Influence of catalyst and solvent on preparation of silica solid core mesoporous shell

Article *in* Journal of the Indian Chemical Society · May 2012

CITATIONS
0

READS
81

4 authors:

N. Venkatathri
National Institute of Technology, Warangal
439 PUBLICATIONS **1,004** CITATIONS
SEE PROFILE

Rajini Anumula
National Institute of Technology, Warangal
38 PUBLICATIONS **163** CITATIONS
SEE PROFILE

Nookaraju Muralasetti
Anil Neerukonda Institute of Technology and Sciences
29 PUBLICATIONS **80** CITATIONS
SEE PROFILE

Ingala Ajitkumar Reddy
National Institute of Technology, Warangal
35 PUBLICATIONS **292** CITATIONS
SEE PROFILE

J. Indian Chem. Soc.,
Vol. 89, May 2012, pp. 1-4

Influence of catalyst and solvent on preparation of silica solid core mesoporous shell

N. Venkatathri*, A. Rajini, M. Nookaraju and I. A. K. Reddy

Department of Chemistry, National Institute of Technology, Warangal-506 004, Andhra Pradesh, India

E-mail : venkatathrin@yahoo.com

Manuscript received 17 September 2010, revised 25 July 2011, accepted 07 September 2011

Abstract : Silica spheres with sub-micrometer sized solid core mesoporous shell structure were prepared. Effect of different catalysts and solvents on synthesis of silica solid core mesoporous shell is studied. Depend on solvent and catalyst the particle size and shape are varied. Experimental results show *n*-propylamine. diethylamine, triethanolamine were entrapped inside the morphology. However ammonia did not incorporated due to its low temperature volatilability. Apart from pH, density of the solvent and catalyst plays important role in particle growth. There is an optimum value of density, above or below which, they did not give precipitate. Use of octadecyltrimethoxy silane normalizes the particle size, when ammonia catalyst is used. Use of triethanolamine instead of ammonia gives silica hollow cuboids.

Keywords : Silica solid core, mesoporous shell, solvent, catalyst, microscopy, amines.

Introduction

Since the invention of mesoporous silica molecular sieves[1,2], a lot of its application were brought out in the fields of catalysis[3], separation[4] and nanoscience[5-7]. In recent years much attention were paid to its morphology[8-12], result in exploring thin films, monoliths, hexagonal prisms, toroids, discoids, spirals, dodecahedron and hollow sphere shapes[13-27]. Among them hollow spheres are having wide applications like catalysis, chromatography, controlled release of drugs, fillers with low dielectric constant, pigments and hosts for optically active compounds[20,25-29]. Silica solid core mesoporous shell are used as template to synthesis hollow nanospheres[26]. Change in any of its synthesis constituent may rise in preparation of interesting materials. Besides use of hollow silica sphere application is restricted due to its restricted shape. Synthesis of other type hollow silica will expand its scope.

The pH value of the reaction gel will affect the morphology of silica particles. To control the pH value of the system, amine is a good choice. Compared with ammonia or NaOH, the types of amine are very simple and they are commercially available widely. The relative strength of amine base is usually expressed as either pK_a or pK_b of conjugate acid[30]. The strong base has a high pK_a value. In our experiments ammonia (pK_a = 9.25), *n*-propylamine (pK_a = 10.7), triethylamine (pK_a = 10.8) and diethylamine (pK_a = 11.0) were used to catalyze the hydrolysis and the condensation of TEOS. The key factor was the pH, density of amines, otherwise the relative strength of amine. All in all the amines used as catalyst was a successful choice.

This paper described a study on influence of different catalyst (e.g. amines) and solvent on synthesis of silica solid core mesoporous shell. The catalysts and solvents having different density, basicity (catalyst) and polarity (solvent).

Experimental

Synthesis of silica solid core mesoporous shell using ammonia catalyst and ethanol solvent was carried out as follows. 3.14 ml of aqueous ammonia (28–30%, Aldrich, USA) was added to a solution containing 74 ml of ethanol (99%, Aldrich, USA) and 10 ml of deionized water. Six milliliters of tetraethoxysilane (TEOS, 98%, Aldrich, USA) was added to the above prepared mixture at 298 K with vigorous stirring and the reaction mixture was stirred continuously for 1 h to yield uniform silica spheres. A solution mixture containing 5 ml of TEOS and 2 ml octadecyltrimethoxy silane (C18TMS, 90%, Aldrich,

USA) was added to the colloidal solution containing the silica spheres (11.4 SiO_2 : 6 NH_4OH : 1 C18TMS : 149 H_2O : 297.5 EtOH) and further reacted for 1 h. The resulting octadecyl group incorporated silica shell/solid core nanocomposite[26] was retrieved by centrifugation, and further calcined at 823 K for 6 h under an air atmosphere to produce the final solid core/mesoporous shell silica material. With the same molar ratio, different catalysts (e.g. amines) and solvents containing reactions were carried out. The results are listed out in Tables 1 and 2.

Table 1. Effect of catalyst on hard core silica shell formation

Sl. no.	Catalyst	Density (g/mL at 25 °C)	Basicity (pK_a)	Yield (%)	Growth period (h)	Particle size (nm)	Particle shape
1.	Amonia	0.600	9.25	77	2	300–400	Spherical
2.	Diethylamine	0.707	11.0	100	2	200	Spherical
3.	*n*-Propylamine	0.719	10.7	100	2	100	Hexagonal
4.	Triethylamine	0.726	10.8	100	2	100	Spherical
5.	*n*-Octylamine	0.782	10.7	–	2–24	–	–
6.	Tetrapropylammonium hydroxide	1.012	–	–	2–24	–	–
7.	Triethanolamine	1.124	–	67	24	50	Cubiod
8	HCl	1.200	-0.7	–	2–24	–	–

Table 2. Effect of solvent on hard core silica shell formation with ammonia as catalyst

Sl. no.	Catalyst	Density (g/mL at 25 °C)	Basicity (pK_a)	Yield (%)	Growth period (h)	Particle size (nm)	Particle shape
1.	*n*-Hexane	0.659	0	–	2–24	–	–
2.	Cyclohexane	0.779	0.2	–	2–24	–	–
3.	Isopropanol	0.785	3.9	58	2	450	Spherical
4.	Ethanol	0.789	5.2	77	2	300–400	Spherical
5.	Acetone	0.791	5.1	46	2	500	Spherical
6.	Octan-l-ol	0.827	4.0	67	2	150	Spherical
7.	Water	1.000	9.0	–	2–24	–	–
8.	Propylene glycol	1.036	–	–	2–24	–	–
9.	Ethylene glycol	1.113	–	–	2–24	–	–

The particle size and shape were analyzed by a Topcon, SM-300 scanning electron microscope (SEM). The copper disc pasted with carbon tape and the sample was dispersed over the tape. The disc was coated with gold in ionization chamber. Transmission electron microscopic (TEM) studies were performed on a JEOL JSM-2000 EX electron microscope operated at 200 kV. The TEM sample was prepared by coating carbon films over Cu grid with sample aqueous suspension (solution was sonicated for 20 min).

Results and discussion

Ammonia catalysed with ethanol experiment without octadecyltrimethoxy silane gave bimodal particle size (200 and 400 nm). On the contrary, in the same procedure with octadecyltrimethoxy silane gave a narrow range of particle size (500 nm).

Influence of catalyst :

Normally organic amines are used as catalyst in molecular sieve synthesis[31]. However it was not used in silica solid core mesoporous shell preparation[32]. When ammonia was used in its synthesis, it was believed that they are not involved in structure build up[33]. If we use organic amine, the same may not occur. Apart from pH change, the amines are expected to entrape in morphology and this can be eliminated by calcination. We have taken *n*-propylamine, *n*-octylamine, triethylamine, diethylamine, triethanolamine, tetrapropyl ammonium hydroxide and HCl apart from ammonia are taken for the

present study. The pH, density and basicity of the amines are expected to play a vital role in particle growth. Another observation we found is with change in density, the time required for particle growth also increases (e.g. *n*-propylamine = 2 h and triethanolamine = 24 h). Except HCl (pH = -0.7) remaining all are basic (pH = 9.25 to 11) in nature. The resulting particle size and shape are given in Table 1. The morphology of the samples are given in Fig. 1. Most of the samples are spherical except *n*-propylamine (hexagonal) and triethanolamine (cuboids) in nanoscale range (100 to 400 nm sizes). Besides *n*-

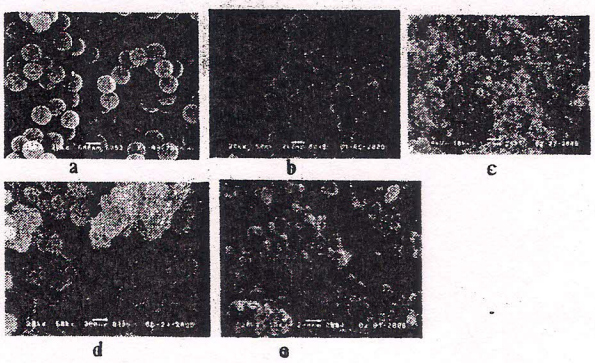

Fig. 1. Scanning electron micrograph of samples synthesized from different catalyst : (a) ammonia, (b) *n*-propylamine, (c) triethylamine, (d) diethylamine and (e) triethanolamine.

octylamine, tetrapropylammonium hydroxide and HCl did not give precipitate. The reason might be due to their higher density. The optimum density required for the particle growth is 0.6 g/mL to 0.782 g/mL. However ethanolamine having density higher to the optimum range, that is 1.124 g/mL also give precipitate. The reason might be due to the presence of dual functional group with higher polarity. The presence of hydroxyl group connected to alkyl chain of amine, which form oligomer to catalyze the precipitation. The particle sizes are decreased with increase in amines molecular size[34]. The reason may be due to the stronger electronic density around nitrogen in bigger molecules activate the nucleation faster which results slow down particle growth and cause smaller particles.

The yields are calculated from the theoretical silica yield. Ammonia yields (Table 1) lesser than remaining amines. It may be due to the the amines are incorporated inside the morphology. The same also supported by the yield data of ammonia with different solvents experiments. Further this is also confirmed by the calcination results The amine catalyzed samples losses more weight compare to ammonia samples. The sample synthesized using ammonia are solid core mesoporous shell morphology as shown by the TEM picture (Fig. 2)[26]. The shell thickness is 40 nm and 400 nm core diameter. The particle size and shape are uniform. The emission electron microscopic picture of sample synthesized using triethanolamine shows to have hollow nanocuboids morphology.

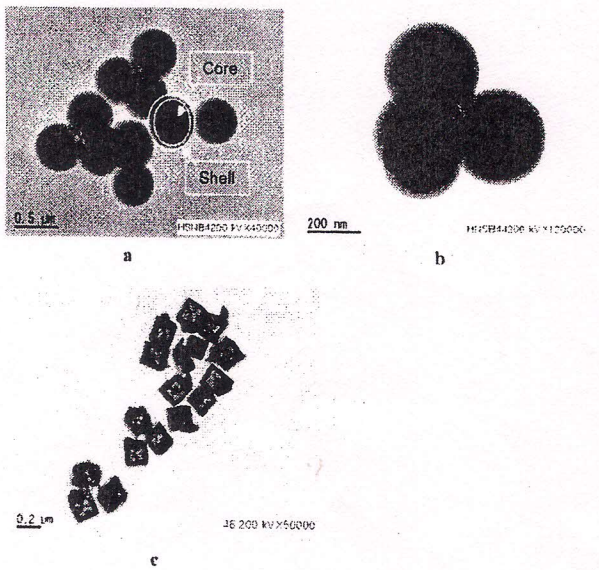

Fig. 2. Transmission electron micrograph of sample synthesized from (a) ammonia (ethanol), (b) triethylamine (ethanol) and (c) triethanolamine (ethanol).

Influence of solvent :

Solvent play a media role in particle growth. Polarity and density[35] of the solvent are playing important role. *n*-hexane, cyclohexane, water, acetone, isopropanol, ethylene glycol, propylene glycol, octan-l-ol, were used instead of ethanol (Table 2). Yields follow parabolic behaviour with respect to density. With polarity the time required to particle growth decreases. The SEM photograph of the samples are given in Fig. 3. All solvents give spherical particles in nanoscale with particle sizes are ranging from 100 to 450 nm. *n*-hexane, cyclohexane, propylene glycol, ethylene glycol did not give precipitate, may be due to excess or lower from optimum density (0.785 g/mL to 0.827 g/mL). Same way polarity also having an optimum range (3.9 to 5.2). There is similarity between the optimum range of catalyst and solvent density (Tables 1 and 2). However, the basicity and polarity are not related. It is reported that with solvent polarity[36] the particle size are decreased. Polarity measured in terms of dielectric constant.

USA) was added to the colloidal solution containing the silica spheres (11.4 SiO_2 : 6 NH_4OH : 1 C18TMS : 149 H_2O : 297.5 EtOH) and further reacted for 1 h. The resulting octadecyl group incorporated silica shell/solid core nanocomposite[26] was retrieved by centrifugation, and further calcined at 823 K for 6 h under an air atmosphere to produce the final solid core/mesoporous shell silica material. With the same molar ratio, different catalysts (e.g. amines) and solvents containing reactions were carried out. The results are listed out in Tables 1 and 2.

Results and discussion

Ammonia catalysed with ethanol experiment without octadecyltrimethoxy silane gave bimodal particle size (200 and 400 nm). On the contrary, in the same procedure with octadecyltrimethoxy silane gave a narrow range of particle size (500 nm).

Influence of catalyst :

Normally organic amines are used as catalyst in molecular sieve synthesis[31]. However it was not used in silica solid core mesoporous shell preparation[32]. When ammonia was used in its synthesis, it was believed that they are not involved in structure build up[33]. If we use organic amine, the same may not occur. Apart from pH change, the amines are expected to entrape in morphology and this can be eliminated by calcination. We have taken *n*-propylamine, *n*-octylamine, triethylamine, diethylamine, triethanolamine, tetrapropyl ammonium hydroxide and HCl apart from ammonia are taken for the

Table 1. Effect of catalyst on hard core silica shell formation

Sl. no.	Catalyst	Density (g/mL at 25 °C)	Basicity (pK_a)	Yield (%)	Growth period (h)	Particle size (nm)	Particle shape
1.	Amonia	0.600	9.25	77	2	300–400	Spherical
2.	Diethylamine	0.707	11.0	100	2	200	Spherical
3.	*n*-Propylamine	0.719	10.7	100	2	100	Hexagonal
4.	Triethylamine	0.726	10.8	100	2	100	Spherical
5.	*n*-Octylamine	0.782	10.7	–	2–24	–	–
6.	Tetrapropylammonium hydroxide	1.012	–	–	2–24	–	–
7.	Triethanolamine	1.124	–	67	24	50	Cubiod
8	HCl	1.200	–0.7	–	2–24	–	–

Table 2. Effect of solvent on hard core silica shell formation with ammonia as catalyst

Sl. no.	Catalyst	Density (g/mL at 25 °C)	Basicity (pK_a)	Yield (%)	Growth period (h)	Particle size (nm)	Particle shape
1.	*n*-Hexane	0.659	0	–	2–24	–	–
2.	Cyclohexane	0.779	0.2	–	2–24	–	–
3.	Isopropanol	0.785	3.9	58	2	450	Spherical
4.	Ethanol	0.789	5.2	77	2	300–400	Spherical
5.	Acetone	0.791	5.1	46	2	500	Spherical
6.	Octan-1-ol	0.827	4.0	67	2	150	Spherical
7.	Water	1.000	9.0	–	2–24	–	–
8.	Propylene glycol	1.036	–	–	2–24	–	–
9.	Ethylene glycol	1.113	–	–	2–24	–	–

The particle size and shape were analyzed by a Topcon, SM-300 scanning electron microscope (SEM). The copper disc pasted with carbon tape and the sample was dispersed over the tape. The disc was coated with gold in ionization chamber. Transmission electron microscopic (TEM) studies were performed on a JEOL JSM-2000 EX electron microscope operated at 200 kV. The TEM sample was prepared by coating carbon films over Cu grid with sample aqueous suspension (solution was sonicated for 20 min).