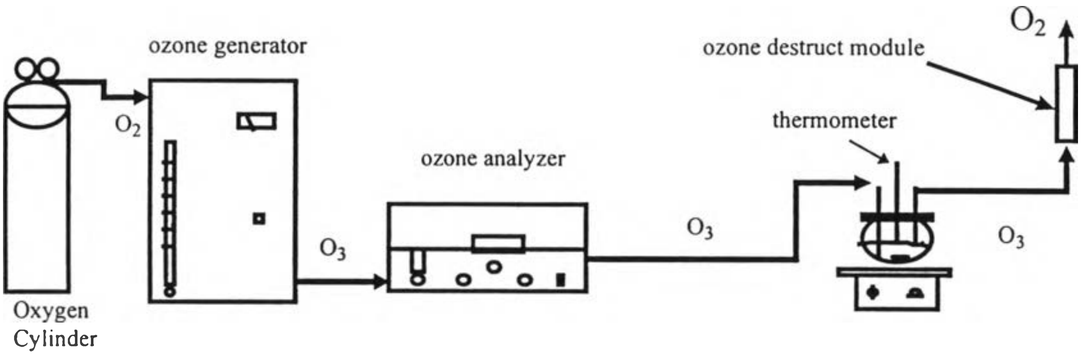

Figure 3.1 Experimental apparatus for ozone oxidation.