Preparation of fumed silica using tetraethyl ortho silicate / effect of reaction temperature on its physical properties

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Abstract

The aim of this work was to prepare fumed silica from tetraethyl orthosilicate and study the effect of reaction temperature on physical properties of fumed silica.

This study was focused on indigenously a system built for the preparation, it consists of four stages which these chemical reaction stage, agglomeration stage, separation stage and calcinations stage. Chemical and physical properties of product "fumed silica" such purity (SiO_2 content), acidity, porosity, pore volume and apparent density had been in measured and evaluated.

The preparation step was performed by chemical reaction in various temperature (200 , 250 , 300 , 350 , 400 , 450 ,500) ^oC at (1) atmospheric pressure.

The chemical reaction occurred can be represented by:

$$Si(OC_2H_5)_4 + 2H_2O \xrightarrow[(200\text{-}500)\ ^oC]{1\ atm} SiO_2 + 4C_2H_5OH$$

After reaction the produced fumed silica is tend to agglomerate, separate from ethanol vapour by cyclone separators, calcinated at (350 ^oC) to remove the residual ethanol vapour.

It was deduced that the chemical reaction at 200 ^oC give fumed silica with higher acidity compered to the reaction at 500 ^oC, with small particle size and high surface area.

Introduction

Silica is one of the commonest materials known, naturally silica occurred in earth in different forms such as qartz, sand, kieseguhr, opal, chert, chalcedony and a part of plants such as barley, bamboo, palms, rice. Silica has almost been found in meteorites. Synthetically silica is divided to three important kinds which they are; gels precipitates and pyrogenic (fumed) silica .

Synthetic silica have many uses in industry, there uses include surface coating, rubber, reinforcement, plastic compounding, liquid carriers, tooth paste abrasive and thickeners, free flow aids, substrates for catalysts, e.g. transition materials and molecular sieve and as a descant[1].

Silica fumed one of the synthetic silica, it primarily consists of amorphous silicon dioxide. The individual particle is extremely small it is called silica smoke because of it fine particle size, large surface area and the high SiO_2 content[2]. It is produced by more than one method, such as that which used tetraethyl orthosilicate [3] or silicon tetrachloride[4,5,6,7,8] or silicon tetrafluride[9,10,11,12] as starting materials.

In Germany this form of fumed silica has been made commercially and called Areosil since 1940. The (Cab-O-Sils) company captured 65% of the market of fumed silica until 1990[13] , and exported to up to 85% of the market by September 2000[14].

This work deals with preparation of fumed silica (highly dispersed silicon dioxide) by reaction gaseous silicon compounds (such as tetraethyl orthosilicate) with water vapour. The reaction passed four stages these are: reaction, agglomeration, separation and calcination.

The effect of reaction temperature on fumed silica properties (i.e. acidity, porosity, pore voleum and bulk density) are studied.

Experimental work

Apparatus

- **Reactor:**

The reactor is tubular, 0.12 m inside diameter and 1.25 m long, and Fabricated from 316 stainless steel with 5 mm thickness. The reactor contained a sensor at the end to sense the temperature and gage pressure with 25 bar.

- **Furnace:**

The furnace is a box containing electrical coil coated the reactor, and type K thermocouple was fitted to a digital temperature controller (Rustart KG 3406 Borenden 1, Type RKH, Max. Tem. 100 ^{o}C) to sense the reactor surface temperature.

- **Agglomerator:**

The agglomerator used in the system is a coil of stainless steel, 1.5 mm in diameter and 10 m long. It is formed as a double coil in one center with 10 and 15 cm, and it has a sensor at the end to sense the outlet agglomerator temperature.

- **Agglomerator Container:**

Agglomerator container was used for cooling by submerging agglomerator in water.

- **Cyclone:**

Two Q.V.F. glass cyclones were used to separate silica from the mixture gases.

- **Filter:**

Two stainless steel sieves with 30 and 40 mesh were used as a filter fixed at the top end of the cyclone.

- **Calciner:**

A programmable electrical furnace (Model N_2O/H_2 Max. Tem. 1340 ^oC) was used in the calcinations of fumed silica product.

- **PH meter:**

Digital PH meter with temperature sensor used for measuring the PH of the solution having the following specification: Pw 9409 Type, England.

- **Electronic Balance:**

With (4) digital reading, ER 180 A Type, A&d company limited , Japan.

Experimental procedure

- **Chemical Reaction:**

The pathway through which the flame hydrolysis reactants, comprising the hydrolysable metal or metalloid feed stock (i.e. tetraethyl orthosilicate) and water, are introduced into the reactor (reaction zone). The reactants may be totally or partially mixed by means of premixing chamber adapted preliminarily. This chamber receive the separate reactant stream and mix them prior to entry therefore into reaction. However, the hydrolysis reactants can also be wholly or partially mixed within reaction zone upon discharge from furnace or reactor mouth.

The feeds stock, water preheated to about 100 ^{o}C and tetraethyl orthosilicate to about reaction temperature (200-500 ^{o}C), air or nitrogen at about ambient temperature can be used to reduce the vapour pressure in reactor. All of these are introduced preliminary to the reactor, or introduced together as mixture to reactor and there heated to (200-500 ^{o}C) by electrical power [14]. The reaction between reactants occur to give silica and ethanol within highly exothermic reaction, the reaction temperature is reached. Silica properties (porosity, surface area, pore size, apparent density and acidity) depend largely on the reaction temperature, within range (200-500 ^{o}C). Flame or reaction temperature is controlled by proportion of tetraethyl orthosilicate and water[13]:

$$Si(OC_2H_5)_4 + 2H_2O \xrightarrow[(200\text{-}500)\ ^{o}C]{1\ atm} SiO_2 + 4C_2H_5OH$$

- **Agglomeration Process:**

The discharge from the reactor contains silica and ethanol vapour at (500-550 ^{o}C). Silica winds its way through the system when the particle stick together to convert extremely fine particles to large particles enough to be taken out by a cyclone separation. Silica and ethanol vapour leave the agglomerator at (300-350 ^{o}C) after cooling.

- **Separation Process:**

Two cyclones separators connected horizontal to collect the silica product from the gas stream. Each cyclones is (15 and 5 cm). Filter of 30 mesh upper diameter fixed for first cyclone, and 40 mesh for the second cyclone.

Each cyclones remove about 80% of the silica has been taken out of the stream after the two cyclones.

- **Calcination Process:**

The solid particles silica were calcined using a programmable electrical furnace at (350 ^{o}C) retention time is (15) min. , the residual ethanol is driven off silica in the calciner. Acidity of silica produce can be controlled by the temperature in the calciner.

Fumed silica properties measured

- **Bulk (or Apparent) Density**

The apparent or bulk density Da can be determined using liquid impregnation method [15]**.** A sample of silica powder was weight after being thoroughly dried in an oven at (350 ^{o}C) for 2 hours. The weight was recorded as W_1. Then this sample was placed in boiling water for (5) minutes, let for (10) minutes to cool and then the liquid was dropped away. The powder sample was put on a tissue paper, wiped slightly and weight W_2. The sample was placed in a stainless steel basket, suspended in cold water and weight using a thin wire attached to a sensitive electronic balance (4-decimals). This weight was W_3.

The bulk (or apparent) density Da can be calculated by the following equation [16]:

$$Da = \frac{(W_1)\ D_w}{W_3 - W_2}$$

Where:

D_w= water density = 1g/cm^3

The results are given in table (A-5) appendix (A).

- **Apparent Porosity:**

Apparent porosity is defined as the ratio of the volume of water of liquid capable of being adsorbed into the particle to the total volume of the particle. Closed pores and open pores, that are so fine prevent liquid penetration, are not included as void space in determining the apparent porosity [17]. The apparent porosity Pa can be determined using

liquid impregnation method described in the pervious paragraph [15] by the following equation [17] :

$$Pa = \frac{W_1 - W_2}{W_3 - W_2}$$

The results are given in table (A-6) Appendix (A).

- **Pore volume:**

The pore volume of silica and other microprobes solids may be calculated by the Gurvitsch rule [16]:

$$Vp = \frac{Xs}{D_w} = \frac{W_2 - W_1}{W_1 D_w}$$

Where:

Vp: is the total volume of open pores (cm^3 / gm).

Xs: is the quantity of liquid adsorbed to completely fill the pores (gm/gm).

The results are given in table (A-7) appendix (A).

Results and Discussion

- **Chemical Analysis of Fumed Silica:**

The chemical composition of fumed silica standard is given in table (A-1). The purity of fumed silica (SiO_2 content) depends on the preparation method, type of alloys of the instruments and purity of raw materials. The purity of silica prepared in the present work was (42.44 %) measured by Ibn Sina State Company (ISSC). The standard purity of silica (SiO_2) is (93 %) . Hence the obtained results were in agreement with operation equipment and available raw materials with medium.

- **Effect of Reaction Temperature on Acidity:**

The acidity of silica product decrease with increasing the reaction temperature. This decrease is due to the resulting ethanol. Silica particles are sintering or coalescing by moisture of ethanol at high temperature. It given an indication that high temperature gives lightly large particles and thus less surface area, while lower temperature gives less particles size thus large surface area.

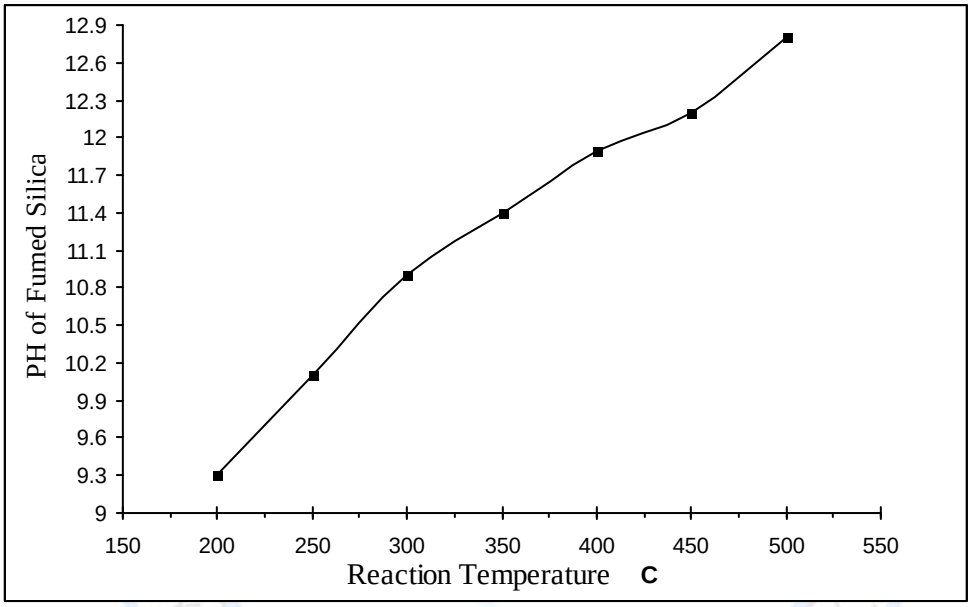

Figure (5.1) The Effect of Reaction Temperature on Acidity

- **Effect of Reaction Temperature on Bulk Density:**

Figure (5.2) show that the bulk density increased as the reaction temperature increased. This behavior is attributing to the large particles with small pore volume because closed the pores during the sintering particles with increasing th reaction temperature.

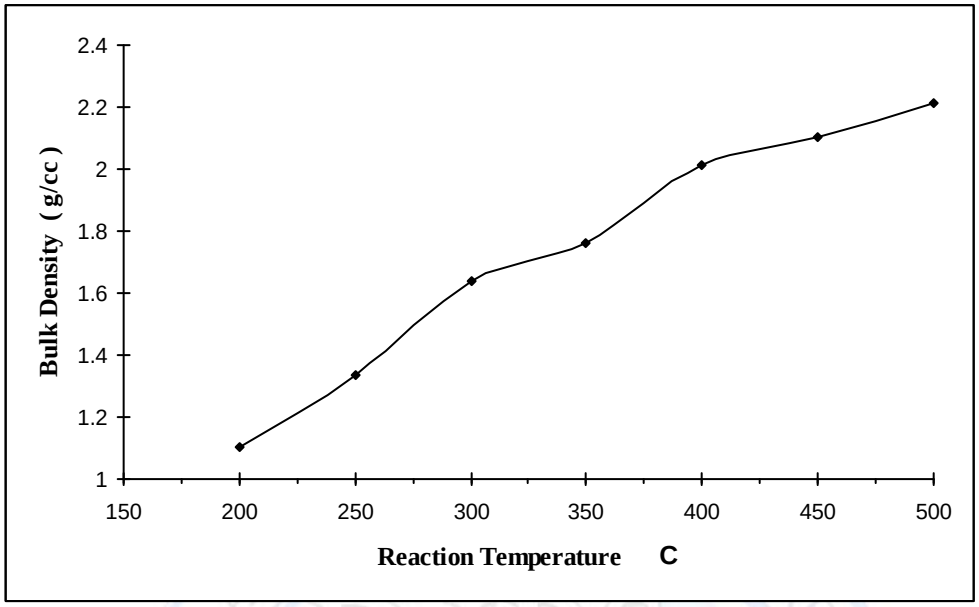

Figure (5.2) The Effect of Reaction Temperature on Bulk Density

- **Effect the Reaction Temperature on porosity:**

Figure (5.3) show the effect of the reaction temperature on the porosity. It is shown that with increasing the reaction temperature, the porosity decrease. This can be attribution to the decrease in the porosity of the media and this because the more of pores are closed by sintering particles. The decreasing porosity will lead to decreasing in surface area too, so to obtained highly surface area silics must be less reaction temperature using.

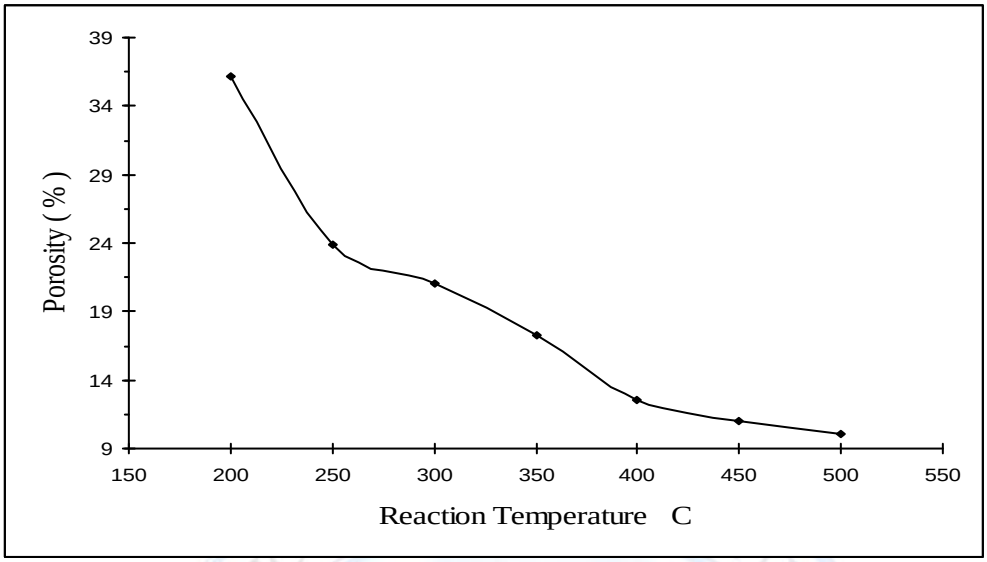

Figure (5.3) The Effect of Reaction Temperature on Porosity

- **Effect the Reaction Temperature on pore volume:**

Figure (5.4) show the effect of reaction temperature on the pore volume. As can be seen the pore volume decreasing with the reaction temperature. This decreasing results as the produced silica particles have more coalescing by ethanol vapor and losses more of pores.

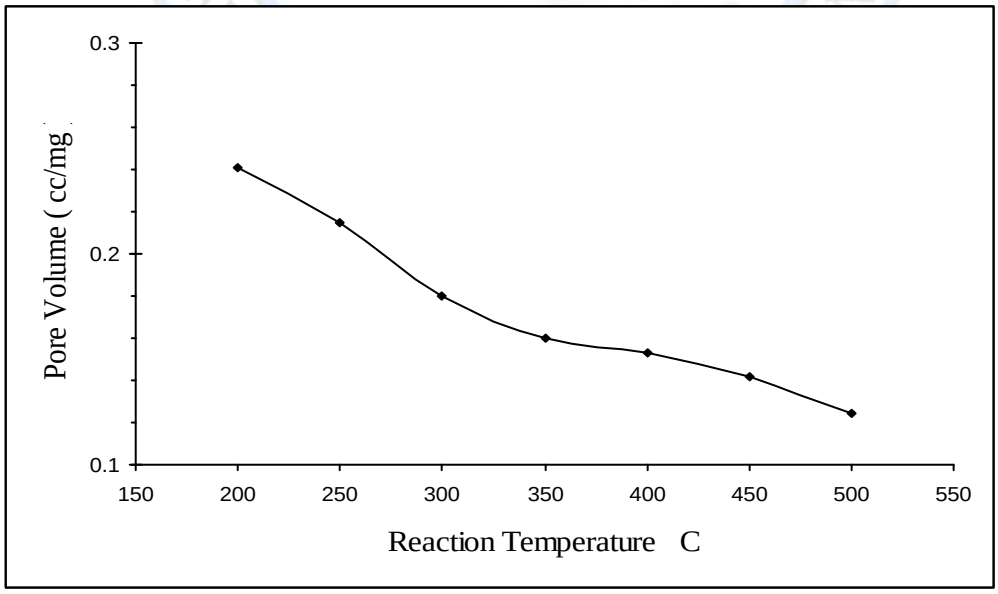

Figure (5.4) The Effect of Reaction Temperature on Pore Volume

Conclusions

According to the results obtained from this study, the following conclusion is deduced:

1- Highly reaction temperature (500 ^{o}C) give more basity (PH=12.8). This leading to large Particles size and low surface area , and at (200 ^{o}C) high acidity (PH = 9.3) , this leading to small particles size and large surface area.

2- High porosity (36.12) % and pore volume (0.2412) were obtained at lower reaction temperature (200 ^{o} C).

3- High density can be obtained at high reaction temperature.

4-Good agglomeration leading to high separation of fumed from reaction mixture.

Appendix A

Table (A - 1) Typical Chemical Analysis (wt % by XRD, as oxides) of Standard and Fumed Silica

Oxide	Typical
SiO_2	93.0
$ZrO_2 + HfO_2$	4.2
Fe_2O_3	0.4
Al_2O_3	0.2
TiO_2	0.02
CaO	0.01
Na_2O	0.01
K_2O	0.01
H_2O	0.5

Table (A – 2) Typical Physical Properties of Standard Fumed Silica

Properties	Typical
Bulk Density	2-3 g/ cm^3
Surface Area	175-200 m^2/g
pH	2-3.5
Particle size	0.015-0.020 mm
Refractive Index	1.55
Residue	0.3 %

Table (A – 3) Properties of Prepared Fumed Silica

Chemical Structure	purity	Acidity PH	Porosity %	Pore volume(cc/g)	Bulk Density(g/cc)
SiO_2	42.44	4.5	36.12	0.2412	1.1032

Table (A – 4) Acidity of Fumed Silica at Various Reaction Temperature

Sample No.	Reaction Temperature ^0C	Acidity pH
1	200	9.3
2	250	10.1
3	300	10.9
4	350	11.4
5	400	11.9
6	450	12.2
7	500	12.8

Table (A – 5) Bulk Density of Fumed Silica at Various Reaction Temperature

Sample No.	Reaction Temperature ^0C	W1 (g)	W2 (g)	W3 (g)	Da (g/cm^3)
1	200	1.5421	1.7324	0.3346	1.1032
2	250	1.6201	1.9113	0.6956	1.3326
3	300	1.4235	1.5326	0.6636	1.6381
4	350	1.9217	2.1938	1.1007	1.7581
5	400	1.5591	1.9351	1.1609	2.0137
6	450	1.2787	1.8381	1.2301	2.1031
7	500	1.1832	1.7326	1.1982	2.2141

Table (A – 6) Porosity of Fumed Silica at Reaction Temperature

Sample No.	Reaction Temperature ^0C	W1 (g)	W2 (g)	W3 (g)	Pa (%)
1	200	1.8328	2.2270	1.1356	0.3612
2	250	1.6201	1.9113	0.6956	0.2389
3	300	1.5931	1.8372	0.6754	0.2101
4	350	1.3253	1.4904	0.5372	0.1732
5	400	1.4235	1.5326	0.6636	0.1255
6	450	1.7581	1.8231	1.2341	0.1104
7	500	1.6175	1.6377	1.4376	0.1010

Table (A – 7) Pore Volume of Fumed Silica at Reaction Temperature

Sample No.	Reaction Temperature ^{0}C	W1 (g)	W2 (g)	Vp (cm^3/ g)
1	200	1.5591	1.9351	0.2412
2	250	1.8328	2.2270	0.2151
3	300	1.6201	1.9113	0.1797
4	350	1.7372	2.0153	0.1600
5	400	1.5931	1.8372	0.1532
6	450	1.9217	2.1938	0.1416
7	500	1.3253	1.4904	0.1246

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