Synthesis of Spherical mesoporous silica (I) : MSU - X

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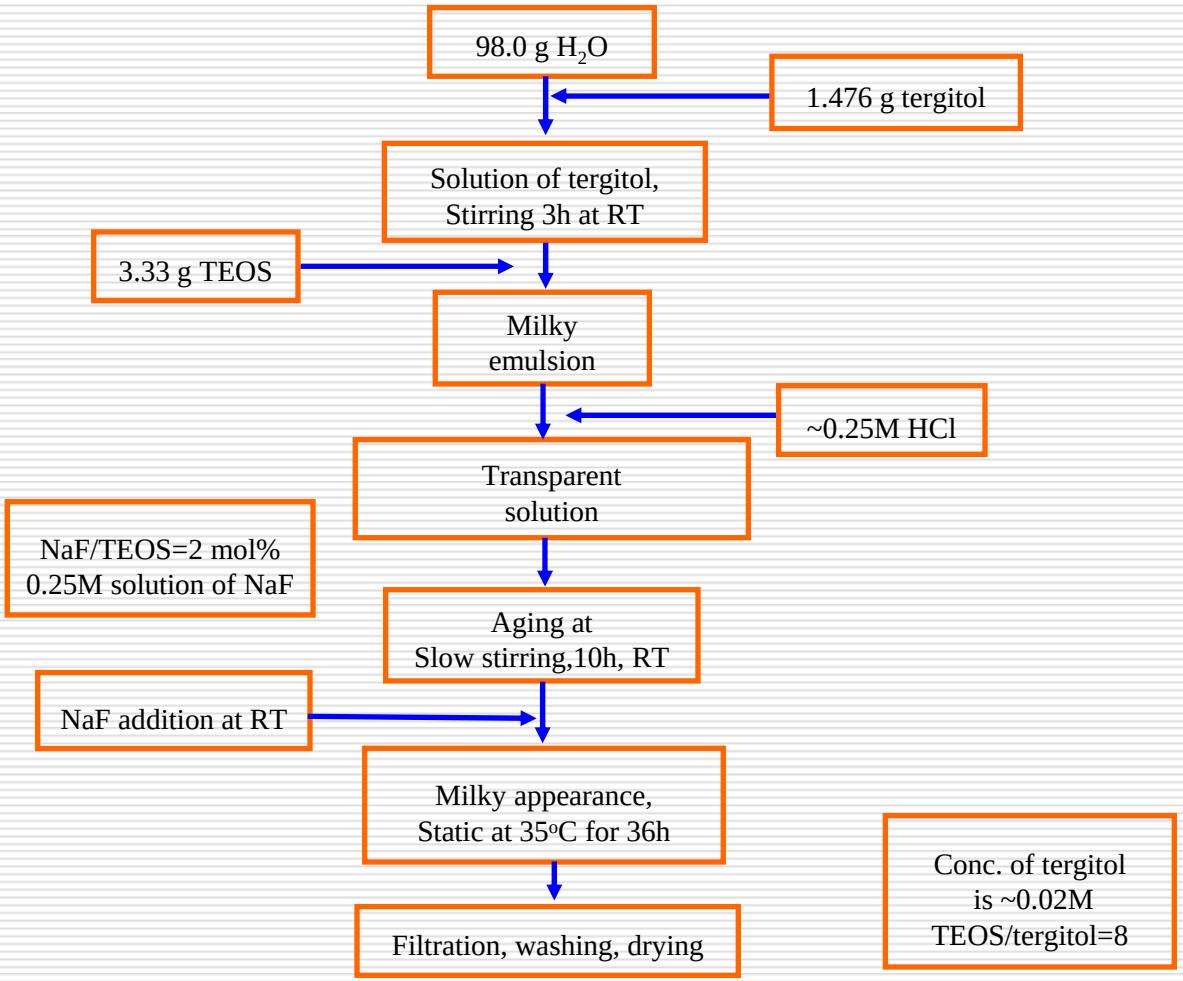
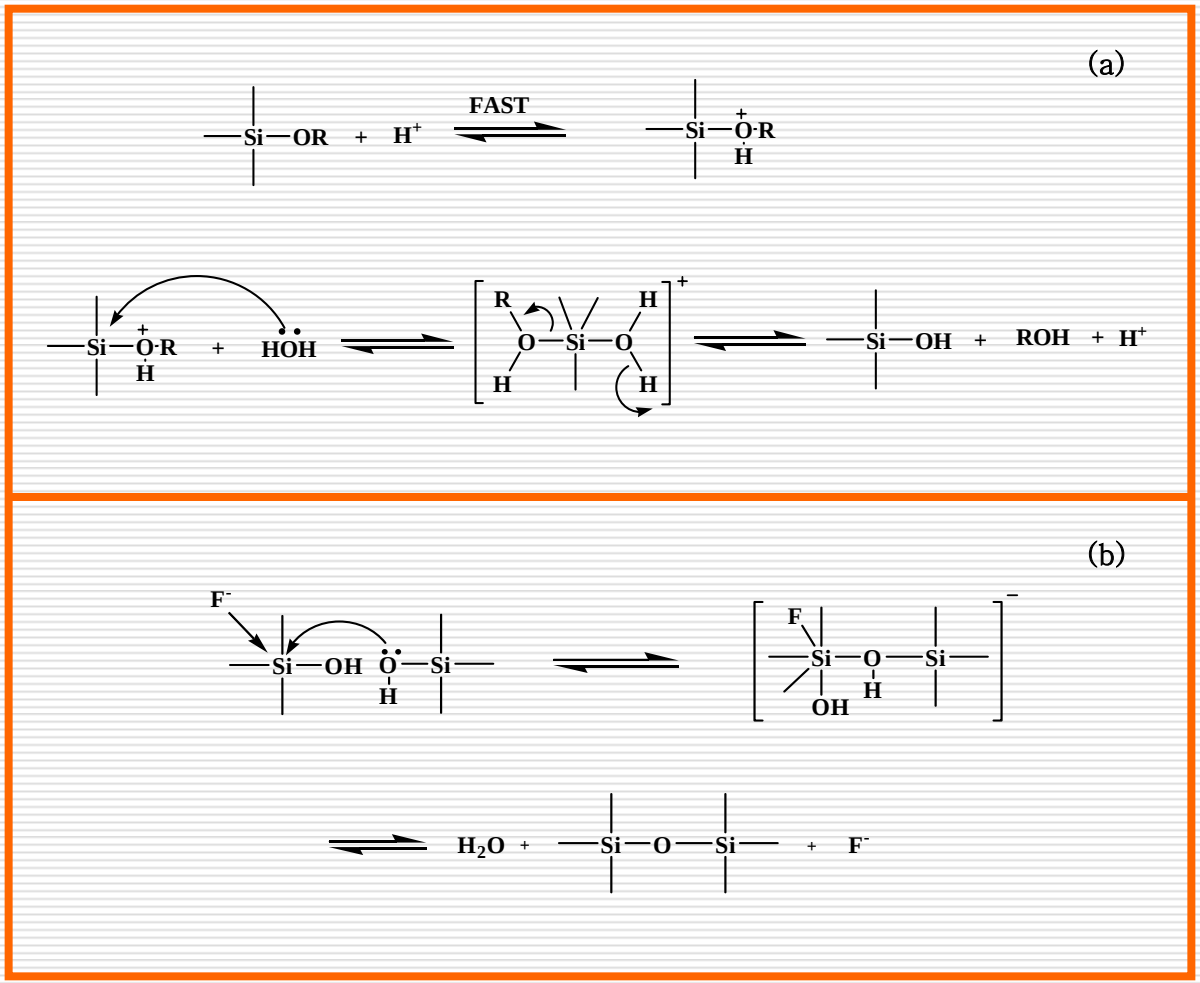
Introduction

- Spherical MSU-1 material was prepared using TEOS as silica source and alkyl polyethyene oxide as a surfactant and made by two-step process. The hydrolysis of TEOS is done in acidic condition and condensation of silica is induced by fluoride ion. It is found that non-stirring static condensation period is essential for the formation of spherical morphology. The growth rate of the particles is examined. The effects of NaF concentration, silica/surfactant molar ratio and condensation temperature on particle size are also probed. The particles are characterized by XRD, SEM, and N_2 adsorption/desorption isotherm analysis. The applicability of the materials to reversed phase HPLC is also Verified.

Experimental

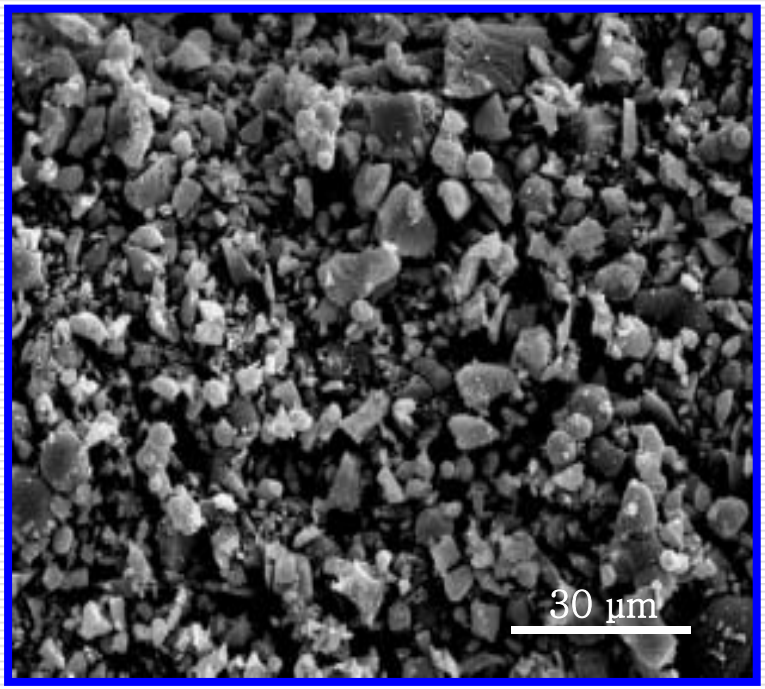


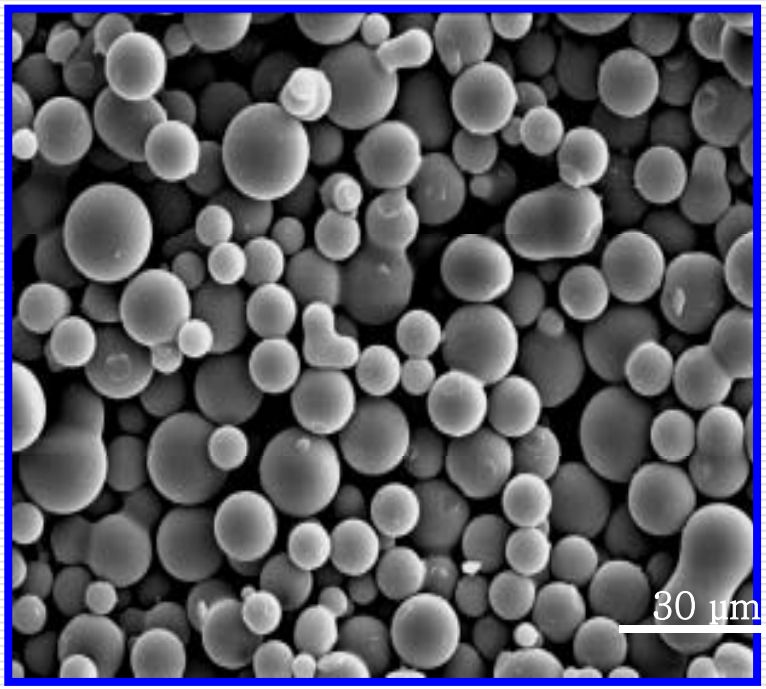
Mechanisms



Results & Discussion

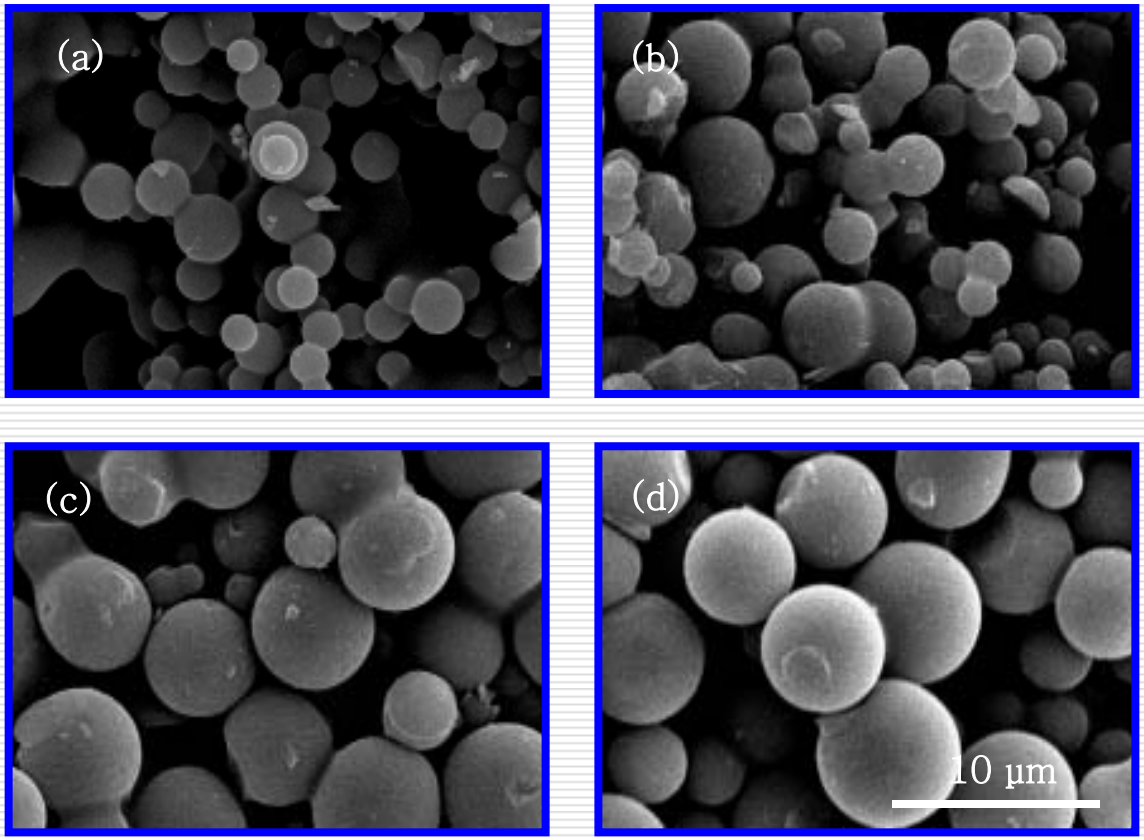
SEM images of the as-made MSU-1 samples
(a) with stirring and
(b) without stirring in the condensation steps





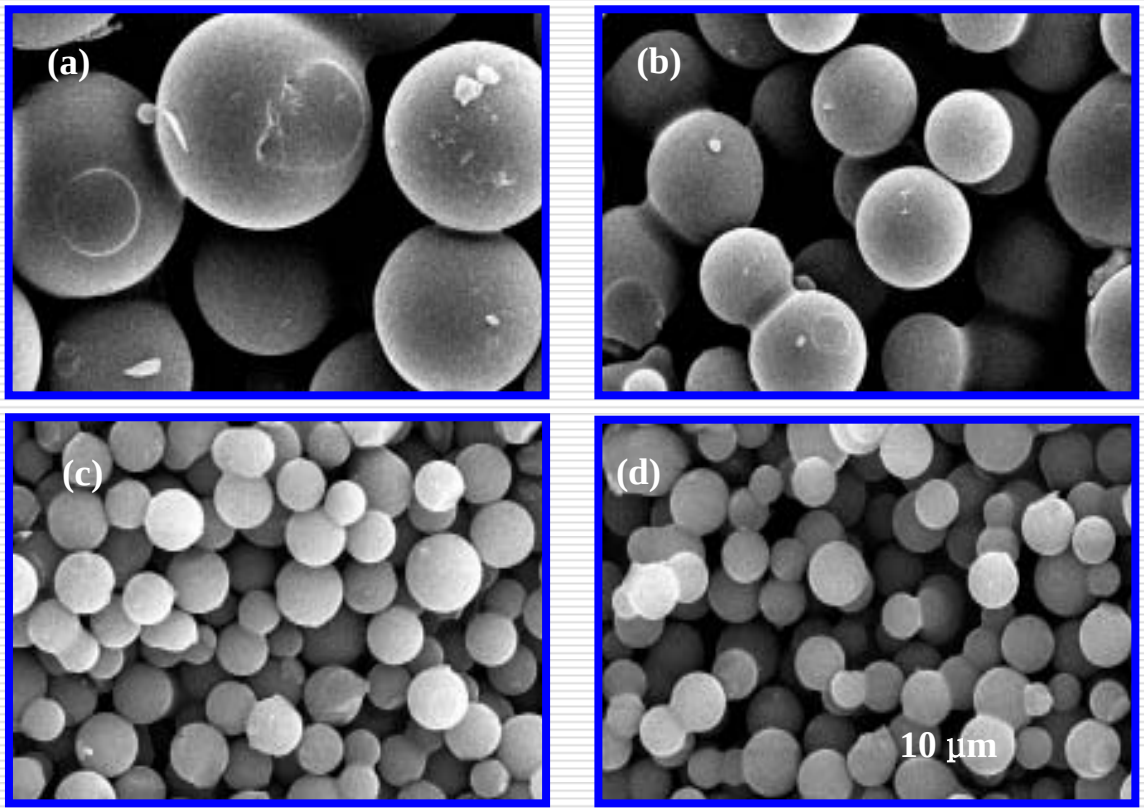
Results & Discussion

SEM images of the as-made MSU-1 samples prepared without stirring in the condensation step for a period of
(a) 30 min, (b) 60 min, (c) 120 min and (d) 3 days



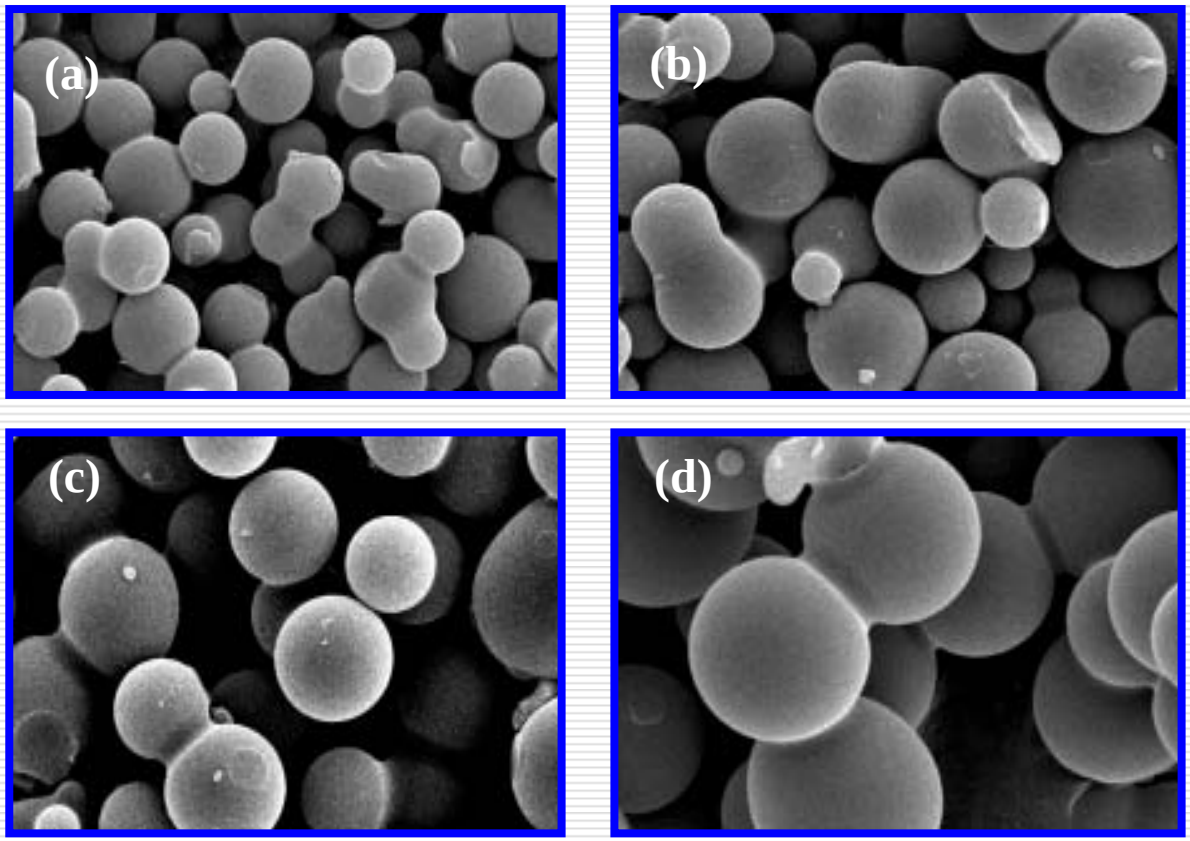
Results & Discussion

SEM images of the samples prepared with varying NaF mole percent over TEOS (a) 1 mol%, (b) 2 mol%, (c) 6 mol% and (d) 10 mol%



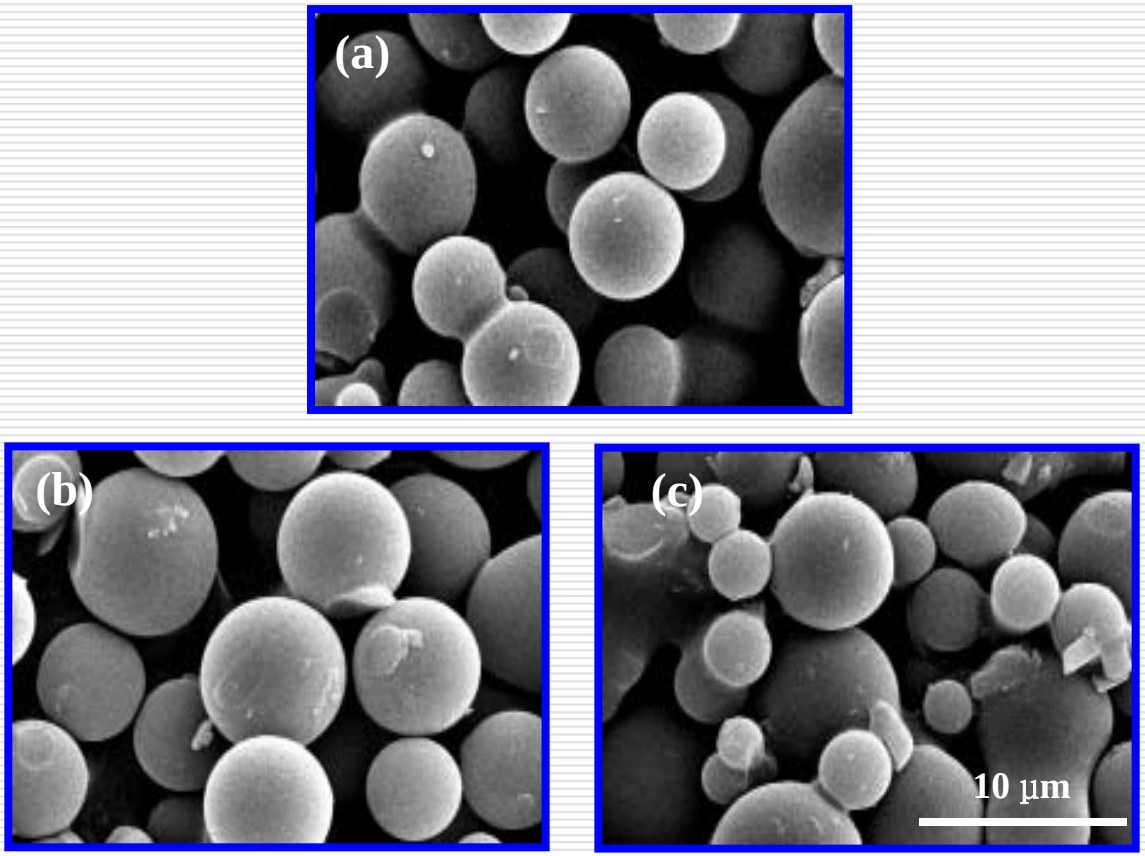
Results & Discussion

SEM images of the samples prepared with varying Si/Surfactant mole ratios of (a) 4, (b) 6, (c) 8 and (d) 10



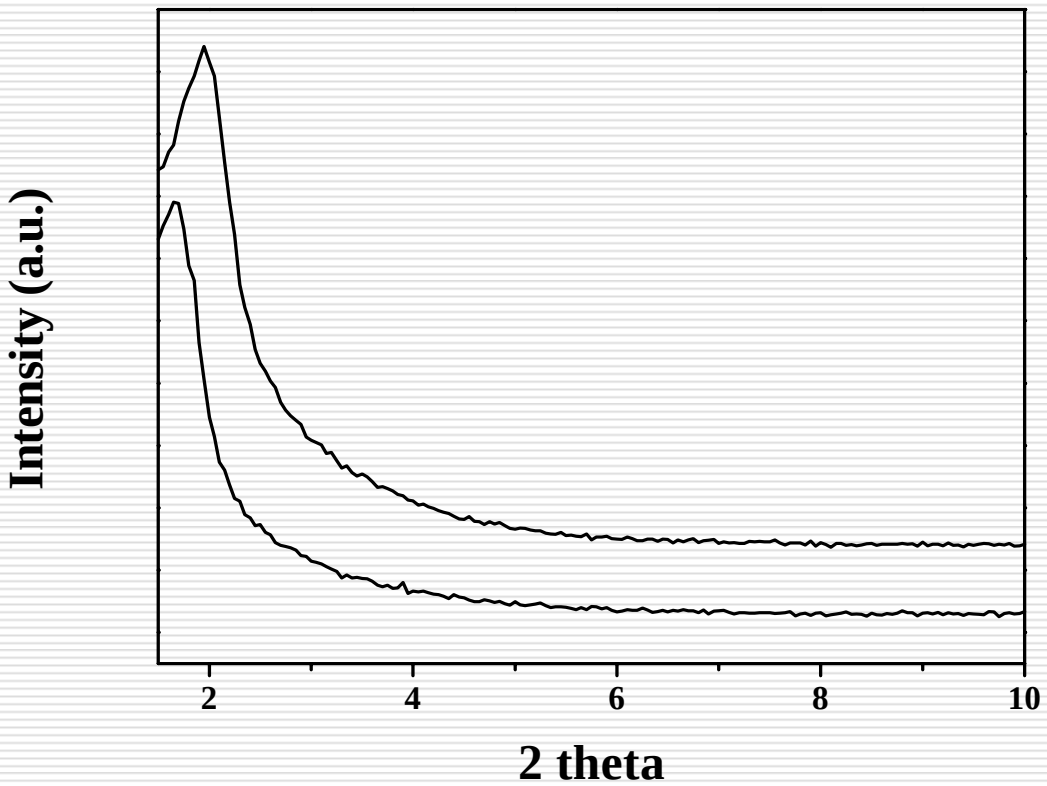
Results & Discussion

SEM images of the samples prepared of different condensation temperatures of (a) 35 ℃, (b) 45 ℃, and (c) 55 ℃



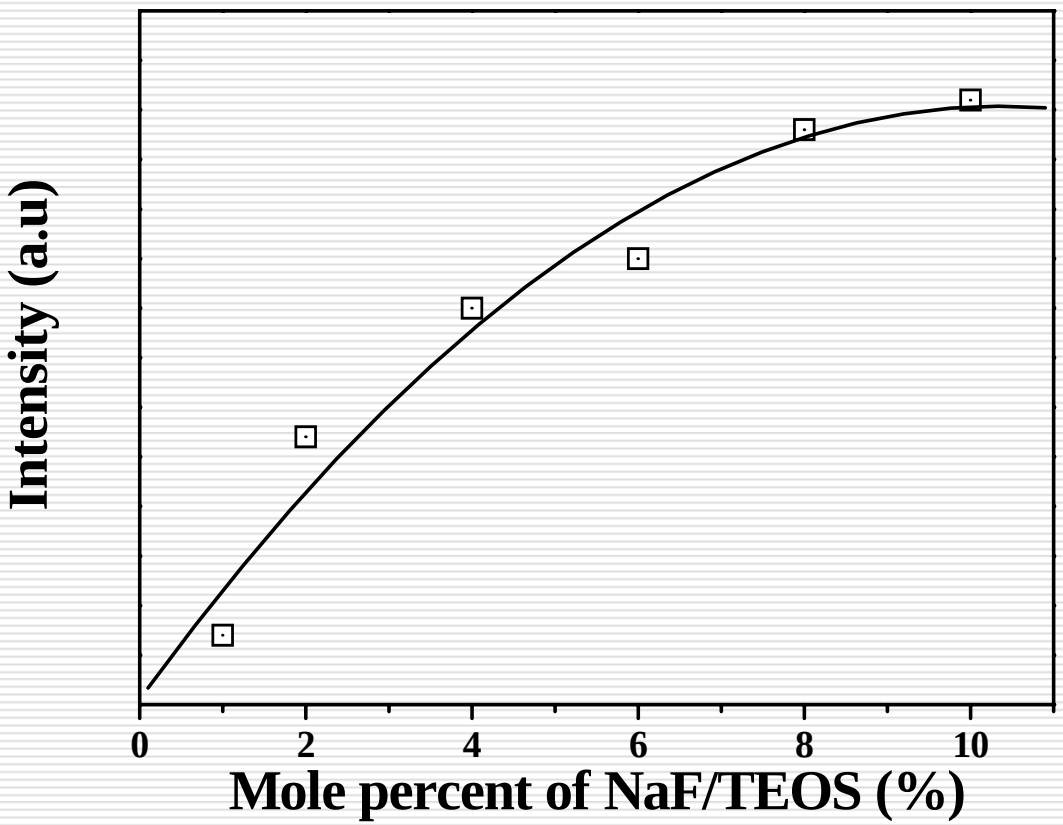
Results & Discussion

Small angle XRD patterns of the MSU-1 samples prepared using NaF/TEOS mole ratio 0.06 (a) as-made and (b) calcined at 620 ℃ for 6 h.



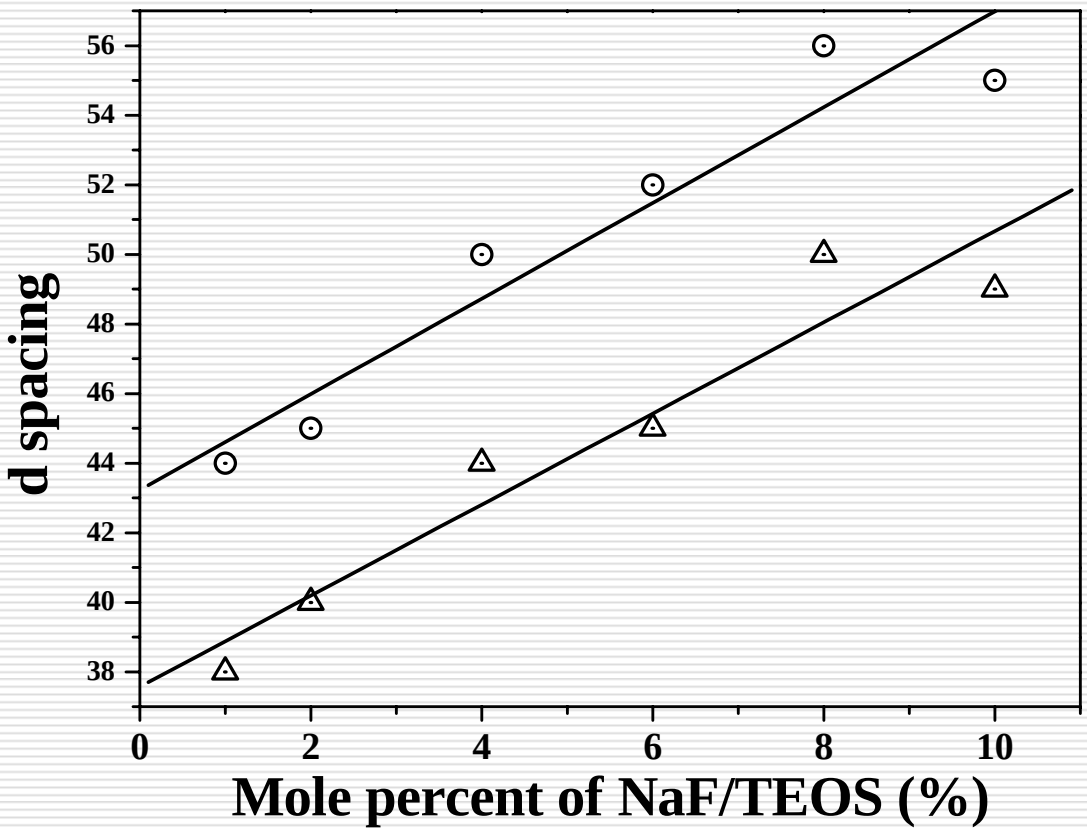
Results & Discussion

The increase in intensities of small angle XRD peaks with the increase of mol % of NaF.



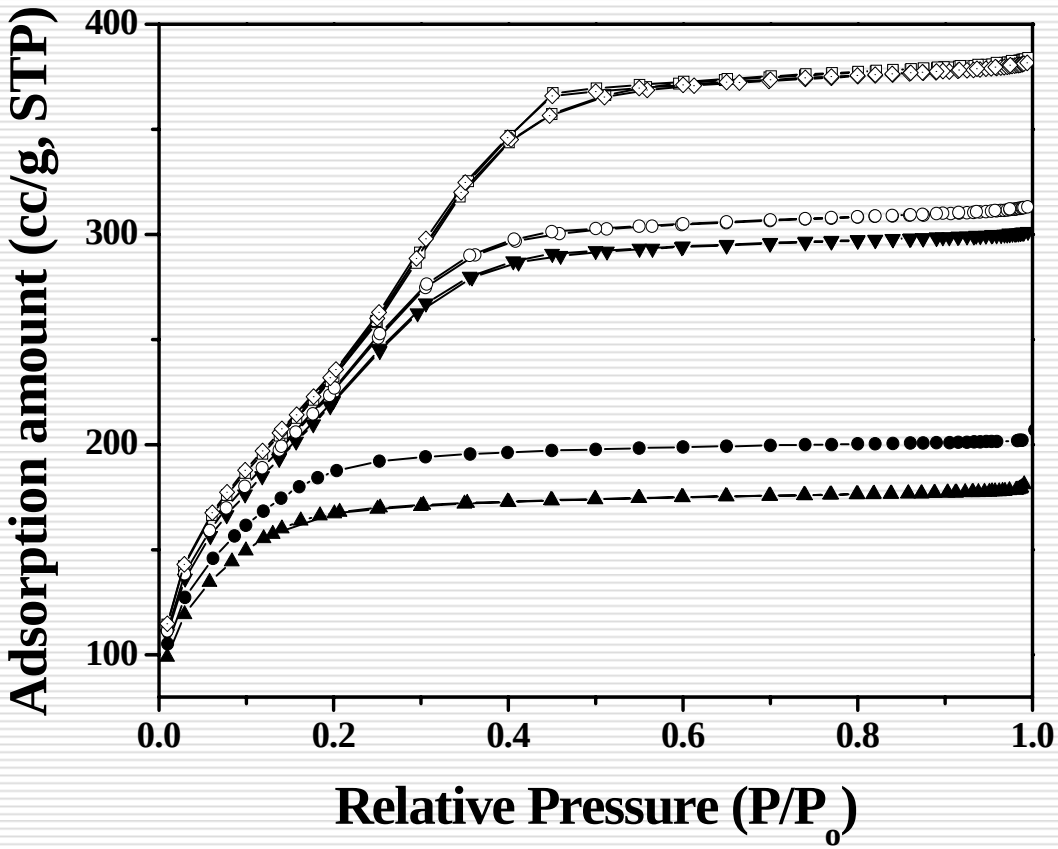
Results & Discussion

The linear increase in d spacing of the XRD peaks with the increase of NaF mole % over TEOS for both the (a) as made and (b) calcined samples.



Results & Discussion

N2-adsorption/desorption isotherm for the silica samples prepared using NaF of ▲ 1 mol%, ● 2 mol%, ▼ 4 mol%, ○ 6 mol%, ◇ 8 mol% and □ 10 mol%.



Results & Discussion

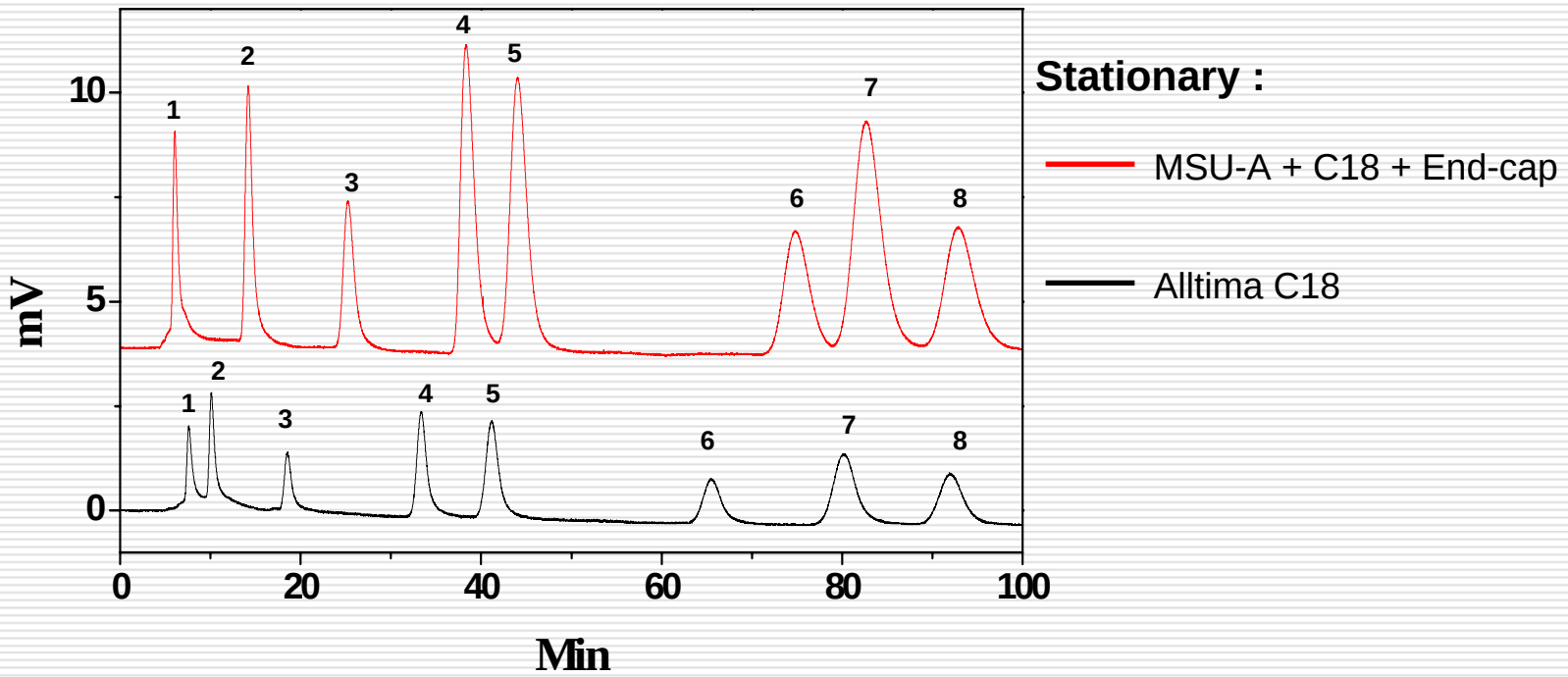
Textural properties of MSU-1 samples prepared with different NaF/TEOS mole ratios different temperatures with Si/Surf. = 8 and aging time = 3 days.

samples	Synthesis temperature	Surface area (m^2/g)	Pore volume (cc/g)	Diameter (Å)*
1 mol%(NaF/TEOS)	35	594	0.28	<20
2 mol%(NaF/TEOS)	35	654	0.31	<20
2 mol%(NaF/TEOS)	45	661	0.31	<20
2 mol%(NaF/TEOS)	45	681	0.32	20
4 mol%(NaF/TEOS)	35	816	0.46	20
6 mol%(NaF/TEOS)	35	837	0.48	21
8 mol%(NaF/TEOS)	35	867	0.58	27
10 mol%(NaF/TEOS)	35	860	0.59	30

(* : pore diameter was calculated by BJH method using desorption branch of the isotherm)

Results & Discussion

Mobile phase : 70/30 v/v% MeOH/H2O
Flow rate : 10μL/min
Solutes
1: 4-Methoxyphenol , 2: Acetophenone , 3: Ethylbenzoate , 4: Ethylbenzene
5: Acenaphthylene , 6: Acenaphthene , 7: Phenanthrene , 8: Anthracene



Conclusions

To have the desired particle morphology and to establish the reproducibility of the process, static condensation period is as important as the separation of the hydrolysis and the condensation steps. Full growth of the particles can be achieved within 2 h instead of aging of three days. By changing the mole ratios of NaF/TEOS and TEOS/Surf., the particle size can be controlled ; amount of NaF and TEOS/Surf. ratio need to be controlled to reduce the particle size. The optimum condensation temperature is in the range of 35 to 45 ℃. The mesoporosity of the materials can be increased with the increasing of the amount of NaF. Pore sizes up to 3.0 nm with pore volume 0.59 cc/g and BET surface area up to 860 m^2/g can be achieved using 10 mol % of NaF. As a mechanism, simultaneously isotropically growth of nanometric micelles and their non-directional aggregation into micrometric spheres may be proposed.