Chapter 3

Nanosilica - Synthesis and Characterization

3.1 Introduction

In the past few years, nanomaterials have attracted tremendous international interest, investment and effort both in scientific research and in industrial development because of their potential applications in various fields. Nanostructured composite materials, when using organic polymer and inorganic fillers, represent a merger between traditional organic and inorganic materials, resulting in compositions that are truly hybrid. Organic-inorganic composites with nanoscale dimensions are of growing interest because of their unique properties, and numerous potential applications such as enhancement of conductivity [4,5], toughness [6], optical activity [7,8], catalytic activity [9], chemical selectivity [10,11] etc. In these materials, inorganic and organic components are mixed or hybridised at nanometer scale with virtually any composition leading to the formation of hybrid/nanocomposite materials [12-22].

Silica has been used in different polymers as a reinforcement material. Examples are in methacrylate [23-26], polyimide [27-28], polyamide [29], rubbery epoxies [30], and acrylic [31]. The specific function of the filler is based on the specific resin system, particle size, surface area, loading and surface modification. Because of the high bond energy in the Si-O bond, SiO₂ has extremely high thermal stability. SiO₂ also possesses a very low thermal
expansion coefficient. The silica containing nanocomposites show remarkable barrier properties to gases and moisture as well as very good resistance to staining [32-34].

Several methods are used to produce nanosilica from various sources [6-12][35-41]. Bomal et al. reported a process for preparing precipitated silica comprising reacting a silicate with an acidifying agent to produce a suspension of precipitated silica and, then, separating and drying the suspension to obtain the precipitated silica as a dried product. The silica obtained has a good dispersibility and very satisfactory reinforcing properties. It also relates to new precipitated silicas which are in the form of powder, of substantially spherical beads or of granules, these silicas being characterized by the fact that they have a BET specific surface of between 90 and 250m$^2$/g. Another study by Teofil Jesionowski studied preparation of amorphous silica via precipitation reaction from aqueous solution of sodium metasilicate and hydrochloric acid in emulsion medium, focusing on determination to optimize the dispersive and morphological properties of silicas. It is revealed that the properties of silicas precipitated from emulsion systems depend on several variables but the amount and concentration of the applied reagents and pH of the emulsion are of critical importance. Kim, Liu and Zachariah have suggested that the aerosol-assisted sol-gel method to produce nanosilica. In this method, Tetra ethoxy silane (TEOS), water and ethanol were allowed to react. Sufficient hydrolysis time was given and then the solution was aerosolized with sodium chloride. Sodium chloride was employed both as an agent to accelerate the kinetics of silica generation and as a templating medium to support the formation and stability of pore structures. Ahamed et al, have synthesized nanosilica from rice hull. The
method involved acid digestion, combustion at 700°C and then milling to produce nanosilica. Kotoki et. al prepared poly vinyl alcohol/silica nanocomposite starting from sodium silicate with dilute hydrochloric acid as catalysts in poly vinyl alcohol. This is a sol-gel method in which the acid plays a catalytic role in enhancing sol-gel condensation of silicon alkoxides within the PVA. The reaction was carried out at 60°C and pH maintained between 1-2. The reaction mixture was passed through cation exchange resin amberlite for the removal of sodium ions. After 24 hrs at ambient temperature it gelled and the samples were dried for 48 hrs at 47°C.

3.1.1 Silica

Silicon is the second most abundant element on earth, after oxygen, making up approximately 25 percent of the earth’s crust by weight; largely found in the form of oxides such as sand and clay (Winter 2003). Silica, in its pure form is colorless to white. Silica is widely and abundantly distributed throughout the earth, both in the pure state and in silicates, (e.g., in quartz, agate, amethyst, chalcedony, flint, jasper, onyx and rock crystal), opal, sand, sandstone, clay, granite and many other rocks. Silica occurs in several forms and is insoluble in water, slightly soluble in alkalies and soluble in dilute hydrofluoric acid.

3.1.2 Types of silica

Commercially available silicas can be broadly classified as Crystalline silicon dioxide, Non-Crystalline, fumed silica, precipitated silica, silica gel and Colloidal silica.

Crystalline silicon dioxide: Crystalline silicon dioxide is one of the most commonly encountered substances in both daily life and in electronics
manufacturing. Crystalline silicon dioxide (in several forms: quartz, cristobalite, tridymite) is an important constituent of a great many minerals and gemstones, both in pure form and mixed with related oxides. Beach sand is mostly silica. Crystalline silicas show discrete reflections in X-ray diffraction from the internal planes formed by the orderly pattern of atoms. The working of silica into glass (usually by the addition of natron -- sodium oxide -- to lower the melting point) has been known since antiquity, with polished glass lenses in eyeglasses and optical instruments dating back more than 5 centuries.

Non-Crystalline silicon dioxide: Non-crystalline, or amorphous silica, is usually prepared by vapor-phase hydrolysis, precipitation or other processes that ensure the absence of crystalline free silica. Three forms of synthetic amorphous silica are classified according to their method of preparation: silica gel (silica G), precipitated silica (silica P) and fumed silica (silica F). There are several naturally-occurring and synthetic amorphous silicas, namely diatomaceous earth, precipitated silica, silica gel, fumed silica and silica fume (thermally generated). In amorphous silica, X-rays are scattered randomly and no discrete reflections are seen. All types of amorphous silica can be converted to crystalline forms when heated to a sufficiently high temperature.

Fumed silica: Fumed silica is derived from vapor-phase hydrolysis of a silicon-bearing halide, such as silicon tetrachloride. It is the byproduct of a high-temperature process when elemental silicon is produced by reacting coke and silica sand (crystalline) in an electric arc furnace. It offers primary particles with diameters from 5 to 40 nm., as well as a low density of silanols, and very few impurities.
Precipitated silica: in precipitated silica, the reaction mixture is held in the alkaline pH region, and offers limited aggregates of primary particles with a diameter of >5 n.m., and specific surface area (<350 m$^2$/g). The production of precipitated silica starts with the reaction of an alkaline silicate solution with a mineral acid. Sulfuric acid and sodium silicate solutions are added simultaneously with agitation to water. The resulting white precipitate is filtered, washed and dried in the manufacturing process. Precipitated silica's basic characteristics, which can be altered during the precipitation process, are particle size distribution, porosity, specific surface area and purity.

Silica gel: for silica gel, the reaction mixture is held in the acidic pH region, and here precipitated silica means a three-dimensional network of particles with low diameter (3 nm.), with a high specific surface area (>350 m$^2$/g). Packets of silica gel are found in all sorts of products because silica gel adsorbs and holds water vapor. In fact, you will find little silica gel packets in anything that would be affected by excess moisture or condensation. Silica gel is nearly harmless and that is why you find it in food products. Silica gel can adsorb about 40% of its weight in moisture and can take the relative humidity in a closed container down to about 40%. Once saturated you can drive the moisture off and reuse silica gel by heating it above 300 degrees F.

Colloidal silica: Colloidal silica has found widespread use for diverse materials in many industries. It is an aqueous, colloidal dispersion of chemically inert silica particles. The particles cut effectively, without deformation, because they combine individual crystals with a large exposed surface area and a high pH activation. Colloidal silica has been used successfully on a variety of materials including aluminium and aluminium
alloys, titanium and titanium alloys, copper and copper alloys, lead and lead alloys, zirconium alloys, semiconductors, printed circuit boards, steels and coal.

3.1.3 Methods of production
3.1.3.1 The sol-gel process

Sol-gel technology has been used extensively in the synthesis of nano silica, as illustrated in Figure 1-1. A sol, by definition, is a suspension of solid particles, with size between 1-1000 nm, in a liquid continuous phase. The sol-gel process refers to the creation of a continuous, solid network through a change of interactions between the colloidal particles; changing the systems characteristics from that of a liquid to that of a gel. The result is a bi-continuous system composed of the continuous, interpenetrating solid and liquid phases. The overall sol-gel process, as the name implies, usually involves two stages: precursors initially form high molecular weight but still soluble oligomeric intermediates, a sol, and the intermediates further link together to form a three-dimensional cross linked network, a gel. The precursors for a sol-gel reaction could be either inorganic salts or organic compounds, such as metal alkoxides.

In general, sol-gel process involves a transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. The starting materials used in the preparation of the "sol" are usually inorganic metal salts or metal organic compounds such as metal alkoxides. The first metal alkoxide was prepared from SiCl₄ and alcohol by Ebelmen in 1844, who found that the compound gelled on exposure to ambient environment. In a typical sol-gel process, the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension, or a "sol". When the
"sol" is cast into a mold, a wet "gel" will form. With further drying and heat-treatment, the "gel" is converted into dense ceramic or glass particles[42-43]. The whole process is illustrated in Figure 3.1.

3.1.3.2 Sol-Gel Reactions

The synthesis of silica gel is easily carried out through either an acid or base catalyzed reaction. The precursors for a sol-gel reaction could be either inorganic salts or organic compounds, known as metal alkoxides. Compared with inorganic salts, reactions of alkoxide precursors have easily controlled reaction kinetics and generate byproducts of alcohols and water, which can be readily removed during the drying process.
Chapter 3

The sol-gel process consists of three basic steps: 1) gelation; 2) ageing; and 3) drying. During gelation, the synthesis of silica polymers occurs through the simultaneous hydrolysis and condensation reactions represented in Figure 3.2 & 3.3.

\[
\text{SiOR} + \text{H}_2\text{O} \rightleftharpoons \text{SiOH} + \text{ROH}
\]

Hydrolysis

\[
\text{SiOR} + \text{HO-Si} \rightleftharpoons \text{Si-O-Si} + \text{ROH}
\]

Condensation

Fig 3.2 Hydrolysis and Condensation reactions during the sol-gel process

![Fig.3.3 Silica gel network formation by (a) acid and (b) base catalyzed hydrolysis and condensation.](image)

3.1.3.3 Effect of catalysts

The fact that the hydrolysis and condensation of alkoxy silicates can be accelerated by using both acids and bases allows for a variety of catalysts to be used in this process. Both hydrolysis and condensation depend greatly on the pH value of the reacting mixture.
Condensation between the precursors results in the formation of a 3-dimensional network, or gel, which grows to encapsulate the solvent phase. It is the relative rates of hydrolysis and condensation that determines the properties of the silica gel formed. Acidic conditions favor hydrolysis leading to the growth of silica filaments, while basic conditions favor condensation and yields colloidal silica. Gelation can be accomplished by a one-step process which involves the use of a single base or acid as catalyst. In addition, a two-step process can also be used by initiating hydrolysis with an acid catalyst and following this with base-catalyzed condensation. A number of factors, including the precursor, temperature, pH, catalyst, and water content, can be manipulated to effect a variation in the reaction rates.

Tetraethoxysilane (TEOS), the most widely used alkoxide precursor, is used as an example below to illustrate the sol-gel process.

In the first step, TEOS is hydrolyzed by mixing with water:

\[
\begin{align*}
\text{C}_2\text{H}_5\text{O} - \text{Si} - \text{OC}_2\text{H}_5 & + 4\text{H}_2\text{O} \rightarrow \text{HO} - \text{Si} - \text{OH} + 4\text{C}_2\text{H}_5\text{OH} \\
\text{OC}_2\text{H}_5 & \text{OC}_2\text{H}_5
\end{align*}
\]

In this reaction, either an acid or a base can serve as catalyst.

The silanols, i.e., hydrolyzed TEOS undergoes further condensation reaction forming siloxane bonds, that is the second step of the sol-gel process:
\[ \text{Si-OH} + \text{HO-Si} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O} \]

or

\[ \text{Si-OR} + \text{HO-Si} \rightarrow \text{Si-O-Si} + \text{ROH} \]

(a)
Linkage of additional Si(OH)$_4$ tetrahedra occurs as a polycondensation reaction and eventually results in a three dimensional SiO$_2$ network. The water and alcohol byproduct molecules generated from the reactions remain in the pores of the silica’s three dimensional networks. They can also, as most often done, be removed during the reaction.

The hydrolysis and polycondensation reactions happen at numerous sites within the TEOS and water mixture upon mixing. When sufficient interconnected Si-O-Si bonds are formed in region they respond cooperatively as colloidal particles, e. g. a sol. The size of the sol particles and the cross linking within the particles depend upon the pH and [H$_2$O]/Si(OR)$_4$ ratio in the solution.
Since sol is a relatively low-viscosity liquid, it can be cast into any shape according to its applications. With time, the colloidal particles and condensed silica species link together to become a three-dimensional network. The physical characteristics of the gel network depend greatly on the size of particles and extent of crosslinking prior to gelation. At the gelation step, the viscosity increases sharply and the system loses its fluidity to form a solid-like object resulting in the general shape of the mold.

The ultrastructure and texture of a gel are established at the time of gelation. After gelation, the next phase in sol-gel fabrication is the ageing process. Although the gel formed in the initial phase entraps the entire solvent volume, the hydrolysis and condensation reactions continue to occur within the gel (Scherer 1988). During this phase, some gel shrinkage is seen along with a corresponding expulsion of solvent. Gels of desired densities can be obtained by simply varying the ageing time (Kistler 1937). Typically, an application for silica gel requires the removal of the solvent phase and this is the final stage of the sol-gel process – the drying step. Drying conditions can have a significant effect on the final gel properties. In drying, as the liquid is removed from the gel, a liquid-vapor interface is developed within the gel and this creates significant capillary pressures as described by the La Place equation:

\[
\Delta p = \frac{2\gamma (\cos \theta)}{r}
\]

where \(\Delta p\) is the capillary pressure difference, \(\gamma\) is the specific surface energy of the liquid-vapor interface, \(\theta\) is the contact angle, and \(r\) is the pore radius. With a pore radius on the nanometer scale, the large stresses generated can result in permanent shrinkage of the gels.
3.1.4 Precipitated silica

Precipitated silicas are pure amorphous silicon dioxide which is ecologically harmless and inert in chemical sense. It is amorphous in nature. The method for obtaining amorphous types of silica could find numerous applications, particularly as polymer fillers. Precipitated silicas are used in elastomers processing with increasing frequency, superceding black fillers in many technologies [44-48]. Shape and size of particles and morphology of silica surface are important variables. An ideal filler should be very well dispersed and its particles should be of spherical shape. It should also feature a very well developed outer surface and contain few, if any, pores [49-51].

Properties of the applied silicas are listed in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Silica industrial by-product</th>
<th>Precipitated silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ %</td>
<td>83.5</td>
<td>89.0</td>
</tr>
<tr>
<td>Water loss, %</td>
<td>2.2</td>
<td>4.8</td>
</tr>
<tr>
<td>pH of water suspension</td>
<td>6.2</td>
<td>6.5</td>
</tr>
<tr>
<td>Specific weight</td>
<td>2.01</td>
<td>2.12</td>
</tr>
<tr>
<td>Particle size, nm</td>
<td>120</td>
<td>25</td>
</tr>
<tr>
<td>Bulk density, g/dm$^3$</td>
<td>290</td>
<td>75</td>
</tr>
<tr>
<td>Packing density, g/dm$^3$</td>
<td>440</td>
<td>210</td>
</tr>
<tr>
<td>Water absorption, g/100g</td>
<td>320</td>
<td>650</td>
</tr>
<tr>
<td>Dibutyl phthalate absorption, g/100g</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

3.1.4.1 Manufacture

Precipitated silicas are produced by chemical reactions and precipitation, which is achieved by neutralizing a solution of sodium silicate with an acid, often sulfuric acid. The by-product, sodium sulfate, is
eliminated via filtration. The remaining silica is then dried and formed based on its final application. The precipitation stage determined the microscopic particle morphology for most of the silica's application properties. Key precipitated silica manufacturing process stages include precipitation, filtration, drying and milling.

During the precipitation stage, product properties may be varied through changes in composition and ratio of reactants, reaction time, temperature and concentration. The important characteristics that result from the precipitation process include physical properties such as structure (oil absorption and compressibility), and chemical properties such as pH, silanol group density and optical properties.

During filtration, drying and milling, salts formed during the precipitation stage are washed out, and depending on the product, the solids content of the filter cake can range from 15-30 percent. As a result, drying is a major cost component in manufacturing precipitated silica.

Fig.3.5 Typical flow diagram for the manufacture of silica from sodium silicate.
3.2 Experimental

Precipitation was chosen for the study for the following reason.

a) It involves the use of commonly available sodium silicate and mineral acids.

b) It is possible to produce nanosized silica particles by proper modification and control of conditions.

c) It does not require very long gelation and drying time as required for sol-gel process.

d) Limited choice of solvents that can prevent phase separation during reaction with the organosilanes.

e) The catalyst used in the sol-gel process may remain as impurities.

f) Silica synthesized by the sol-gel process was observed to contain many lattice defects.

g) The impurities would be easily removed by washing with distilled water.

The method adopted in this study is based on the work of Kotoky and Dolui on the PVA/Silica nanocomposite. In the mentioned work, PVA material was used to synthesize nanosilica, which remains in the material to form PVA/Silica composite with sodium silicate and HCl as the starting material. Since in the present work, the required product is nanosilica and not the PVA/Silica nanocomposite, the amount of PVA is reduced to a lower mole ratio. As alkaline medium supports the precipitation reaction and also ammonia reacts with sodium silicate to produce silica, a slightly alkaline medium can be maintained by adding ammonia.
The reaction medium was stirred continuously for a period of 2 hours and the temperature was maintained at 60°C. This serves two purposes.

a. It enables uniform PVA distribution in the reaction solution, so that it could act as a matrix to collect the formed particles. In the absence of heating PVA agglomerates out in the reaction medium.

b. It also enables the conversion of silicic acid formed by the reaction between HCl and Sodium silicate into silica.

The reactions are given below.

\[
\begin{align*}
\text{Na}_2\text{SiO}_3 + 2 \text{HCl} & \rightarrow \text{SiO}_3 + 2\text{NaCl} \\
\text{H}_2\text{SiO}_3 & \rightarrow \text{SiO}_2 + \text{H}_2\text{O} \\
\text{NH}_3 + \text{HCl} & \rightarrow \text{NH}_4\text{Cl} \\
\text{Na}_2\text{SiO}_3 + 2 \text{NH}_4\text{Cl} + 2\text{H}_2\text{O} & \rightarrow \text{H}_2\text{SiO}_3 + 2\text{NaCl} + 2\text{NH}_4\text{OH}
\end{align*}
\]

The acid plays a catalytic role in enhancing the co-condensation of silicon oxides within the PVA matrix. Acid provides extensive Hydrogen bonding to both the polymer and the developing polysilicate network enabling system homogeneity.

It is expected that the addition of PVA would produce a matrix into which synthesized silica would be incorporated, thus producing silica in the nano scale. The interaction between the hydroxyl groups of PVA and the hydroxyl groups of silanol from hydrolyzed silica would result in co-condensation.

The synthesized silica after complete drying is proposed to be calcined to remove the PVA matrix and hence obtaining purer silica. Since the end use
of the synthesized silica is to produce nanocomposite with polymer, no effort is proposed to be made to remove PVA. The presence of organic molecule (PVA) eliminates the need for the usage of coupling agent during nanocomposite preparation.

3.2.1 Preparation of Chemicals

Sodium silicate solution of two different concentrations, 15% and 30% were prepared for the study.

Hydrochloric acid of strength 3.5N was used.

AR grade ammonia was used as such without any dilution.

Poly Vinyl Alcohol of 1%, 5% were used in the experiments.

The optimized reaction conditions include the concentration of sodium silicate as 15%, HCl of 3.5N and 1% PVA solution.

3.2.2 Procedure

The reaction was initially conducted on a laboratory scale with a reactor with a reactor volume of 500cm$^3$ for studying the kinetics and later developed into a large scale, based on a total volume of 8 litres to get a more uniform product that can be used for polymer modification.

The required quantities of sodium silicate, HCl, PVA and ammonia in the mole ratio 1:1.96:0.000286: 0.00615 was prepared.

A homogeneous mixture of 3.5N HCl, 1% PVA and ammonia in the desired ratio was made initially and it is then added to Sodium silicate solution (15%) with constant stirring and a constant heat supply of 60°C. During the addition of chemicals, there was instant solidification at one point
and stirring becomes difficult. So distilled water was added to keep the reaction mixture in a 40% slurry form. The reaction mixture was stirred continuously for 2 hours. After the stirring, heat supply was cut off and the reaction mixture was kept at room temperature and the reaction was allowed to continue. After the completion of reaction time, the resultant slurry was kept at room temperature for 24 hrs. It was then filtered, washed, dried at a temperature of 100°C for 5 hrs and then milled to produce fine particles.

3.2.3 Experimental set up

The experimental set up consists of the following parts.

a) Reactor
b) Stirring and heating arrangement
c) Filtration assembly
d) Drying assembly

Reactor

The experiments were carried out initially on a laboratory scale and then to a large scale. In a small scale a 250 ml borosil beaker was used as reactor but in a large scale a stainless steel cylindrical vessel with a volume of 20 litres is being used.

Stirring cum heating arrangement

For experiments on a large scale, a motor driven stirrer with two sets of blades was used to provide necessary agitation of the slurry. The reactor was kept in a constant temperature bath which was set for 60°C. The speed of the stirrer can be varied from 0-100 rpm. The speed of the stirrer was varied from 30 rpm to 60 rpm based on the concentration of the slurry and the optimum was found to be 40 rpm.
Vacuum filtration was done using a leaf filter. The filtration assembly consists of the following parts.

a) The cylindrical vessel containing the slurry
b) Stirrer
c) Leaf filter covered with filter cloth
d) Graduated jar
e) Tubing
f) Stop cocks 1 & 2
g) Mercury manometer
h) Vacuum pump
The vessel containing the slurry is kept as a suspension using a stirrer. Keeping stop cock 1 (which is nearer to the leaf) vacuum is made to develop inside the jar using a vacuum pump and it is measured using a manometer. Vacuum is kept at a particular value, i.e. about 30 cm Hg using stop cock 2.

Now stop cock 1 is opened. Now vacuum will enter the filter. Due to the pressure difference filtrate will be sucked into the graduated jar. The cake will be deposited on the surface of the leaf. It is lifted up when it is full and the cake is dislodged and dipped into the slurry again. This is repeated till almost all the silica particles in the slurry have been removed. A small portion of the wet cake deposited is taken, dried and weighed.

**Drying assembly**

Hot air oven with a temperature setting adjustable to 300°C was used. The oven maintains the set point by turning on and off the hot air circulation
through the drying chamber. The oven was given the required temperature set point and it was ensured that the temperature was achieved by means of the indicator. The cake obtained after filtration was scrapped out and spread out evenly on a glass plate using a glass rod. Glass plate was then placed in the middle tray of the oven and dried for the required time.

Filtration was done using a leaf filter and the cakes obtained were washed with distilled water several times and then dried in an oven at a temperature of 120°C for 5 hours. Dried cakes are then ground to obtain fine powder of silica.

3.2.4 Surface modification of silica

Explanation of the reinforcing action of fillers in polymers would require consideration of several factors which affect polymer properties, including chemical character of a polymer and a filler, type of filler, polymer-filler phase relation, polymer adhesion to filler’s surface, conditions of polymer formation in the presence of a filler and other. The surface modification should be considered in order to improve chemical affinity of the silica to elastomer. Several modifying compounds and on various ways of inducing filler surface modification are reported [52-56].

Silane coupling agents are a very attractive group of compounds capable of promoting reciprocal action of silica fillers and elastomers [56-59].

Activity of silica fillers reflects to a significant extent the chemical character of their surface. The latter may be altered using various reactions which lead to chemical bonds between functional groups, a modifying substance and a filler. With this aim, coupling agents of silane [60-62], borate [63] or titanate [64-65] are used. The application of silane coupling agents is principally aimed at decreasing the hydrophilic character of silicas and at
introducing onto the surface of silica, particles of new functional organic groups capable of reacting with the polymer.

![Nucleation Growth Aggregation Agglomeration](image)

**Fig. 3.8** Stages of colloidal growth of precipitated silica.

Figure 1 shows schematically the processes that are believed to be active during synthesis along with the structural features resulting from complex growth processes active during synthesis. We can control both the structure of the aggregate/agglomerate and to optimize the structure for effective reinforcement by interfacial modification during the synthesis.

### 3.2.5 Modification Procedure

The procedure for the surface modification of silica particles are outlined in figure 2. The basic steps involved are hydrolysis and condensation of organoalkoxysilanes. This was done by the addition of HNO₃ and NH₄OH as catalysts. The silica particles (0.1g/ml) with agitation and sonication were dispersed homogeneously in an aqueous solution with agitation and sonication. A dilute solution of HNO₃ was added to the dispersion. In the acidic condition an organoalkoxysilane (0.2M) was added to the silica dispersion and the mixture was stirred at 60°C for 3 minutes for the hydrolysis. Then in the basic condition resulting from the addition of NH₄OH solution the mixture was stirred continuously at 60°C for 1 hour for the
condensation. The surface modified particles thus obtained were filtered, washed with distilled water. The particles were then dried overnight in a drying oven at 120°C.

The modified particles were then characterized by various techniques such as TEM, SEM, FTIR, TGA etc.

![Flow chart for the surface modification of silica particles.](image)

3.2.6 Characterization

The characterization of synthesized silica particles were done using various techniques which are described below.

3.2.6.1 Bulk density

Determination of bulk density of the material was done as per ASTM-D-1895. Two important terms used are apparent density and bulk density.
Apparent density is the weight per unit volume of a material including voids inherent in the material. Bulk density is defined as the weight per unit volume of a material. It is primarily used for pellets. The test can provide a gross measure of particle size and dispersion, which can effect material flow consistency and reflect packaging quantity.

**Apparent density**

Measuring cup, a cylindrical cup of 100±0.5 ml capacity having a diameter equal to half of the height. For e.g. 39.9 mm inside diameter by 79.8 mm inside height.

Funnel, having a 9.5 mm diameter opening at the bottom and mounted at a height 38 mm above the measuring cup.

Apparent density value is recorded as g/cm³.

Specimen: Powder or Pellets

Procedure

Close the small end of the funnel with hand or a suitable flat strip and pour 115± 5 cm³ samples into the funnel. Open the bottom of the funnel quickly and allow the material to flow freely into the cup. If caking occurs in the funnel, the material may be loosened with a glass rod. After the material has passed through the funnel immediately scrap off the excess on the top of the cup with a straight edge without shaking the cup. Weigh the material cup to the nearest 0.1g. Calculate the weight in grams of 1 cm³ of the material.

3.2.6.2 Energy dispersive X-ray spectrometer

The chemical stochiometry of silica nanoparticles is investigated with EDX, (EDS,HITACHI, S-2400).
3.2.6.3 Surface area

Surface area of the silica nanoparticles were measured using BET method. Surface area analysis was done using Micromeritics BJH surface analyzer. Model 060 Gemini 2360 instrument (liquid N\textsubscript{2}, 77K). Measurements were carried out at liquid nitrogen atmosphere.

Surface area is determined by the equation,

\[ S_{\text{BET}} = 4.353 \, V_m \]

Where \( S_{\text{BET}} \) is the surface area in \( m^2/g \) and \( V_m \) is the moalr volume of adsorbate gas (N\textsubscript{2}) at STP.

3.2.6.4 X-Ray diffraction (XRD)

Particle size of the sample was determined using X-Ray diffraction (XRD) technique. XRD patterns were collected using Bruker, AXS D8 advance diffractometer at the wavelength CuK\( \alpha = 1.54\, \text{\AA} \), a tube voltage of 40 KV and the tube current of 25 mA.

Crystallite size is calculated using Scherrer equation,

\[ L_{hkl} = \frac{k\lambda}{\beta \cos \theta} \]

Where \( L_{hkl} \) is the crystallite size perpendicular to the direction of the (hkl) crystal plane,

\( \beta \) - half width of the diffraction peak

\( k \) - constant factor of the crystal shape = 0.9

\( \lambda \) - wavelength of the incident X-ray

\( \theta \) - half of the Bragg angle (degree)
3.2.6.5 *Fourier transform infrared spectroscopy*

The shape of a spectrum can be qualitatively interpreted into the compound responsible for the spectrum. Ultraviolet and visible spectra of solutions contain generally featureless information for identifying the compound, but infrared spectra show a great deal of peak characteristics of the compound, which allows the identification by matching known spectra of the compound.

Fourier transform infrared spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm\(^{-1}\) by organic molecules. Different functional groups and structural features in the molecule absorb at characteristic frequencies. The frequency and intensity of absorption are the indication of the band structures and structural geometry in the molecule. FTIR absorption spectra were collected using Thermo Avtar 370 spectrometer.

3.2.6.6 *Transmission electron microscopy*

The morphology and particle size of nanosilica were observed using transmission electron microscope (TEM). The TEM images were taken on Philips TEM CM 200 model.

3.2.6.7 *Scanning electron microscopy*

Scanning electron microscope (Cambridge Instruments, S 360 Stereo scanner-version V02-01, England) was used to investigate the morphology of the nanosilica sample.

3.2.6.8 *Thermogravimetric analysis*

Thermo gravimetric analyzer (TGA, Q-50, TA Instruments) was used to study the thermal stability of nanosilica. Approximately 5 mg of the samples were heated at a rate of 20° C/min to 800°C. The chamber was continuously swept with nitrogen gas at the rate of 60ml/min.
3.2.7 Kinetic studies on synthesis of nanosilica from sodium silicate

Chemical kinetics and reactor design are at the heart of producing almost all industrial chemicals. The selection of a reaction system that operates in the safest and most efficient manner can be considered economically feasible. So a study on the chemical kinetic principles associated in the synthesis of silica will lead to the design of a better process that can meet our requirements on a large scale.

Chemical kinetics is concerned with the rate at which the chemical reactions take place, the mechanism and rate-limiting steps that can the reaction process[66]. In order to design a process it is important to have knowledge of the chemical and physical behaviour of the fluids within the reactor.

As a first step towards design, it is necessary to account for the various chemical species entering and leaving a reaction system. This is achieved through overall material balance on individual species in the reacting system. Then the design equations for common industrial reactors are developed.

3.2.7.1 Classification of reactions and definition of reaction rate

There are many ways of classifying chemical reactions. The wide classification is based on the number and types of phases involved. That is, they are classified into two types.

i) Homogeneous and  ii) Heterogeneous

A reaction is homogeneous if it take place in one phase alone. Eg : most gas phase reactions, most liquid phase reactions which are non-catalytic or catalytic in nature.
A heterogeneous reaction is one which requires the presence of at least two phases to proceed, at that rate.

**Reaction rate**

There are several ways of expressing a reaction rate. For this we must select one reaction component and define the rate in terms of this component $i$.

If the rate of change in the number of moles of this component due to reaction is $dN_i/dt$, then based on unit volume of reacting fluid,

$$ r_i = \frac{1}{V} \left( \frac{dN_i}{dt} \right) = \text{moles } i \text{ formed/(volume of fluid)(time)} $$

There are many variables that may affect the rate of a chemical reaction. In homogeneous system the temperature, pressure and composition are important variables. But in heterogeneous reactions due to the more number of phases involved we must consider the heat and mass transfer effects also.

The rate equation

Consider the single phase reaction,

$$ AA + bB \rightarrow rR + sS $$

The most useful measure of the reaction rate for reactant $A$ is then

$$ -r_A = \frac{1}{V} \left( \frac{dN_A}{dt} \right) = \text{(amount of } A \text{ disappearing)/(volume)(time)}, [\text{mol/m}^3 \cdot \text{s}] $$

where $-r_A$ is the rate of disappearance of $A$.

The rates of reactions of all materials are related by

$$ -r_A/a = -r_B/b = r_R/r = r_S/s $$

The rate of reaction is influenced by composition and the energy or temperature of the material.
Thus $-r_A = f[(\text{temp. dependent terms}) \cdot (\text{Concn. dependent terms})]$.

Example, $-r_A = kC_A^a$

$$= k_0 e^{-E/RT} \cdot C_A^a$$

where $k = k_0 e^{-E/RT}$ and $E$ is the activation energy.

**Simple reactor types**

The various types of ideal reactors used for homogeneous and for isothermal and non-isothermal operations are,

a) Batch Reactor (BR)

b) Plug Flow Reactor (PFR)

c) Mixed Flow Reactor (MFR)

**Batch reactor**

In batch reactor, the reactants are initially charged into a container, are well mixed, and are left to react for a certain period. The resultant mixture is then discharged. This is an unsteady state operation where the composition changes with time, however at any instant the composition throughout the reactor is uniform.

**Plug flow reactor**

In plug flow reactor the pattern of flow is considered as plug flow. There is no mixing in the axial direction inside the reactor though there may be lateral mixing of fluid elements. The residence time of all elements of fluid in the reactor is same.
**Mixed flow reactor**

This is another ideal steady state flow reactor. The other names of this reactor are the back mix reactor, continuous stirred tank reactor etc. In this reactor the contents are well stirred and uniform throughout and the exit stream has the same composition as the fluid within the reactor.

**Batch reactor- Performance Equation**

A batch reactor has neither inflow nor outflow of reactants or products while the reaction is being carried out.

A material balance equation written for component A which is taken as the limiting component is given below.

Input = Output + disappearance + accumulation ............................................ (1)

\[ 0 = 0 + \text{rate of loss of reactant A within the reactor due to chemical reaction} + \text{rate of accumulation of reactant A within the reactor} \]

or

\[ (-r_A)_A V \text{ (moles of A reacting), (vol. of fluid)} = -\frac{dN_A}{dt} \text{ moles/time (time)(vol. of fluid)} \]

i.e. \[ (-r_A)V = \frac{d}{dt} \left[ N_{A0}(1-x_A) \right] \]

\[ = N_{A0} \frac{dx_A}{dt} \] .............................................. (2)

Rearranging and integrating gives,

\[ t = N_{A0} \int_{x_A^o}^{x_A^f} \frac{dx_A}{(-r_A)V} \] .............................................. (3)

If the fluid density remains constant, eq.(3) becomes,
Space time and Space velocity

Space time and space velocity are the proper performance measures of flow reactors. Space time (τ) is defined as the time required to process one reactor volume of feed at specified conditions. Space velocity (s) is the number of reactor volumes of feed at specified conditions which can be treated in unit time. Both these terms are related as,

\[ \tau = \frac{1}{s} \]

\( \tau \) has the unit of time.

\( s \) has the unit of \( (\text{time})^{-1} \).

\[ \tau = \frac{1}{s} = \frac{C_{Ao}V}{F_{Ao}} \]

where \( C_{Ao} \) is the initial concentration of A, (moles of A entering)/(volume of feed),

\( V \) is the volume of the reactor, \( (\text{m}^3) \)

\( F_{Ao} \) is the feed rate (moles of A entering/time)

\[ \tau = \frac{V}{V_o} = \frac{\text{reactor volume}}{\text{vol. feed rate}} \]

3.2.7.2 Collection and analysis of reactor data

Batch reactors are used to determine rate law parameters for homogeneous reactions. This is usually done by measuring concentration as a
function of time and then using either differential or integral method of analysis to determine the reaction order ‘n’ and specific reaction rate , k.

**Differential method of Rate analysis**

For irreversible reactions of the type involved in the synthesis of silica, it is possible to determine the reaction order ‘n’ and specific rate constant ‘k’ by differential method. This method is applicable when the reaction conditions are such that the rate is essentially a function of the concentration of only one reactant.

For the irreversible reaction

\[ A + B \rightarrow \text{products} \]

With the rate law

\[ -r_A = k \ C_A^a C_B^b \]

where a and b are both unknown, then reaction could be first run in excess of B so that \( C_B \) remains constant during the course of reaction and

\[ -r_A = k' \ C_A^a \] where \( k' = k C_B^b \)

In the same manner b is also found out.

Now consider the reaction involved in the synthesis of silica. In the reaction between sodium silicate and hydrochloric acid it is assumed that the reaction rate is proportional to the concentration of HCl and all the calculations are based on the amount of HCl converted during synthesis.

The reaction is carried out isothermally in a constant volume batch reactor and the concentration recorded as a function of time.
Then, \((-r_A) = (-dC_A/dt) = kC_A^n\)...................................................... (6)

Taking logarithm of both sides of equation (6),

\[\ln (-dC_A/dt) = \ln k + n \ln C_A\].......................................................... (7)

Now plot \(\ln (-dC_A/dt)\) as a function of \(C_A\) and determine the slope which will be the order of the reaction. See the fig.3.10 (a)&(b) given below.

![Fig.3.10(a)&(b) Determination of rate constant and reaction order by differential method.](image)

The specific reaction rate can be found by first choosing a concentration in the plot, say \(C_A\) and then finding the corresponding value of \((-dC_A/dt)\). After raising \(C_A\) to the \(n^{th}\) power, divide \((-dC_A/dt)\) to determine \(k\).

\[k = \frac{-dC_A}{dt \cdot C_A^n}\]

The values of \((-dC_A/dt)\) can be found either graphically or by numerical methods. In graphical method, plot \(C_A\) vs time. Draw tangents at various points and find the slopes. This gives the values of \((-dC_A/dt)\).
**Integral method**

To determine the reaction order by this method, guess the reaction order and integrate the differential equation used to model the batch system. If the order we assume is correct the appropriate plot of concentration-time data should be linear. The integral method is used most often to evaluate the specific reaction rate constants at different temperatures and to determine the activation energy.

In the integral method, the rate data should be a function of concentration corresponding to a particular rate law that is linear with time.

For a second order reaction,

\[
-\frac{dC_A}{dt} = kC_A^2
\]  

(8)

Rearranging and integrating eq.(8),

\[
\int_{C_{A_0}}^{C_A} \frac{-dC_A}{C_A^2} = k \int_0^t dt
\]

\[
\frac{1}{C_A} - \frac{1}{C_{A_0}} = kt
\]

In this case a plot of \(\frac{1}{C_A} - \frac{1}{C_{A_0}}\) vs \(t\) yield a straight line with slope \(k\).

The unit of \(k\) for nth order reactions is \((\text{time})^{-1}(\text{concentration})^{1-n}\).

### 3.2.7.3 Estimation Methods

The amount of HCl reacted was estimated by titration method using NaOH solution and phenolphthalein indicator. Known volumes of sample collected from the reactor were titrated against 0.035N NaOH solution. The end point is pink colour. This procedure was continued till the concentration of HCl that remain unconverted in the reaction mixture was almost constant.
3.3 Results and discussion

3.3.1 Characterization

3.3.1.1 Bulk density

The primary identification of the material was done by determining the bulk density of the material. The samples prepared in the lab are characterized by determining the bulk densities and it is given in the table.

Table 3.2 Densities of silica samples.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Bulk density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial silica</td>
<td>1.03</td>
</tr>
<tr>
<td>Sample 1</td>
<td>1.39</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

3.3.1.2 Energy dispersive X-Ray spectrometer

The nanosilica prepared was found to have less amount of impurities. The EDX spectrum of samples 1 & 2 are given in the figures 3.9 & 3.10. The percentage of Si in the nanosilica samples prepared in the laboratory are listed in table 3.2. A similar spectrum is obtained for commercial silica.

Fig.3.9 EDX spectrum of nanosilica sample 1.
3.3.1.3 Surface area

Representative samples were selected from those prepared with and without modification for surface area determination. Table 3.4 shows surface area for commercial nanosilica, Sample 1 and Sample 2.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Atomic %</th>
<th>Element %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>96.86</td>
<td>97.03</td>
</tr>
<tr>
<td>Sample 2</td>
<td>98.54</td>
<td>99.01</td>
</tr>
<tr>
<td>Commercial silica</td>
<td>98.12</td>
<td>98.8</td>
</tr>
</tbody>
</table>

Table 3.4 Surface areas of silica samples.

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Samples</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Commercial silica</td>
<td>175</td>
</tr>
<tr>
<td>2</td>
<td>Sample 1</td>
<td>180</td>
</tr>
<tr>
<td>3</td>
<td>Sample 2</td>
<td>278</td>
</tr>
</tbody>
</table>

It is clear that surface area of silica prepared in the lab is more than commercial silica. Also the surface modified particles have greater surface than the other samples.
3.3.1.4 XRD Studies

The XRD patterns of silica samples are given in figures 3.11(a) & (b). Since silica is amorphous there is no sharp peaks observed. From the one which is seen at an angle of 22° the crystallite size was determined as 24 nm.

---

**Fig. 3.11(a).** XRD patterns of commercial silica.

**Fig. 3.11(b).** XRD patterns of sample 1.
3.3.1.5 IR spectroscopy

The IR spectrum of different samples of silica are shown in the fig.3.12(a),(b)&(c).

![IR spectrum of different samples of silica](image)

Fig.3.12 IR spectrum of (a) Commercial Silica (b) modified silica
The IR spectra give only qualitative (and not quantitative) information about a sample. By comparison of the corresponding peaks, it can be concluded that all samples consist predominantly of silicon oxide. The IR spectrum of commercial and unmodified silica showed a characteristic peak around 1085 cm\(^{-1}\) which is due to the Si-O bond. There are no peaks in the region of 1500 – 3000 cm\(^{-1}\). However, the second sample shows two small peaks in the vicinity of 3000\(^{0}\)A. This means that organo groups have been attached to silica as a result of modification.

3.3.1.6 Scanning electron microscopy

Scanning electron microscopy (SEM) allows the visualization of materials at very high magnifications. Depending on the instrument and materials properties, it is capable of providing resolutions down to the nanometer scale.

The surface morphology as determined by scanning electron microscopy reveals that the method of preparation has a significant effect on the structure and shape of the particles. It is clear from the figure that the silica particles prepared have spherical shape. The effect of modification is also evident from the SEM pictures. The commercial silica particles is found to be present in the form of agglomerates when compared to modified silica particles which is identical to that of unmodified silica.
3.3.1.7 Transmission electron microscopy

The TEM image of the different silica samples is given in figure 3.15. The size of the particles was determined from the scale bar given in the picture. The average size of the particles was calculated and found to be equal to 15 nm. The corresponding diffraction pattern is also shown in fig.3.16 and it is identical to that of amorphous particles.
3.3.1.8 Thermogravimetric analysis

Thermogravimetric analysis of the synthesized silica and commercial silica nanoparticles was done to check the thermal stability. The changes occurring during the heat treatment are given the fig.3.17. TGA shows that there was no peaks which may be due to the perfect drying of the samples prior to Thermal analysis. The nanosilica sample 2 shows very good thermal stability even at higher temperatures.
3.3.2 Determination of kinetic parameters

In the reaction between sodium silicate and HCl the rate of reaction depends on the amount of HCl converted. Hence to evaluate the rate constant \( k \), the concentration of HCl in the reaction medium is determined at definite intervals.

The information necessary for finding out the performance of the reactor used for silica synthesis are the rate constant and order of the reaction [67-69]. Based on this data the process can be scaled up to industrial level which can offer great potential for using silica for polymer modification.

The rate constant for the reaction of sodium silicate with HCl is determined based on the observation that the acid plays a significant role in the formation of silica particles. The concentration of HCl is used as a measure to find the reaction order and rate constant. The rate constant for the
reaction is found out by estimating amount of HCl converted with time. The concentrations of sodium and ammonia are assumed to be constant during the course of reaction. The reaction rate is written to be of the form,

\[-r_A = kC_A^n\]  \hspace{2cm} (9)

where \(-r_A\) = rate of disappearance of HCl with time = \(-dC_A/dt\)

\(C_A\) is the concentration of HCl, mol/litre

\(k\) = rate constant for the reaction, litre/mol.min

\(n\) = order of the reaction.

Taking logarithm on both sides of equation (1),

\[\ln(-r_A) = \ln k + n \ln C_A\]  \hspace{2cm} (10)

A plot of \(\ln(-r_A)\) vs \(\ln C_A\) is made. The slope and intercept of the straight line obtained is determined. From these, the values of rate constant ‘k’ and reaction order ‘n’ are found out. The \((-dC_A/dt)\) values are obtained either numerically or by graphical method [70-71]. In the graphical method \(C_A\) vs time is plotted [72]. The slopes of the tangents drawn at various points in curve are taken as \(-dC_A/dt\).

The plot of concentration vs time is shown in fig. 3.18. From this graph \(-dC_A/dt\) is calculated and are listed in Table3.4
Fig.3.18 plot of concentration vs time

Table 3.4 Concentration-time data

<table>
<thead>
<tr>
<th>Time, minutes</th>
<th>$C_A , \text{mol/litre.min}$</th>
<th>$(dC_A/dt)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.591</td>
<td>0.24</td>
</tr>
<tr>
<td>15</td>
<td>1.401</td>
<td>0.042</td>
</tr>
<tr>
<td>30</td>
<td>1.033</td>
<td>0.013</td>
</tr>
<tr>
<td>45</td>
<td>0.875</td>
<td>0.009</td>
</tr>
<tr>
<td>60</td>
<td>0.75</td>
<td>0.006</td>
</tr>
<tr>
<td>75</td>
<td>0.645</td>
<td>0.004</td>
</tr>
<tr>
<td>90</td>
<td>0.578</td>
<td>0.003</td>
</tr>
<tr>
<td>105</td>
<td>0.526</td>
<td>0.002</td>
</tr>
<tr>
<td>120</td>
<td>0.438</td>
<td>0.001</td>
</tr>
</tbody>
</table>
The plot of $\ln -r_A$ vs $\ln C_A$ is shown in fig.3.19. The plot is a straight line and the slope of this line is equal to 2 which show that the reaction is of second order. Also from the intercept the value of the rate constant is found to be 0.0166 litre/mol.min.

3.3.2.1 Determination of $k$ by Non-linear least squares analysis

This is a useful method to determine the rate law parameters [73-74]. In non-linear least squares analysis we search for those parameter values that minimize the sum of squares of the differences between the measured values and the calculated values for all the data points. Here we make estimates of parameter values such as reaction order and specific rate constants in order to calculate the rate of reaction, $r_c$. Then search for those values that minimize
the sum of the squared differences of the measured reaction rate, \( r_m \), and the calculated reaction rates, \( r_c \). Now select the value if the parameters such that sum of \( (r_m - r_c)^2 \) is minimum. The variance is calculated according to the equation,

\[
\sigma = \frac{S^2}{(N-K)} = \frac{\sum (r_{im} - r_{ic})^2}{N-K}
\]

where \( N \) - is the number of runs

\( K \) - Number of parameters to be determined.

\( r_{im} \) - measured reaction rate for run \( i \)

\( r_{ic} \) - calculated reaction rate for run \( i \)

Now consider the silica synthesis reaction, the rate equation is assumed to be of the form \(-r_A = k C^n_A\) where \( k \) is the reaction rate and \( n \) is the reaction order. For these parameters values were chosen and the rate is calculated as \( r_{ic} \) at each concentration at which an experimental point was taken. Then the sum of the squares of the difference \( (r_{im} - r_{ic}) \) was found out. This procedure is continued by further varying \( k \) and \( n \) until their best values, that is, those values that minimize the sum of squares. The values of \( k \) and \( n \) that minimize the sum of squares were taken as the theoretical values and the data were tabulated in table.3.5. It was then compared with the experimental values and the percentage error is determined. This is shown in fig.3.20.
Table 3.5 Minimizing the sum of the squared differences

<table>
<thead>
<tr>
<th>Data</th>
<th>Trial 1 k = 1, n=1</th>
<th>Trial 2 k = 0.017, n = 3</th>
<th>Trial 3 k = 0.05, n = 3</th>
<th>Trial 4 k = 15, n = 2</th>
<th>Trial 5 k = 0.017, n = 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run</td>
<td>C_A</td>
<td>r_m</td>
<td>(r_m - r_e)^2</td>
<td>r_m - r_e</td>
<td>(r_m - r_e)^2</td>
</tr>
<tr>
<td>1</td>
<td>3.59</td>
<td>0.24</td>
<td>3.35</td>
<td>11.22</td>
<td>2.073</td>
</tr>
<tr>
<td>2</td>
<td>1.40</td>
<td>0.042</td>
<td>1.359</td>
<td>1.85</td>
<td>0.096</td>
</tr>
<tr>
<td>3</td>
<td>1.03</td>
<td>0.013</td>
<td>1.021</td>
<td>1.04</td>
<td>0.042</td>
</tr>
<tr>
<td>4</td>
<td>0.88</td>
<td>0.009</td>
<td>0.866</td>
<td>0.75</td>
<td>0.025</td>
</tr>
<tr>
<td>5</td>
<td>0.75</td>
<td>0.006</td>
<td>0.744</td>
<td>0.55</td>
<td>0.015</td>
</tr>
<tr>
<td>6</td>
<td>0.65</td>
<td>0.004</td>
<td>0.644</td>
<td>0.42</td>
<td>0.025</td>
</tr>
<tr>
<td>7</td>
<td>0.58</td>
<td>0.003</td>
<td>0.575</td>
<td>0.33</td>
<td>6.65 x 10^{-3}</td>
</tr>
<tr>
<td>8</td>
<td>0.53</td>
<td>0.002</td>
<td>0.525</td>
<td>0.28</td>
<td>5.78 x 10^{-4}</td>
</tr>
<tr>
<td>9</td>
<td>0.44</td>
<td>0.001</td>
<td>0.438</td>
<td>0.19</td>
<td>3.7 x 10^{-3}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>16.63</td>
<td>4.299</td>
<td></td>
</tr>
</tbody>
</table>

\[
S_1^2 = 16.63 \\
\sigma_1^2 = \frac{16.63}{2} = 8.315
\]

\[
S_2^2 = 4.299 \\
\sigma_2^2 = \frac{4.299}{2} = 2.15
\]

\[
S_3^2 = 0.17 \\
\sigma_3^2 = \frac{0.17}{2} = 0.085
\]

\[
S_4^2 = 2.61 \times 10^{-3} \\
\sigma_4^2 = \frac{0.00261}{2} = 0.0013
\]

\[
S_5^2 = 0.402 \\
\sigma_5^2 = \frac{0.402}{2} = 0.201
\]

Trial No: 4 gives the lowest value for \( \sigma^2 \). Hence it is chosen.

\[\therefore\text{Theoretical value of rate constant } k \text{ is takes as } = 0.017 \text{ litre/mole.min}\]
From the figure, the percentage error was determined from the extent of deviation of the line with the 45° diagonal, where the rates have equal values. The deviation is calculated as 6.25% which is satisfactory as it is less than 10%.

### 3.3.3 Scale up and reactor modeling

After optimizing the parameters for the synthesis of silica, the next step was to produce it in a large scale for polymer modification. Scale up of laboratory experiments to pilot plant or full scale production is usually done based on laboratory data. To make this successful, a thorough understanding of the chemical kinetics is required. In this work, after determining the specific reaction rate, $k$, from a batch experiment we used it in the design of a full-scale reactor.
3.3.3.1 Characteristic behaviour of reactors

The design equation developed for three basic types of reactors are based on the assumption that the reaction mixture behaviour according to the ideal flow patterns characteristic of such reactors.

Although practical reactors can not completely fulfill these assumptions, many cases may be approximated by ideal react oral models without any serious error being introduced. On the other hand, there are a number of cases in which deviation from ideal reactor becomes so significance that an excessively large error good result if the design were based entirely on ideal models. Such deviations can some times be taken care of by introducing correction factors in to the ideal reactor models, but purely empirical methods of scale up and design are also frequently employed.

In addition to the non-ideal behaviour, those reactors characteristic that govern the degree of conversion and the product composition should also be considered. They include reactor type and size, reaction temperature and pressure.

3.3.3.2 Non-ideal flow

Deviation from ideality assumed in developing the basic reactor design equations are presenting practical reactors and the extent of non-ideality often varies considerably, depending on the scale and type of reactor. Important types of deviation from two ideal flow reactors are

Deviation from plug-flow reactor
a) Channeling of the reacting fluid through the catalyst packing and the presence of stagnant fluid pockets.

b) The presence of velocity and temperature gradients in the radial direction, and

c) The presence of stagnant fluid pockets.

Deviation from back-mix reactor

a) Short-circuiting and bypassing of the reacting fluid. That is certain portions of the fluid may proceed directly from the feed inlet to the product discharge port without mixing with the contents of the reactor.

b) Internal recycling of the fluid.

c) The presence of stagnant fluid pockets.

3.3.3.3 Characterization of non-ideal flow

Deviations from ideality imply that the different portions of reacting fluid follow separate flow patterns through the reaction vessels, resulting in a wide distribution of residence times. Such deviations from ideality represent inefficiency in the reactor performance and cause reduction in the production capacity. To alleviate this condition, there are various methods used to characterize the magnitude of deviation - the so-called stimulus-response techniques that utilize a tracer.

Three typical techniques of introducing a tracer into the reaction vessel are the step input, the pulse input and the cyclic input. The information thus obtained is applicable to the determination of conversion in a reactor, either
directly or in combination with one of the several mathematical models proposed to account for non-ideal flow condition.

3.3.3.4 Residence time distribution (RTD)

Information obtainable from the stimulus techniques by using a tracer is the distribution of residence times for various elements of reacting fluid.

RTD of a reactor is a characteristic of mixing that occurs in a chemical reactor. The RTD exhibited by a given reactor yields distinctive clues to the type of mixing occurring within it and is one of the most informative characterizations of the reactor.

The distribution of times for the stream of fluid leaving the vessel is called the residence time distribution, RTD or exit age distribution \( E \) of the fluid. \( E \) has the unit of time\(^{-1}\).

It is convenient to represent the RTD in such a way that the area under the curve is unity or

\[
\int_0^\infty E \, dt = 1
\]

*Tracer response curves*

Two types of response curves are obtained from the tracer experiment. In both curves, a dimensionless tracer signal (or concentration) \( C/C_0 \) is plotted against dimensionless time \( \tau \). \( C_0 \) is the input concentration, whereas \( C \) is the tracer concentration measured at the exit. The response curve to a step input is termed an F-curve. The second type, called a C-curve is the response to a pulse tracer injection.
The method of obtaining the RTD from the tracer experiments is shown in the following relation

\[ E = C = \left( \frac{C}{C_0} \right) \text{ step input} \]

\[ E = \frac{dF}{dt} = \frac{d}{d\tau} \left( \frac{C}{C_0} \right) \text{ step input} \]

**Application of residence time distribution data**

The RTD data resulting from the tracer experiment can be used to predict the performance of the reactor with good accuracy only for processes involving first order reactions. For reactions other than first order tracer data alone is not sufficient to determine its performance, in addition to RTD, an adequate model of the non ideal reactor flow pattern and knowledge of the quality of mixing or "degree of segregation" are required to characterize a reactor properly.

**a. RTD in ideal reactors**

**RTDs in batch reactors**

The RTDs in plug flow reactors and batch reactors are simplest to consider. All the atoms leaving such reactors have spent precisely the same amount of time within the reactors. The distribution function in such a case is a spike of infinite height and zero width, whose area is equal to 1; It occurs at \( t = V/v \) or \( \theta = 1 \) where \( \theta \) is the dimensionless time. Mathematically, this spike is represented by the dirac delta function.

\[ E(t) = (t - \tau) \]
The dirac delta function has the following properties.

\[ \delta(x) = \begin{cases} 0 & \text{when } x \neq 0, \\ \infty & \text{when } x = 0. \end{cases} \]

b. Single CSTR-RTD

In an ideal CSTR the concentration of any substance in the effluent stream is identical to the concentration within the reactor. Hence RTD is obtained by taking material balance on an inert tracer that has been injected as a pulse at time \( t=0 \) into a CSTR. The material balance equation is given below.

\[
\text{In} - \text{out} = \text{accumulation} \tag{11}
\]

\[
0 - V C = \frac{V \cdot dc}{dt} \tag{12}
\]

where \( V \) is the volume of the reactor, \( v \) is the volumetric flow rate and \( C \) is the concentration of the tracer either in the effluent or in the reactor.

Separating the variables and integrating eq.(2) with \( C=C_0 \) at \( t=0 \) yields

\[
C(t) = C_0 e^{-vt} \tag{13}
\]

This relationship gives the concentration of the tracer in the effluent at time \( t \).

\( E(t) \) for an ideal CSTR is given by

\[
E(t) = C(t) \frac{C(t)}{\int_0^\infty C(t)dt} \tag{14}
\]

\[
= \frac{C_0 e^{-vt}}{\int_0^\infty C(t)dt} \tag{15}
\]
In terms of the dimensionless parameter $\theta$,

$$E(\theta) = e^{-\theta} \text{ where } \theta = t/\tau$$

c. **Reactor modeling with RTD**

There are many situations in which the fluid in a reactor is neither well mixed nor approximates plug flow. So various models were developed and used for predicting conversion in real reactors based on the information obtained from RTD. These models are classified according to the number of adjustable parameters that are extracted from RTD data and are given below.

1) **Zero adjustable parameters**
   a. Segregation model
   b. Maximum mixedness model

2) **One adjustable parameter model**
   a. Tanks -in-series model
   b. Dispersion model

3) **Two adjustable parameter model**

Real reactors modeled as combinations of ideal reactors.

The mixing of reacting species is one of the major factors controlling the behaviour of chemical reactors. For reactions of first order the conversion is independent of concentration. Consequently mixing with the surrounding molecules is not important. Therefore once the RTD is determined we can predict conversion that will be achieved in real reactor provided that specific reaction rate for the first order is known. For reactions of higher order models used must contain information about micromixing in addition to that of
macromixing. Macromixing produces a distribution of residence times without specifying how molecules of different ages encounter one another in the reactor.

A fluid in which globules of a given age do not mix with other globules is called a macro fluid, while a fluid in which molecules are free to move everywhere is called a microfluid. These two extremes of late and early mixing are referred to as complete segregation and maximum mixedness respectively.

**Segregation model**

In a CSTR, the entering fluid is assumed to be distributed uniformly throughout the reacting mixture. The mixing is assumed to take place even on the microscale, the elements of different ages mix together thoroughly to form a completely micromixed fluid. If the fluid elements of different ages do not mix together at all, the elements remain segregated from each other and the fluid is termed completely segregated.

In a segregated flow model, we visualize the flow through the reactor to consists of a series of globules. They do not interchange material with other globules in the fluid during their period of residence in the reaction environment. In addition each globule spends a different amount of time in the reactor. The principles of this model are based on clumping all the molecules that have same residence time in the reactor into the same globule. The reactor performance was first described by Danckwertz & Zweitering.

Because there is no molecular interchange between globules, each acts essentially as its own batch reactor. The reaction time in any one of these
batch reactors is equal to the time that the particular globule spends in the reaction environment given by the E function.

Thus fluid elements have different compositions. The mean composition in the exit stream will have to account for these two factors, the kinetics and the RTD.

\[
\begin{align*}
\text{Mean concentration of reactant in the exit stream} &= \text{concentration of reactant remaining in an element of age between } t \text{ and } t + dt \\
\text{fraction of exit stream which is of age between } t \text{ and } t + dt
\end{align*}
\]

In symbols this becomes,

\[
\left( \frac{C_A}{C_{A_0}} \right)_{\text{at exit}} = \int_0^\infty \left( \frac{C_A}{C_{A_0}} \right)_{\text{for element of age } \Delta t} E \Delta t
\]

or in terms of conversion,

\[
X_A = \int_0^\infty X_A \text{ element } E \Delta t
\]

\[
\left( \frac{C_A}{C_{A_0}} \right)_{\text{all age intervals}} \sum \left( \frac{C_A}{C_{A_0}} \right)_{\text{element } E \Delta t}
\]

For a second order reaction taking place in a batch reactor the conversion is given by the equation,

\[
\left( \frac{C_A}{C_{A_0}} \right)_{\text{all age intervals}} = \frac{1}{1 + k C_{A_0} t}
\]
For an nth order reaction,

\[
\left( \frac{C_A}{C_{A_0}} \right)_{\text{element}} = \left[ 1 + (n - 1)C_{A_0}^{n-1}kt \right]^{\frac{1}{n-1}}
\]

The steps involved in the scale up are discussed below.

1. A mole balance on a batch reactor that is well mixed is

\[
\frac{dC_A}{dt} = r_A
\]

1. The rate law was assumed as \(-r_A = kC_A^2\)

2. Combining the rate law and the mole balance,

\[
\frac{-dC_A}{dt} = kC_A^2
\]

For isothermal operation, the equation can be integrated,

\[
\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} = \int_0^t kt dt
\]

Integrating yields,

\[
\frac{1}{C_A} - \frac{1}{C_{A0}} = kt
\]

A plot of \((1/C_A - 1/C_{A0})\) versus time yields a straight line with slope equal to \(k\).

The value of \(k\) determined from previous experiment was 0.0166 mole/litre.min can be used here. Hence the rate law becomes
-r_A = 0.0166 \ C_A

3. This rate law was used in the design of CSTR.

For a batch reactor, the mean residence time is calculated as follows.

In terms of conversion,

\[
C_{A_0} \int \frac{dx_A}{(1 - x_A)^2} = 1x0.878 / (0.122x0.0166x3.59x60)
\]

\[
= 2.04 \text{ hours.}
\]

The results of the kinetic studies obtained from a batch reactor are used for finding out the conversion in a CSTR.

The residence time distribution function, E, is calculated using the equation,

\[
E = \frac{1}{\tau} \ e^{\tau t}
\]

The batch equation for a second order reaction is,

\[
\left( \frac{C_A}{C_{A_0}} \right)_{\text{element}} = \frac{1}{1+kC_{A_0}t}
\]
Table 3.6

<table>
<thead>
<tr>
<th>t, min</th>
<th>$E = 1/\tau \cdot e^{-\tau \cdot t}$</th>
<th>$(C_A/C_{A_0})_{element}$</th>
<th>$(C_A/C_{A_0})_{element} \cdot E \cdot \Delta t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0083</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>0.0073</td>
<td>1.862</td>
<td>0.0592</td>
</tr>
<tr>
<td>30</td>
<td>0.0065</td>
<td>2.723</td>
<td>0.0358</td>
</tr>
<tr>
<td>45</td>
<td>0.0057</td>
<td>2.585</td>
<td>0.0333</td>
</tr>
<tr>
<td>60</td>
<td>0.0050</td>
<td>3.446</td>
<td>0.0219</td>
</tr>
<tr>
<td>75</td>
<td>0.0045</td>
<td>5.308</td>
<td>0.0127</td>
</tr>
<tr>
<td>90</td>
<td>0.0039</td>
<td>6.169</td>
<td>0.0095</td>
</tr>
<tr>
<td>105</td>
<td>0.0034</td>
<td>7.031</td>
<td>0.0074</td>
</tr>
<tr>
<td>120</td>
<td>0.0030</td>
<td>7.893</td>
<td>0.0058</td>
</tr>
</tbody>
</table>

$\Sigma(C_A/C_{A_0})_{element} \cdot E \cdot \Delta t = 0.186$

From the table,

$$C_A/C_{A_0} = \Sigma(C_A/C_{A_0})_{element} \cdot E \cdot \Delta t$$

$$= 0.186$$

Therefore conversion in a CSTR is,

$$X_A = 1 - 0.186 = 0.814$$

$$= 81.4\%$$

3.4 Conclusions

Silica particles can be prepared from sodium silicate by precipitation method in poly(vinyl alcohol) medium. The size of the silica particles obtained is found to be in the nanoscale from TEM analysis. The average size
of the particles is 15nm. This is lower than the commercial silica particles as it is obvious from the surface area values. SEM studies revealed the influence of reaction parameters during synthesis. Unmodified particles exist as small agglomerates when compared to modified particles. Thermogravimetry shows the thermal behaviour and purity of the product formed. XRD pattern revealed that the prepared silica samples are amorphous.

Kinetic studies on synthesis reaction provided important information required for the design of reactors for producing silica in a large scale for polymer modification. The value of the reaction rate constant k is determined from a batch experiment as 0.0166 litre/mole.min which is found to be consistent with the theoretical methods. The reaction is found to be of second order and these data can be used for analyzing the performance of the continuous reactors used for the synthesizing silica on a large scale.

References

[31] Qiu, k. and Huang, Z. Polymer 38, 521 (1997).
[38] Stoher W., Fink A., Bohn E., J. Colloid Interface Sci., 26 (1968), 62.
Nanosilica – Synthesis and Characterization


