INTRODUCTION

Amorphous aluminosilicate nanoparticles are used in many applications including ceramics, catalysis, pharmaceutical, electronic packaging and chemical-mechanical polishing\textsuperscript{1-5}. In particular, special attention has recently been paid to methods for controlling the nanospheres, size and distribution, because they exhibit peculiar and desirable properties in the wafer polishing process. Monodisperse silica nanospheres were first synthesized by Stober et al. using sol-gel method which induces high purity in the resulting particles\textsuperscript{6}. Bogush and Zukoski reported the influence of reaction parameters such as ammonia and water contents on the particle size and distribution\textsuperscript{7}. Recently silica nanospheres have been considered effective candidates for chemical-mechanical polishing materials, so several investigators have reported ways to control particle size by using reactor type and varying the concentrations of ammonia, water and alcohol solvent\textsuperscript{8-11}. They also examined the influence of reaction method (such as semi-batch reaction and batch reaction) on particle size and distribution. A relatively slow rate of hydrolysis of TEOS occurred during the semi-batch process, which resulted in larger silica particles and a narrower size distribution\textsuperscript{12}. Even though several studies detail how various controlling factors affect the size and distribution of aluminosilicate nanospheres, there are no systematic reports about the effect of kinetics, heteroatom, surfactant on nanosphere formation.

EXPERIMENTAL

In a typical procedure to synthesize silica nanosphere, 3.3g of sodium aluminate (99\%, s.d.fine, India) was mixed well with 0.7g of sodium hydroxide (99\%, s.d.fine, India) and 129g of distilled water. This mixture was stirred well until a clear solution was obtained (solution A). Another solution B was made by thorough mixing of 46.47g of silica sol (30\%) and 18.3g of ethylene diamine (EDA, 99\%, Aldrich, U.S.A). Solution A and B were mixed well to make a clear mixture and charged into a teflon lined steel autoclave. Growth was carried out at 177\(^\circ\)C for 5 days. The product was removed and washed with deionised water and the sample was dried at 110\(^\circ\)C for 24h. It was subjected to various physicochemical characterizations. Synthesis carried out for 10 days and the sample was taken for comparison purpose.

X-ray diffraction patterns were recorded on a Rigaku (D/MAX III VC) instrument in the 2q
region of 5-45°. Scanning electron microscope pictures were taken using a JEOL JSM 5200 microscope: chemical analysis was carried out by XRF using a Rigaku 3070 X-ray Spectrometer. Carbon and nitrogen were estimated by microanalysis. The framework IR spectra were recorded in the diffuse reflectance mode using 5% sample in KBr (Nicolet 60SXB). To study the nature of the surface hydroxyl groups in the transmittance mode, self-supported wafers (~10mg/cm²) and an IR cell with controlled environment chamber were used. The sample was activated in situ at 673K under vacuum (10⁻⁶ torr) for 4h and then cooled to 323K before recording the spectrum (4cm⁻¹ resolution, averaged over 500 scans). 

**RESULT AND DISCUSSION**

Nanospheres was synthesized at 5 days compared to the complete grown grains crystal sample in ten days (Fig. 1). XRD patterns shows that both are Ferrierite type zeolite molecular sieve. Elemental analysis of the calcined samples gave the chemical composition as 1.75Na₂O [Al₂O₃: 22SiO₂]. The aluminium and sodium can be removed on 0.1 N HCl treatment by overnight. The elemental composition of both the samples were same. The morphology of the nanospheres are spherical with 200 nm particle size, where the other sample was 6 x 17 mm in size.

Table - 1 summarizes the effect of synthesis procedures on nanospheres shapes and sizes; images are shown in Fig. 1-3. The silica nanoparticles were synthesized using 1.85Na₂O: Al₂O₃: 15.2SiO₂: 59.2H₂O: 19.7C₂DN at 177°C. The particles had round shapes, except those prepared at 10 days, which had grain shapes with narrow size distribution. During that time the particles growth had completed. Another sample (No. 2) prepared using surfactant with aluminium. Sample prepared without aluminium shows a fully grown crystals. Non-aqueous media synthesized sample with vanadium and silicon gives nanospheres (sample 3), in absence of silicon gives fully grown crystals (sample 6).

The TG/DTA curves of the template containing nanosphere (sample 1) shows that the main difference between the two TG/DTA is that the nanosphere sample were loose all the template in two steps, the first endothermic loss at 103°C (7.42% loss) is due to the loss of physisorbed template and water the second exothermic step at 325°C (3.69% loss) is due to the oxidative decomposition of the template. As the particle size is small the decomposition is easier in this case. Where the fully grown samples (sample 4) loss in five stages. In the low temperature region up to 586K, endothermic weight loss occurs in two stages (6.56% and 1.88%) mainly due to the loss of adsorbed water and template. In the temperature region of 586 to 1086K, there are three stages of

Fig. - 1: Scanning electron micrograph of a) sample 4 and b) sample 1
exothermic weight loss (1.41%, 4.22%, and 3.59% respectively) due to the oxidative decomposition of the organic template occluded in the sample. The probable oxidation stages as follows: in the 586 – 642 K region occluded template molecules in the pores oxidatively decompose with burning of a part of the hydrocarbon, while in the region 642 – 817 K, protonated template molecules interacting strongly with the framework charge and the fragments of templates decomposed and adsorbed at lower temperatures are partially oxidized leaving behind a coke residue. In the last stage (817 – 1086 K), this coke is eliminated by oxidation. Based on the total loss due to template removal and the carbon and nitrogen analysis (2.21%C, 2.04%N for nanospheres, and 4.40% C, 4.15% N for grains). The \(^{27}\text{Al}\) and \(^{29}\text{Si}\) MAS NMR spectra of nanospheres and grains shows that the \(^{27}\text{Al}\) NMR spectra of the samples contain a single symmetrical \(^{27}\text{Al}\) line at 52.80 ppm with respect to Al\((\text{H}_2\text{O})_6^{3+}\) indicating a single tetrahedral aluminium species, confirming the high purity of the samples. The two \(^{29}\text{Si}\) peaks in grain sample shows peaks at -107.00 and -111.51 ppm are due to the Si present in Si:\[3\text{Si}:\text{Al}\] and Si:\[4\text{Si}\] environments respectively. In nanosphere only one peak at 112.45 ppm, for Si:\[4\text{Si}\] environment was appeared. Small shoulder peaks at 123.63 and 134.20 also appeared for environmentally different Si:\[4\text{Si}\] species.

The FTIR spectrum of the as-synthesized nanosphere and grain in the framework region gives bands for the different modes of tetrahedral linkages give bands at 1232(sh), 1062(vs), 1208(sh), 797(s), 696(w), 581(s), 528 (sh), 460(sh), 424(s) cm\(^{-1}\). However the nanocrystalline sample

\begin{table}[h]
\centering
\caption{Influence of various synthesis parameters on synthesis of aluminosilicate nanospheres}
\begin{tabular}{|c|c|c|c|}
\hline
S. No. & Gel composition (molar ratio) & Temperature \(^{\circ}\text{C}\) & Time (days) & Particle size \\
\hline
1. & 1.85Na\textsubscript{2}O: Al\textsubscript{2}O\textsubscript{3}: 592H\textsubscript{2}O: 19.7C\textsubscript{2}DN & 177 & 5 & 200 nm \\
2. & SiO\textsubscript{2}: 0.02 Al\textsubscript{2}O\textsubscript{3}: 0.27 (CTMA)\textsubscript{2}O: 0.13 (TMA)\textsubscript{2}O: 60 H\textsubscript{2}O & 100 & 5 & 250 nm \\
3. & 1Al\textsubscript{2}O\textsubscript{3}: 1.8P\textsubscript{2}O\textsubscript{5}: 0.3SiO\textsubscript{2}: 0.02V\textsubscript{2}O\textsubscript{5}: 4.5HEM: 45EG. & 200 & 15 & 500 nm \\
4. & 1.85Na\textsubscript{2}O: Al\textsubscript{2}O\textsubscript{3}: 15.2SiO\textsubscript{2}: 592H\textsubscript{2}O: 19.7C\textsubscript{2}DN & 177 & 10 & 6 x 17 \(\mu\text{m}\) \\
5. & SiO\textsubscript{2}: 0.27 (CTMA)\textsubscript{2}O: 0.13 (TMA)\textsubscript{2}O: 60 H\textsubscript{2}O & 100 & 5 & 8 \(\mu\text{m}\) \\
6. & 1Al\textsubscript{2}O\textsubscript{3}: 1.8P\textsubscript{2}O\textsubscript{5}: 0.3SiO\textsubscript{2}: 0.02V\textsubscript{2}O\textsubscript{5}: 4.5HEM: 45EG. & 200 & 15 & 2 \(\mu\text{m}\) \\
\hline
\end{tabular}
\end{table}

\(\text{C}_2\text{DN} = \) ethylene diamine, CTMA = cetyltrimethylammonium, TMA = tetramethyl ammonium, HEM = hexamethylenimine and EG = Ethylene glycol

Fig. - 2: Scanning electron micrograph of a) sample 5 and b) sample 2
The bands can be assigned to asymmetric stretching, symmetric stretching, pore opening and bending vibrations of T-O-T linkages described in earlier literature.

The transmittance spectrums of the calcined samples in the –OH stretching region shows three bands at 3736, 3592 and 3552 cm⁻¹ are noticed for grains. Nanospheres gave bands at 3733, 3656, and 3637 cm⁻¹. The band at 3736 cm⁻¹ can be assigned to terminal Si-OH groups. The other two bands are assigned to bridging hydroxyl groups (Si-OH-Al) situated in the pores confined by the ten and eight membered rings respectively.

Conclusions

We have synthesized diverse silica nanoparticles using various types of procedures. Silica nanospheres samples were prepared by reducing the time duration (5 days compared to 10 days) of the completely grown grains. Scanning electron microscope proves the nanospheres samples are uniform with 200 nm particle size. The characterization of the synthesized material by XRD, TG/DTA, FT-IR and MAS-NMR also studied.

ACKNOWLEDGEMENTS

The author thanks Brain Pool Program, South Korea for a fellowship.

REFERENCES

1. Iler, R.K.: The Chemistry of Silica, Wiley, New York (1979).
2. Sacks, M.D., Tseng, T.Y. J. Am. Ceram. Soc. 67: 526 (1984).
3. Masuda, R., Takahashi, W. and Ishii, M. J. Non-Cryst. Solids. 121: 389 (1990).
4. Yamashita, A., Demiya, M., Mori, H. and Maekawa, T. J. Ceram. Soc. Jpn. 100 1444 (1992).
5. Taira, M. and Yamaki, M. J. Mater. Sci. Mater. Med. 6: 197 (1995).
6. Stoer, W. Fink, A. and Bohn, E. J. Colloid Interface Sci. 26: 62 (1968).
7. Bogush, G.H. and Zukoski, C.F. J. Non-Cryst. Solids 104: 95 (1988).
8. Park, S.K., Kim, K.D. and Kim, H.T. Colloids Surfaces A: Physicochem. Eng. Aspects 197: 7 (2002).
9. Kim, K.D. and Kim, H.T. J. Sol-Gel Sci. Tech. 25: 183 (2002).
10. Sadasivan, S., Rasmussen, D.H., Chen, F.P. and Kannabiran, R.K. Colloids Surfaces A: Physicochem. Eng. Aspects 132: 45 (1998).
11. Kim, K.S., Kim, S.S., Kim, S.K., Kim, J.K. and Kim, W.S. Hwahak Konghak 38: 817 (2000).
12. Voronkov, M.G., Mileshkevich, V.P. and Yuzhelevski, Y.A. The Siloxane Bond, Consultants Bureau, New York, (1978).