Synthesis of Porous Silica by co-Micelle Emulsion Templating Technique Using PEG/Acrylamide and 2–(Acryloyloxy)–N,N,N–Trimethylethanaminium Chloride/Acrylamide as Templates

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Abstract

Co-micelle emulsion templating (co-MET) technique is a new method to synthesize uniform and ordered porous silica from tetraethylortosilicate precursor using double polymer as templates. In this study, co-MET technique was conducted by varying template type (namely PEG/acrylamide and 2–(acryloyloxy)–N,N,N–trimethylethanaminium chloride/acrylamide) and percentage of polymer (2.5%, 5%, 10%, 15% and 20% for PEG and 0.5%, 1%, 2.5%, 5%, 10% for 2–(acryloyloxy)–N,N,N–trimethylethanaminium chloride). The resulting porous silica were then characterized by SEM-EDS, BET and XRD to investigates the pore character and structure of silica. Based on SEM-EDS and BET analysis, it is shown that the amount and the type of polymer gave a significant effect to the structure formation of the porous silica. Cationic polymer as templates gave higher surface area and uniform pore size than neutral polymer templates. Polymer concentration of 2.5% gave the best result for both template types, resulting an interconnected mesopore silica with surface area of 615 m^2/g for PEG and 1137 m^2/g for 2–(acryloyloxy)–N,N,N–trimethylethanaminium chloride.

Introduction

Porous ordered silica have attracted wide interest due to its diverse potential appications such as in catalysis[1], separation/molecular sieves[2], absorbents[3], and bioadsorptions[4,5]. Those are usually related to the virtue characteristic of silica which includes high stabilities both thermally and chemically, large surface area, as well as good compatibility with other materials.[6] Many attempts have been conducted to create porous ordered silica having specific characteristic for the desired application, mostly using polymer as templates.

Moreover, meso/macroporous silica materials are new solid inorganic silica framework with interconnected mesopore structures in their macropore walls. They have the potential to provide high diffusion and throughput rates in addition to the unique benefits of ordered mesoporous materials.[7] This material can overcome the limitations of the structured mesoporous materials such as MCM-41, SBA-15, MCF and FDU which are generally lacking of macroporosity.[8,9,10,11]

Mehdi N.S. and co-workers[7] have developed a method of synthesizing silica with co-micelle/emulsion templating (co-MET) techniques, which produces meso/macroporous silica. In their work, triblock polymer of ethylene oxide/propylene oxide/ethylene oxide and acrylamide were used as regulator of meso- and macroporosity. The structure of silica obtained by co-MET techniques gave both meso- and macropore structures connected to each other. This allows the material to be used for various application processes involving large molecules such as in catalysis, adsorptions, biosensors, and bioseparations. Therefore we are challenged to find the effect of another neutral polymer templates (PEG 4000) and cationic templates known as adamquat 80 MC (2–(acryloyloxy)–N,N,N–trimethylethanaminium chloride) to the formation of porous silica structures using co-MET techniques with some modification.

Materials and Experimental Procedures

Materials

The chemicals used were tetraethylortosilicate (TEOS) (Sigma Aldrich) as silica precursor, polyethylene glycol (PEG) 4000 (Merck), HCl 0.9 M, acrylamide purum 98% (Sigma Aldrich), 2–(acryloyloxy)–N,N,N–trimethylethanaminium chloride (industrially known as Adamquat 80 MC), ammonium persulfate (APS) (Sigma Aldrich),

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N,Nmethylenebisacrylamide (MBAM) (Sigma Aldrich), N,N,N',N'-tetramethylethylenediamine (TMEDA) (Sigma Aldrich), paraffin oil (ρ=0.86 g/mL), demineralized water.

co-MET Procedures using PEG 4000/acrylamide template

Meso/macroporous silica was synthesized using co-MET technique[7] with some modifications. Co-MET silica was synthesized by first dissolving PEG 4000 (2.5, 5, 10, 15 or 20 w/v%) in water and mixing for 24 hours at room temperature. Hydrolyzed tetraethylorthosilicate (TEOS) solution was prepared using the method reported by Brennan et al. with modification.[12] TEOS (33.75 mL), water (10.5 mL), and hydrochloric acid (0.15 mL of 0.9 MHCl) were sonicated in an ice bath until formation of a homogeneous solution, then stored in a sealed container at -4°C for two weeks before use. Monomer solution was prepared as reported by Zhang and Cooper.[13] Acrylamide (2.555 g) and the cross-linker methylene-bisacrylamide (MBAM) (0.518 g) were dissolved in water (6.667 mL).

Monomer solution (3 mL) and PEG 4000 solution (4 mL) were mixed with 1.6 mL of 0.9 M hydrochloric acid at room temperature for 15 minutes, followed by the dropwise addition of hydrolyzed TEOS (3 mL) with continued mixing. Mineral oil (36 mL) containing the coinitiator N,N,N',N'-tetramethylethylenediamine (TMEDA) (0.110 mL) was added resulting in formation of the emulsion. A second initiator, ammonium persulphate (0.3 mL, 20 w/v% in water) was then added and mixing continued for a further 5 minutes. Finally the emulsion was injected via a nozzle of 0.8 mm diameter into a 1000 mL beaker glass partially filled with mineral oil containing TMEDA (23 mL) at 65°C. The co-MET silica beads were formed as a result of polymerization during sedimentation of the emulsion droplets. The beads were collected and stored in an incubator at 50°C for 48 hours. Finally, the beads were calcined in air for 10 hours at 550°C.

co-MET Procedures using 2–(acryloyloxy)–N,N,N–trimethylethanaminium chloride /acrylamide template.

Synthesis of meso/macroporous silica using 2–(acryloyloxy)–N,N,N–trimethylethanaminium chloride/acrylamide template performed by the same procedures as in PEG/acrylamide template, but the percentage of cationic polymers were 0,5; 1; 2,5; 5; and 10% respectively.

Characterization of silica

The successful synthesis of meso/macroporous silica can be evidenced from the results of the characterization of SEM-EDS, XRD, FTIR and BET.

Results and Discussion

The XRD pattern in Figure 1 shows broad peaks at 2θ = 23° which is a characteristic peak of silica. The absence of a sharp peak indicates that the silica is amorphous for both template types. The peaks also indicate that the material contain pure SiO2 in accordance to EDS data in Table 1.
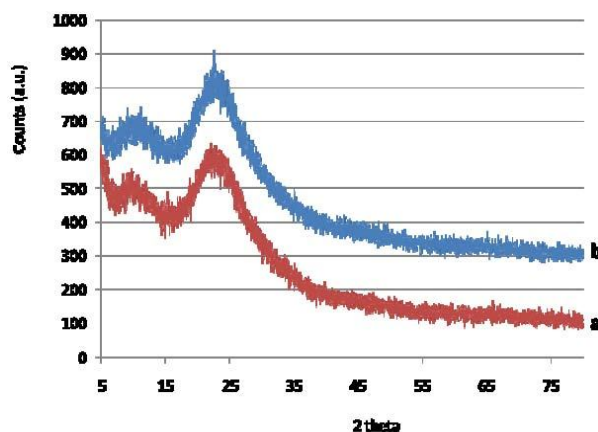

Figure 1. X-Ray Diffraction Patterns of silica synthesized by co-MET techniques using a) 2–(acryloyloxy) –N,N,N–trimethylethanaminium chloride/ Acrylamide Template, and b) PEG 4000/Acrylamide Template

Table 1. Composition of silica (by EDS)

Element	Mass Percentage (%)	
	PEG/acrylamide template	2–(acryloyloxy)–N,N,N–trimethylethanaminium chloride/acrylamide template
O	48.47	48.42
Si	51.53	51.58

FTIR spectra of meso/macroporous silica are shown in Figure 2. In the spectrum of silica, there is a wide band in the region between 3500-2800 cm^{-1}. This is a typical of hydrogen bonding from -OH group on solid samples which indicates strong hydrogen bonds. While the band at 1063 cm^{-1} shows the Si-O-Si group. FTIR spectra also show that polymer concentration as template has no effect on peak shift on spectrum. It does not affect silica content of the resulting solid material since the template is removed during calcinations.
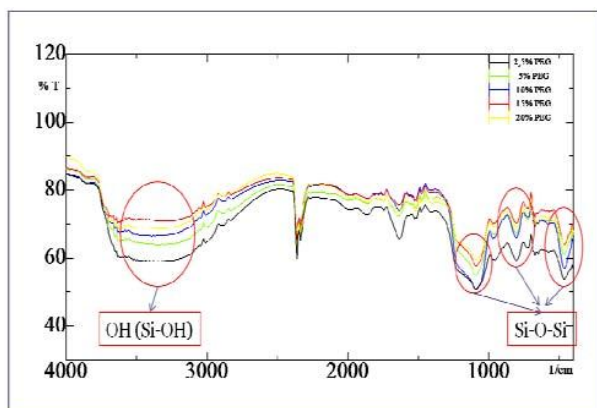

Figure 2. Combined FTIR spectra of silica synthesized by co-MET techniques using PEG/acrylamide as templates

SEM images with a magnification of 2500 times show that the structure of macroporous silica increasingly formed and clearly visible along with the increasing concentration of the polymer template. At a concentration of 5%, both for nonionic and cationic polymer templates, macropore structures of silica were clearly visible compared to other polymer concentrations.
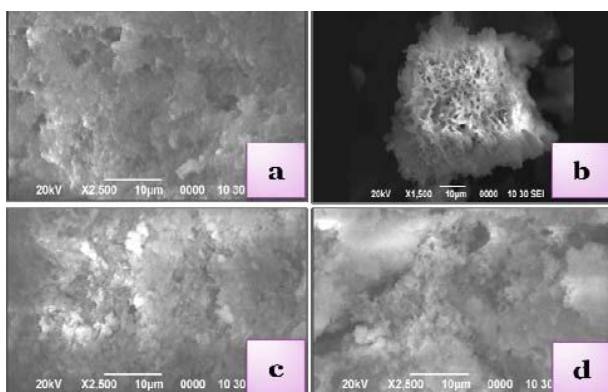

Figure 3. SEM images of various silica synthesized by co-MET techniques using PEG/acrylamide templates by varying PEG concentration: a) 2.5%, b) 5%, c) 10%, d) 15%
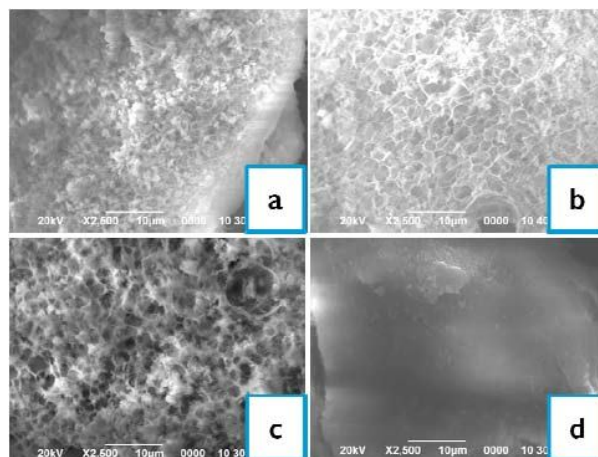

Figure 4. SEM images of various silica synthesized by co-MET techniques using 2–(acryloyloxy)–N,N,N–trimethylethanaminiumchloride/acrylamide template by varying cationic polymer concentration : a) 1%, b) 2.5%, c) 5%, d) 10%

Nitrogen adsorption-desorption isotherm curve of silica are shown in Figure 5. Both samples gave isotherm curves which form the hysteresis loops which indicate the presence of inequality of its adsorption and desorption process. This is means that silica synthesized by co-MET techniques is porous materials. Silica synthesized using PEG 4000/acrylamide template (a) shows the isotherm type IV with the capillary condensation occurs at P/Po $\approx$ 0.8 (except for PEG 5%) which indicates the presence of mesoporous structures. At PEG concentration of 5%, capillary condensation tends to occur at higher pressure (P/Po $\approx$ 0.95), which indicates macropores that present and dominate the silica structures. This is correlated with smaller pore volume as in Table 2. Isotherm adsorption curve of silica synthesized using 2-(acryloyloxy)-N, N, N-trimethylethanaminium chloride are similar to those of silica synthesized using ethylene oxide/propylene oxide/ethylene oxide triblock copolymer as reported by Sarvi et al.[7] The capillary condensation occurs at P/Po around 0.75, and then further capillary condensation occurs at P/Po $\approx$ 0.95 which indicates the presence of both mesopore and macropore structures in the material.
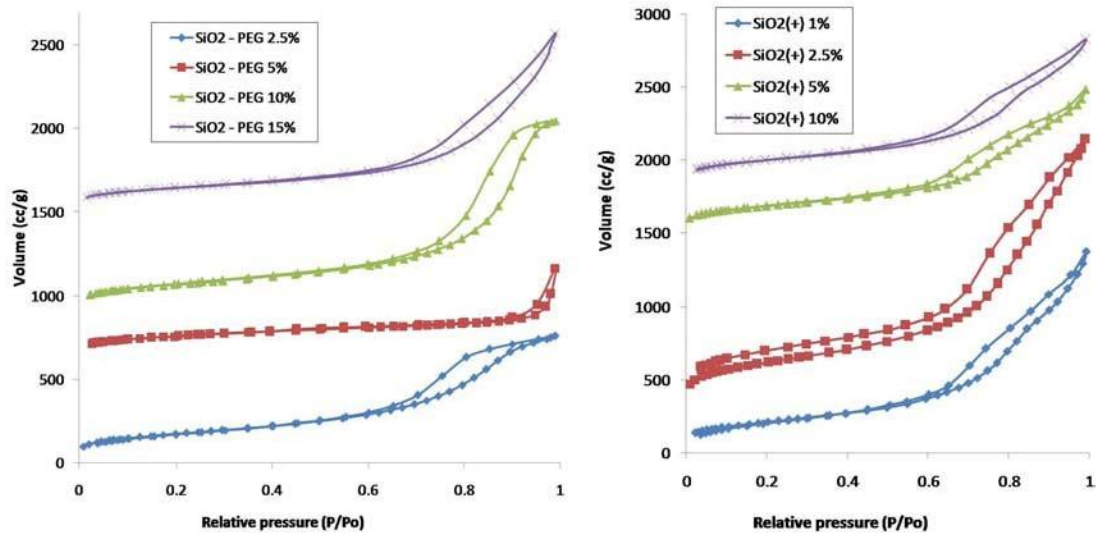
Figure 5. Nitrogen adsorption/desorption curve of silica synthesized by co-MET techniques using (a) PEG 4000/acrylamide template, and (b) 2 – (acryloyloxy) – N, N, N – trimethylethanaminium chloride/acrylamide.

Table 2. Textural properties of silica synthesized by co-MET technique using (a) PEG 4000 5%/acrylamide template and (b) 2–(acryloyloxy)–N,N,N–trimethylethanaminium chloride /acrylamide template [$SiO_2(+)$]

Sample	PEG concentration (w/v%) in water	Adamquat 80 MC concentration (w/v%) in water	BET Surface area (m^2/g)	V total (cc/g)	Average pore radius (Å)
SiO_2-PEG 1	2.5		615.0	1.177	38.27
SiO_2-PEG 2	5		545.0	0.8691	31.91
SiO_2-PEG 3	10		592.2	1.772	59.85
SiO_2-PEG 4	15		500.3	1.655	66.15
$SiO_2(+)$ 1		1	752.7	2.129	56.57
$SiO_2(+)$ 2		2.5	1137	2.852	50.18
$SiO_2(+)$ 3		5	657.0	1.522	46.35
$SiO_2(+)$ 4		10	698.8	1.586	45.38

The results of BET calculation methods (Table 2) show that the use of cationic polymers (2-(acryloyloxy)-N, N, N-trimethylethanaminium chloride) gave a greater surface area compared to the use of a nonionic polymer as a template (PEG 4000). Moreover at polymer concentration of 2.5%, the ratio of the difference is almost doubled (1137 m^2/g to 615 m^2/g). The results also show that cationic polymer templates used in this work give higher surface area than those of ethylene oxide/propylene oxide/ethylene oxide triblock copolymer previously reported by Sarvi et al. (638 m^2/g using copolymer concentration of 10%).[7] In addition, cationic polymer templates give more uniform and narrow pore size distribution as can be seen in Figure 6. This is likely caused by the effect of the positive charge on the polymer chain which causes the hydrolysis and polymerization of TEOS to be more evenly distributed between the polymer chains (bearing silicate groups are basically negatively charged). Once the template is removed by calcination, it would form silica with more evenly distributed pores. In addition, the use of cationic polymers template also gave smaller average pore radius with increasing of the polymer template concentration. While the use of nonionic polymer PEG 4000, tends to gave the opposite results.
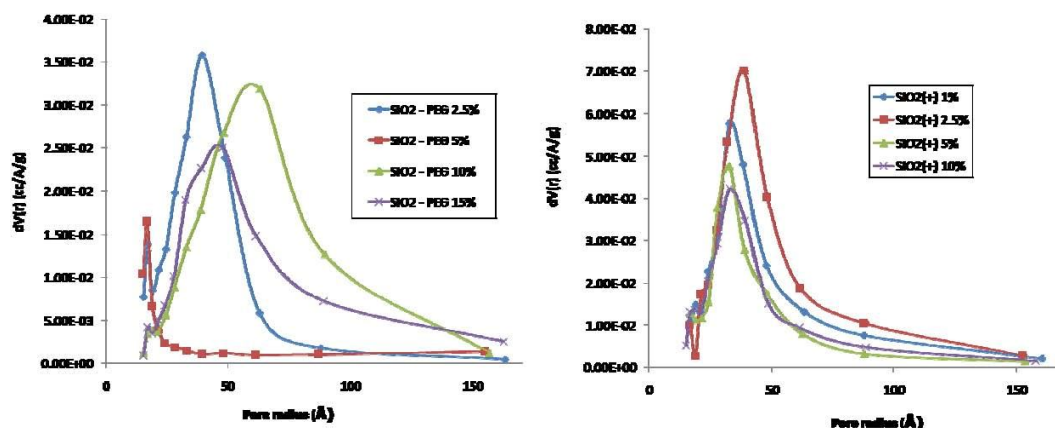
Figure 6. Pore size distribution of silica synthesized by co-MET techniques using (a) PEG 4000/acrylamide template, and (b) 2 – (acryloyloxy) – N, N, N – trimethylethanaminium chloride/acrylamide.
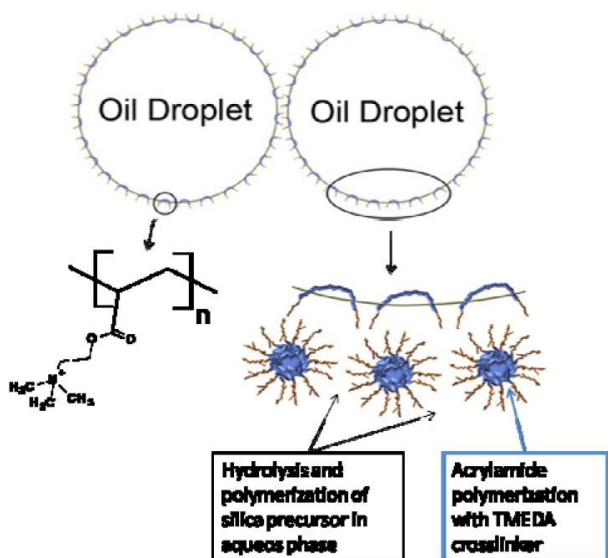

Figure 7. Schematic representation of the formation of meso/macroporous silica by co-MET techniques using 2–(acryloyloxy)–N,N,N–trimethylethanaminium chloride/acrylamide template (picture from Sarvi et al. with some modifications)[7]

Figure 7 shows schematic representation of the formation of meso/macroporous silica using 2–(acryloyloxy)–N,N,N–trimethylethanaminium chloride/acrylamide template. Cationic polymers serve as oil droplet stabilizer, and also form micelles in aqueous phase. The micelle formation serves as the home of acrylamide polymerization reactions that play an important role in the formation of macropore structure of silica. While silica precursors (TEOS) hydrolyze in aqueous phase in the presence of hydrochloric acid. Furthermore, silicate polymerization occurs to form silica frame network. This process takes place in aqueous phase, on the sidelines of cationic polymer chain. The presence of positive charges on polymer chain helps stabilize the micelles so that the resulting macropore structures are maintained and ordered. In addition, the existence of the positive charge also makes the polymer more uniformly dispersed in aqueous phase, resulting in a more regular mesoporous structure.

Conclusion

Co-micelle emulsion templating (co-MET) technique is a new method to synthesize uniform and ordered porous silica from tetraethylortosilicate precursor using double polymer as templates. Polymer concentration of 2.5% gave the best result for both templates, with surface area of 615 m^2/g for PEG/acrylamide and 1137 m^2/g for 2–(acryloyloxy)–N,N,N –trimethylethanaminium chloride/acrylamide template.

Acknowledgements

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