Preparation and Characterization of Colloidal Silica in Alkaline and Constant Range of pH

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ABSTRACT: *In this study, alkaline colloidal silica was prepared by titration of an alkaline solution such as sodium silicate with silicic acid in constant range of pH .This constant range of pH was achieved by using concentrated soduim silicate solutions as pH adjusting solutions during titration.The sodium silicate solutions having a variety of concentrations were passed through ion-exchange resin to prepare the silicic acid solutions. Various effective parameters on the method were investigated. In this research, the results show the mean particle size and surface area of prepared colloidal silica are influenced by formation temperature, titration rate, silicic acid and alkaline solutions concentration. Low titration rate of slicic acid, high formation temperature and low concentration of silicic acid and alkaline solution would help the particle growth to form the larger particle size of colloidal silica.*

INTRODUCTION

For more than one century, colloidal silica has been applied in many industries, eg as binder for inorganic paint, stiffener for hard coating reagent and especially as abrasive particles for chemical mechanical polishing slurries [1,2]. It is also used in production of paper .

Nearly, all of the processes which have been proposed and employed for producing colloidal silica use the low-cost sodium silicate solutions as main raw material. These methods include dialysis [3], electrodialysis [4], acid neutralization [5] peptization [6] and ion exchange [7,8].

Since the ion exchange method is controllable more easily than the other methods, it is the most popular method for industrial production of colloidal silica

nowadays. The homogenous nucleation and the surface growth play important roles in the mechanism of particle formation via ion exchange method. There is much discussion of this process in the literatures.

Chenge liu et al. [9] investigated the relationship between the rate of growth and factors such as pH values, particle size as well as the mole ratio of SiO_2/Na_2O. *Hayraptan et al.* studied effect of pH on the growth processes of the silicia sol colloidal particles [10]. Perhaps, It can be said that *Tsai* and his coworkers accomplished most of the studies about production of colloidal silica via ion exchange method [11-14]. They added silicic acid to a heating alkali solution containing KOH. They accomplished this experiments in two ways, constant

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volume and concentaration, then investigated influence of effective parameters on these two processes. They also studied modification of colloidal with aluminum ions.

In this study, colloidal silica was made via titration of alkaline sodium silicate solutions by means of silicic acid solutions in constant range of pH. Then, the influence of effective parameters on the process such as formation temperature, titration rate, alkaline solutions and silicic acid solutions concentration on the particle properties has been investigated.

EXPERIMENTAL

Preparation of Colloidal Silica

In the first series of experiments, by use of the commercial sodium silicate (29.5 % wt. SiO_2 and $SiO_2/Na_2O=3$) and DI water, Sodium Silicate Solution with 2,4,6 and 8 % wt. SiO_2 were prepared. Then, with passing 2000 mL of these solution through a column filled by a cation exchange resin in hydrogen form (Purolite C-100E), the silicic acid solutions were prepared. 10.30 g of the same sodium silicate was diluted by DI Water up to 300 g for preparing an alkaline solution (1 % wt SiO_2) The silicic acid solutions were added to the boiling alkaline solution with a constant flow rate of 10 mL/min by a peristaltic pump (JESCO DOSDX12D). Aqueous solutions with different concentration of sodium silicate were used in order to adjust pH in the range of 9.5-10 to assure that product will be an alkaline colloidal silica not a gel.

In the second raw of experiments, silicic acid solutions with 4 % wt. SiO_2 were prepared such as above. Four alkaline soduim silicate solutions were prepared through diluting 2.58, 5.15, 10.30 and 20.60 g sodium silicate up to 300 g by DI water. These four solutions were heated to the desire temperatures (70, 85 and 100 °C, respectively). The silicic acid solution was added to these four solutions at constant rates of 5,10 and 15 mL/min.

It must be mentioned, for all solutions the total time of the reaction was the same (200 minutes). The experimental box diagram and apparatus are shown in Figs. 1 and 2, respectively.

Characterization

The formed products were characterized by particle size distribution, zeta potential (Malvern Zeta Sizer 3000 HSA), TEM(Philips, CM 200-FEG) and accelerated
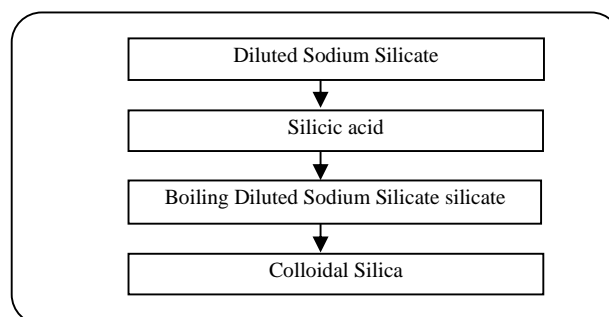
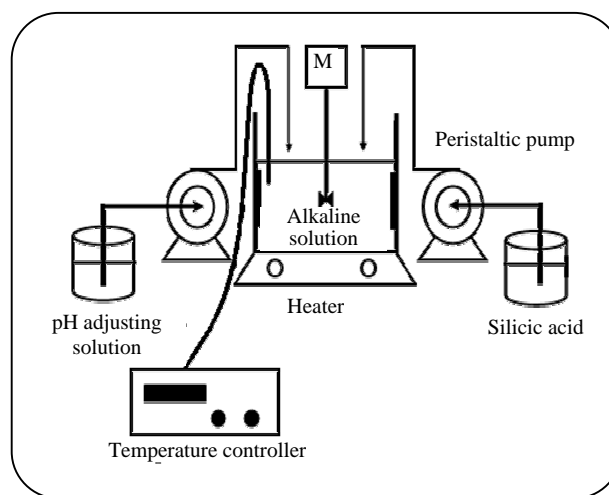**Fig. 1: The experimental Box Diagram of colloidal silica formation.**

Fig. 2: The shematic representation apparatus used.

aging test. The stability of colloidal silica is very important in its application. The accelerated aging test can be taken by decreasing the slurry pH value and increasing the store temperature. The sodium ions were removed from the products and pH value from 9.5-10 to 2-3 by mixing colloidal silica with action exchange resin and the next step is separation. The acidified slurries were placed in the oven at 65 °C for 7 days. When the slurry did not gel in the accelerated aging test, the case was identified as stable; otherwise it was unstable if it gelled in the accelerated aging test.

The specific surface area of products were also determined via titration method [15]. The concentrations of SiO_2 (% wt.) and Na_2O (% wt.) in prepared samples were determined via gravimetery [16] and flame photometery (Flame Photometer Model PFP7) methods, respectively. The most of products were stable in these conditions and the pH of sols was fixed between 9.5-10 by using adjusting pH solutions and pH meter (Model BLD 8252).
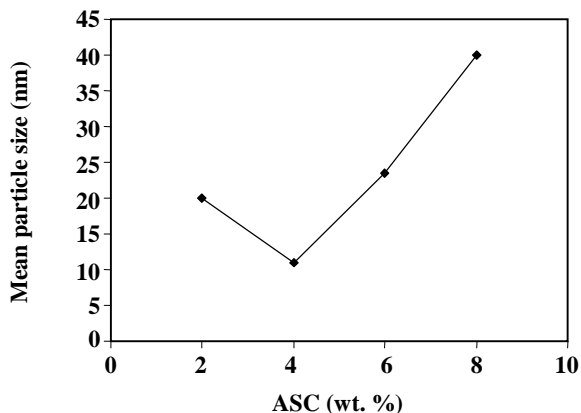
Fig. 3: The influence of the silicic acid concentration on the mean particle size of colloidal silica (100 °C).
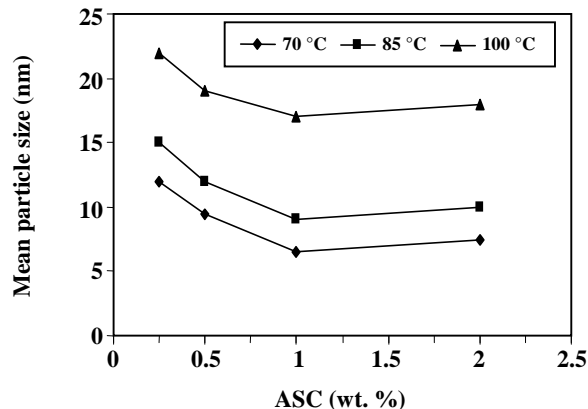

Fig. 5: The influence of the ASC on the mean particle size of colloidal silica as titrated with 10 mL/min.
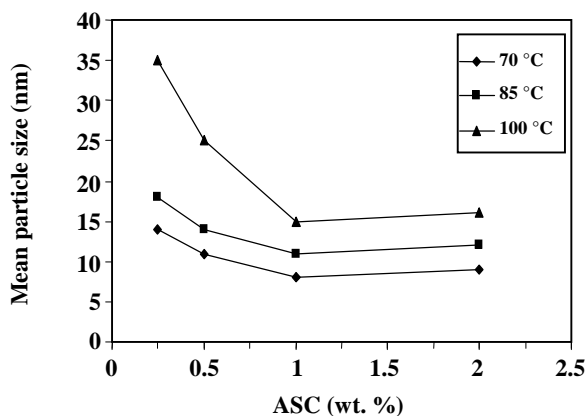

Fig. 4: The influence of the ASC on the mean particle size of colloidal silica as titrated with 5 mL/min.
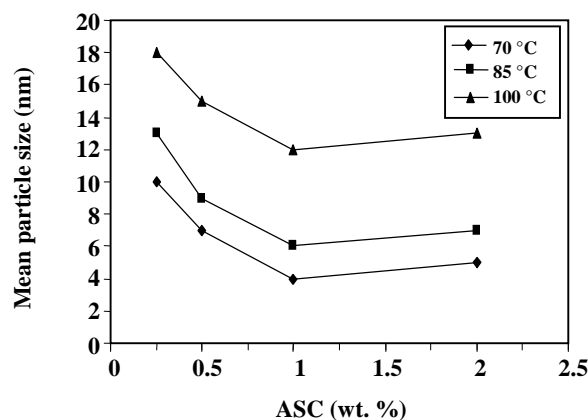

Fig. 6: The influence of the ASC on the mean particle size of colloidal silica as titrated with 15 mL/min.

RESULTS AND DISCUSSION

The effect of silisic acid concentration (SAC) on the particle size of colloidal silica in the first experiments is given in Fig. 3. Different SAC in the range of 2-8 % wt. SiO_2 and the constant concentration of alkaline sodium silicate solution with 1 % wt. SiO_2 were used in the first experiments. It is apparent from Fig. 3 that the mean particle size of ultimate colloidal silica decreases with increasing SAC up to 4 % wt. SiO_2 and then increases up to 8 % wt. SiO_2. According to collision theory in titration, whenever the concentration of titrant is increased, the nucli formation rate exceeds the nucli growth. So, we see that the particle size decreases due to increasing the SAC from 2 % wt. to 4 % wt. On the other hand, when SAC increases more than 4 % wt., i.e., 6 or 8 % wt., the particle size increases. This is because of rapid pH decrease in the point where the drops of silicic acid

contact with the alkaline solution and rapid microgel formation instead of colloidal silica. So, we should expect the particle growth as it has been shown (Fig. 3).

The formation of small gels along the agitator and wall of the mixer after increasing SAC is a good evidence for this interpretation.

According to above, silisic acid with 4 % wt. SiO_2 was selected as titrant for the next series of expriments. So, in the second series of experiments, a silicic acid solution with constant concentration of 4 % wt. was added to alkaline solutions with concentrations of 0.25, 0.5, 1. and 2 % wt. SiO_2. It can be seen from Figs. 4-6, the mean particle size of colloidal Silica decreases up to 2 % wt. and then increases in this point. This trend has a more sharp slope in the temperature 100 ^{o}C. The first decrease is belived to be conformed with collision theory in titration. Acording to this theory, with decreasing concentration of

reactants, the ultimate particle size will increase. But when the alkaline solution concentration (ASC) increases (up to 2 % wt. SiO_2) the ionic strenght of solution increases. While the primary silica particles are formed, they can attach each other easier due to the effect of opposite charges of the solution and decreasing electrical double layer thickness of silica particles. As a result, the nucli growth exceeds the nucli formation rate and the size of particles increases with a very slow rate. This trend is the same in all of temperatures 70,85 and 100 °C.

Figs. 4-6 also show that the upper formation temperature seems to be effective for the nucli growth rather than formation of nucli. This is more obvious for upper temperature such as 100 °C than low temperatures like 70 and 85 °C. It is probably because of increasing particles kinetic energy, decreasing surface adsorption and consequently decreasing particles charge. In these conditions, all of these effects cause more collision between particals and finally particles growth [9].

The above interpretation is in accordance with the trend of products surface area. It can be seen from Figs. 7-9, for the first three samples, the surface area increases with increasing ASC and for the last sample decreases, and as we know in colloidal silicas the surface area has a reverse relation with particle size.

The mean particle size of colloidal silica is increased by increasing the formation temperature or decreasing ASC, which is similar to the cases with the slow rate of titration. By comparing Figs. 4-6, it can be seen that the mean particle size of colloidal silica formed by slow titration rate are generally larger than that formed by the quick titration rate. It is probably caused by the time difference between the surface growth and titration rate. If titration rate is faster than the surface growth, the added silicic acid might not have enough time to consume itself on the surface of the seeds. It would induce the concentration accumulation of silicic acid, and cosequently the homogenous nucleation occurs. The colloidal silica formed in these conditions has small particle size. Otherwise, if titration rate is slower than the surface growth, the time of surface growth seems to be enough. The surface growth would dominate the mechanism of particle formation.

Fig. 10 shows the morphologies of colloidal silica which were formed at various temperatures. Many nano
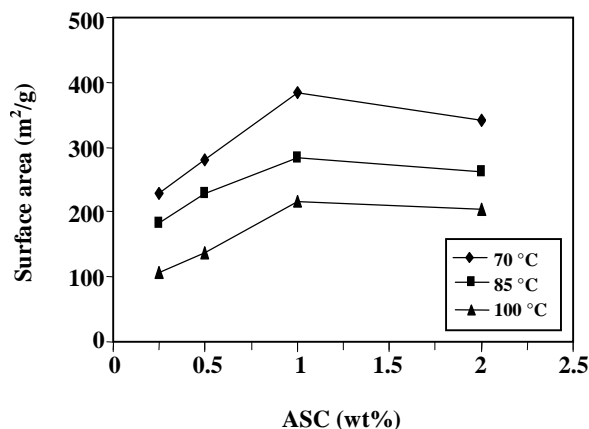

Fig. 7: The influence of the ASC on the surface area of colloidal silica as titrated with 5 mL/min.
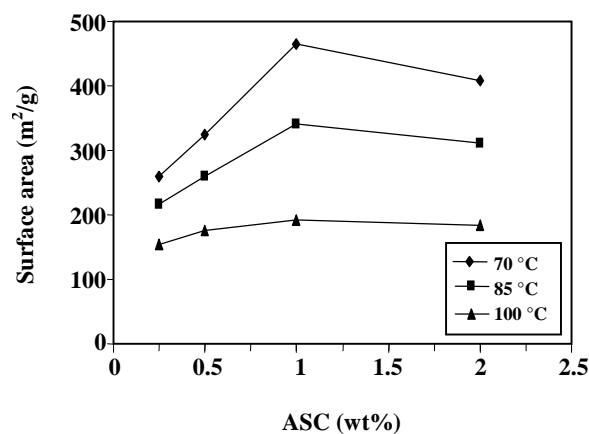

Fig. 8: The influence of the ASC on the surface area of colloidal silica as titrated with 10 mL/min.
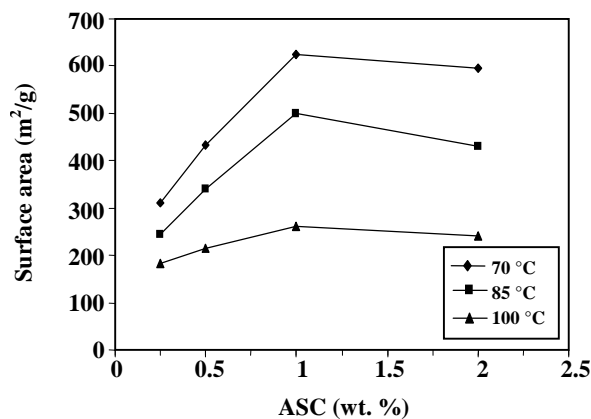

Fig. 9: The influence of the ASC on the surface area of colloidal silica as titrated with 15 mL/min.

Table 1: The effect of formation condition on the Stability of colloidal silica.

ASC (Wt. %)	5 mL/min			10 mL/min			15 mL/min		
	70 ℃	85 ℃	100 ℃	70 ℃	85 ℃	100 ℃	70 ℃	85 ℃	100 ℃
0.25	unstable	unstable	unstable	unstable	unstable	unstable	unstable	unstable	unstable
0.50	Stable	Stable	unstable	Stable	Stable	unstable	Stable	Stable	unstable
1	Stable	Stable	Stable	Stable	Stable	Stable	Stable	Stable	Stable
2	Stable	Stable	Stable	Stable	Stable	stable	Stable	Stable	stable

Table 2: The SiO_2 content of produced colloidal silicas (% wt.).

ASC (Wt. %)	5 mL/min			10 mL/min			15 mL/min		
	70 ℃	85 ℃	100 ℃	70 ℃	85 ℃	100 ℃	70 ℃	85 ℃	100 ℃
0.25	5.24	10.33	13.58	8.21	15.11	20.21	10.31	20.82	24.50
0.50	5.85	10.72	13.83	8.43	15.42	21.52	10.91	21.05	25.37
1	6.03	12.09	14.33	9.56	16.07	22.25	11.72	22.54	26.30
2	6.47	12.5	15.35	9.87	16.85	22.70	11.95	23.09	27.65

Table 3: The Na_2O content of produced colloidal silicas (% wt.).

ASC (Wt. %)	5 mL/min			10 mL/min			15 mL/min		
	70 ℃	85 ℃	100 ℃	70 ℃	85 ℃	100 ℃	70 ℃	85 ℃	100 ℃
0.25	0.07	0.13	0.19	0.11	0.18	0.25	0.13	0.27	0.32
0.50	0.08	0.15	0.20	0.12	0.19	0.27	0.13	0.28	0.33
1	0.09	0.17	0.21	0.13	0.20	0.28	0.15	0.29	0.37
2	0.09	0.18	0.22	0.14	0.21	0.28	0.16	0.29	0.40

grades and spherical bubbles were traped in the small colloidal silica aggregation which can be observed in Fig. 10-a. The serious agglomeration occurred between small particles at 70 °C. The nano size and spherical colloidal silica was formed and could be distinct from each others as the formation temperature reaches above 85 °C as shown in Fig. 10-b,c.

Fig. 11 shows the zeta potential of formation colloidal silica in various pH values. The iso electrical point (IEP) is at pH value of about two. It has consistency with the colloidal silica made by the other traditional methods.

Table 1 shows the forming condition and the stability of colloidal silica. The colloidal silica formed in the solution of lowest SiO_2 (0.25 wt. %) concentration was gelled in the acceleration aging test at all formation temperatures. The colloidal silica formed at 100 °C in 0.5 wt. % SiO_2 also gelled in this test. The high formation temperature would accelerate the reaction of surface growth to form the larger particle colloidal silica. It also led the solution to be gelled. The ASC and the formation temperature are important factors not only on particle growth but also for the stability of colloidal silica. The titration rate doesn't affect clearly the stability of colloidal silica under these conditions as shown in table 1.

Tables 2 and 3 show the total content of SiO_2 and Na_2O in the amples. According to contents of these two tables and table 1, it is clear that in this concentration range the stability just depended on pH and mean particle size. So if these parameters are controled, the desirable stability will be achieved, otherwise, even if the concentration of the silica sol is low, the silica sol wouldn't be stable.

CONCLUSIONS

The effect of the process parameters such as SAC, ASC, formation temperature and titration rate on the properties of the colloidal silica at constant pH were
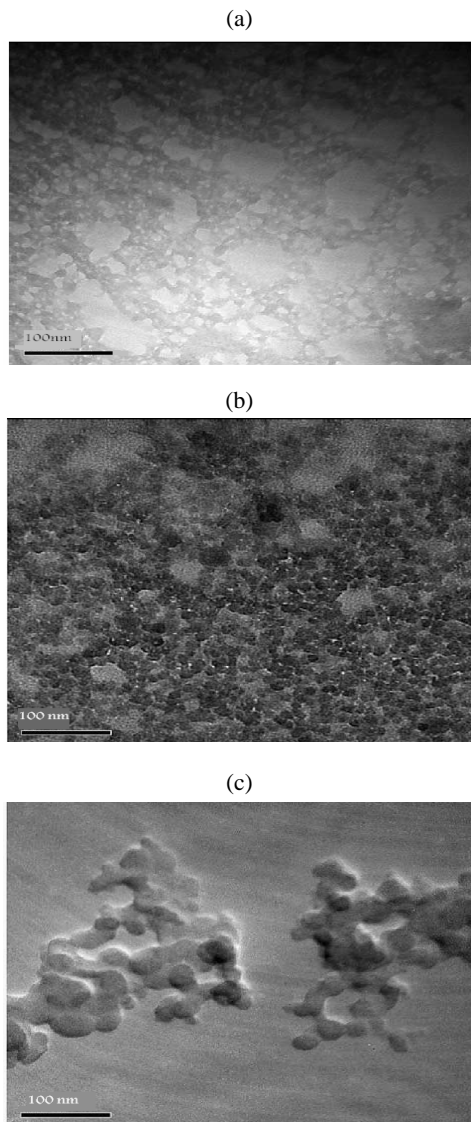
(a)

(b)

(c)

Fig. 10: TEM morphology of colloidal silica formed in 0.25 % wt. alkaline solution at a) 70 °C, b) 85 °C, c) 100 °C.
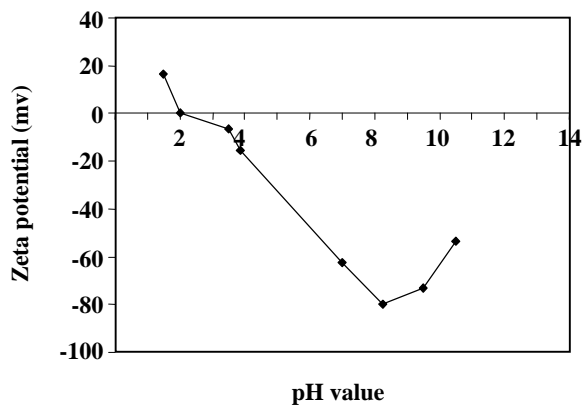

Fig. 11: pH value vs.zeta potential of colloidal silica.

investigated. The mean particle size of colloidal silica increases with increasing formation temperature and decreasing SAC, ASC and the titration rate of silicic acid. we can prepare stable alkaline colloidal silica in a wide range of particle size with controlling theses parameters in the pH of 9.5-10. The formed colloidal Silica also had an IEP at pH of about 2.

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