Materials Science Research India Volume **3**(1a), 23-26 (2006)

A NOVEL SYNTHESIS PROCEDURE AND ITS CHARACTERIZATION OF SILICA NANOSPHERE

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(Received: May 28, 2006; Accepted: June 13, 2006)

ABSTRACT

Three different procedures are reported for the synthesis of silica nanosphere. In all the method either agglomeration time, addition of hetero atom or use of surfactants plays a vital role. In absence of it give a full fledged crystal. This method is applicable to, irrespect of template, aluminium and silica source. The particles are in nanosphere with size in range from 100 to 500 nm. It is a convenient procedure than the conventional non-aqueous media synthesis.

Key words: Aluminosilicate, Nanospheres, Hydrothermal synthesis, XRD, SEM, TG/DTA, FT-IR and MASNMR.

INTRODUCTION

Amorphous aluminosilicate nanoparticles are used in many applications including ceramics, catalysis, pharmaceutical, electronic packaging and chemical-mechanical polishing[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[6]. Bogush and Zukoski reported the influence of reaction parameters such as ammonia and water contents on the particle size and distribution[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[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[12].

The mechanism of the aluminosilicate nanospheres was generally suggested to be via hydrolysis of silica source and alumina source to form the singly hydrolysed monomer. Subsequently, this intermediate reaction product condenses and eventually forms aluminosilicate.

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^{o}C for 5 days. The product was removed and washed with deionised water and the sample was dried at 110^{o}C for 24h. It was subjected to various physicochemical characterizations. Synthesis carried out for 10days 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

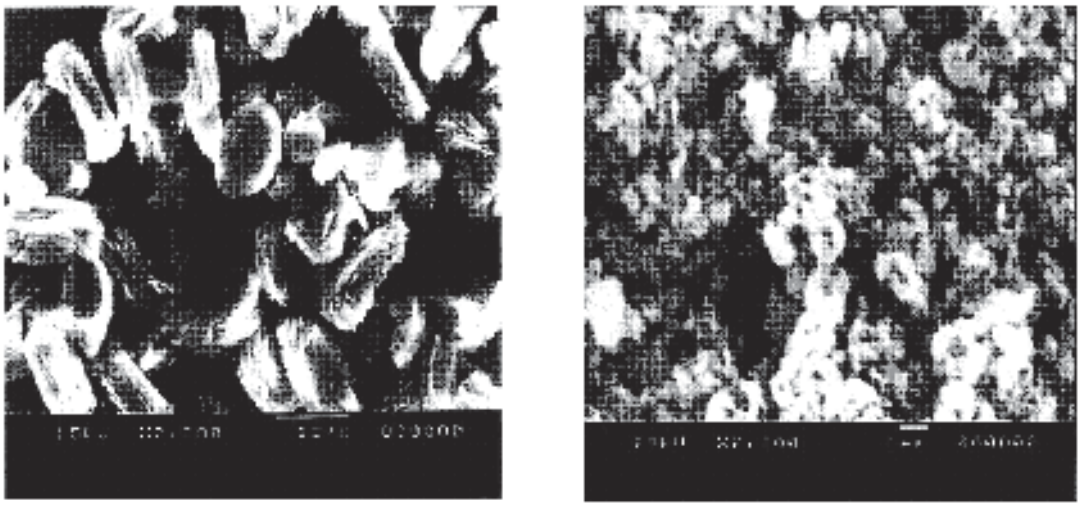
region of 5-45°. Scanning electron microscope pictures were taken using a JEOL JSM 5200 microscope: chemical analysis was carried out by XRF using a Rigaku 3070 X-ray Spectrometer. Carbon and nitrogen were estimated by microanalysis. The framework IR spectra were recorded in the diffuse reflectance mode using 5% sample in KBr (Nicolet 60SXB). To study the nature of the surface hydroxyl groups in the transmittance mode, self-supported wafers (~10mg/cm^{-2}) 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). ^{27}Al and ^{29}Si MAS NMR spectra were recorded on a Bruker MSL 300 spectrometer. ^{29}Si NMR spectra were recorded at 59.6 MHz, 2ms (45°) pulse width and repetition time of 2s. ^{27}Al NMR spectra were recorded at 78.2 MHz, 1ms pulse width and 500 ms repetition time. Tetramethylsilane (for silicon) and 1M $Al(NO_3)_3$ solution (for aluminium) were used as standards.

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 $1.75Na_2O$ [Al_2O_3: $22SiO_2$]. 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 $1.85Na_2O$: Al_2O_3: $15.2SiO_2$: $592H_2O$: $19.7C_2DN$ 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



a **b**

Fig. - 1:Scanning electron micrograph of a) sample 4 and b) sample 1

Table - 1: Influence of various synthesis parameters on synthesis of aluminosilicate nanospheres

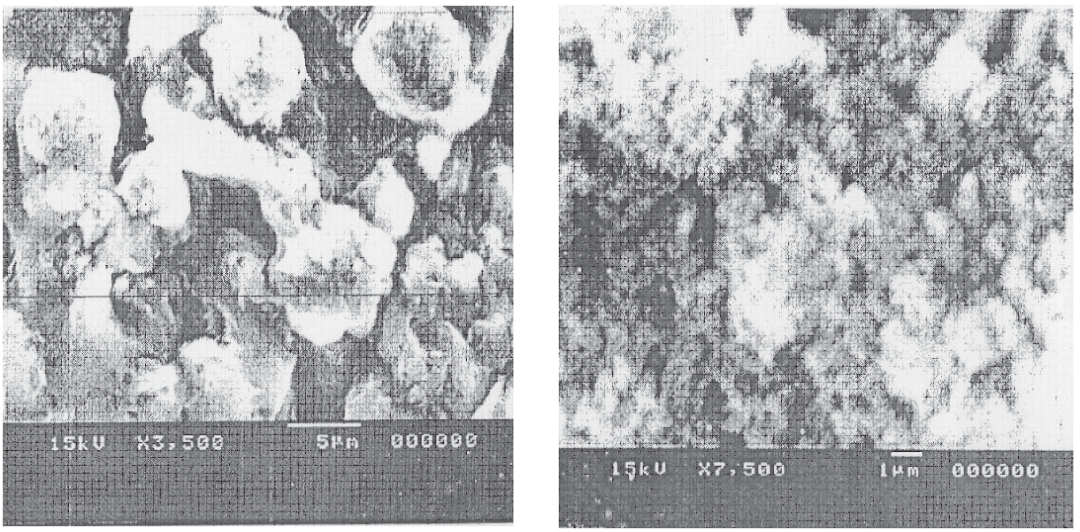
S. No.	Gel composition (molar ratio)	Temperature (°C)	Time (days)	Particle size
1.	$1.85Na_2O$: Al_2O_3: $15.2SiO_2$: $592H_2O$: $19.7C_2DN$	177	5	200 nm
2.	SiO_2 : 0.02 Al_2O_3 : 0.27 $(CTMA)_2O$: 0.13 $(TMA)_2O$: 60 H_2O	100	5	250 nm
3.	$1Al_2O_3$: $1.8P_2O_5$: $0.3SiO_2$: $0.02V_2O_5$: 4.5HEM: 45EG.	200	15	500 nm
4.	$1.85Na_2O$: Al_2O_3: $15.2SiO_2$: $592H_2O$: $19.7C_2DN$	177	10	6 x 17 µm
5.	SiO_2 : 0.27 $(CTMA)_2O$: 0.13 $(TMA)_2O$: 60 H_2O	100	5	8 µm
6.	$1Al_2O_3$: $1.8P_2O_5$: $0.3SiO_2$: $0.02V_2O_5$: 4.5HEM: 45EG.	200	15	2 µm

C_2DN = ethylene diamine, CTMA = cetyltrimethylammonium, TMA = tetramethyl ammonium, HEM = hexamethyleneimine and EG = Ethylene glycol

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).

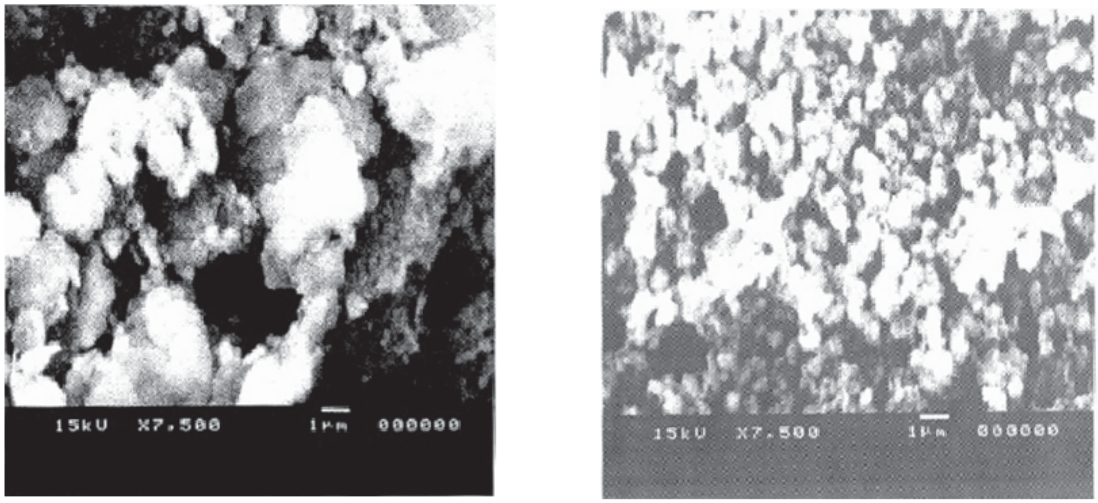
The ^{27}Al and ^{29}Si MAS NMR spectra of nanospheres and grains shows that the ^{27}Al NMR spectra of the samples contain a single symmetrical ^{27}Al line at 52.80 ppm with respect to $Al(H_2O)_6^{3+}$ indicating a single tetrahedral aluminium species, confirming the high purity of the samples. The two ^{29}Si peaks in grain sample shows peaks at -107.00 and -111.51 ppm are due to the Si present in Si:[3Si:Al] and Si:[4Si] environments respectively. In nanosphere only one peak at 112.45 ppm, for Si:4Si environment was appeared. Small shoulder peaks at 123.63 and 134.20 also appeared for environmentally different Si:4Si 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



a **b**

Fig. - 2: Scanning electron micrograph of a) sample 5 and b) sample 2



a **b**

Fig. - 3: Scanning electron micrograph of a) sample 6 and b) sample 3

gave peak at 700(w) as shoulder peak. 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 MASNMR also studied.

ACKNOWLEDGEMENTS

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

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