

Effect of pH in Mesoporous Silica Synthesis

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Abstract

Mesoporous silica was tailored by using diluted triblock copolymer F127. The synthesised silica structure was characterized by TEM and N₂ sorption isotherm. 3D-hexagonal arrangement of 5-30 nm pore sizes obtained. The pore sizes and ordering were affected by pH change in synthesis mixture. Although well-ordered hexagonal arrangement of mesoporous was dominant in acidic conditions, the mesoporous silica synthesized in neutral or basic conditions indicates gel-like structures with no mesoporous. The presence of low pH sol-gel reaction, followed by high pH reaction through addition of alkaline during synthesis, not only produced mesoporous materials, but also provided pore size controlling.

Keywords: mesoporous, triblock copolymer, pH, 2D-hexagonal, gellike, pore size controlling.

1. Introduction

Mesoporous ceramic oxides with large specific surface areas have potential applications in chemical and physical processes, especially for chromatography and catalysis [1]. Since the discovery of MCM-41 in 1992 [2], many research groups have focused their interest on mesoporous materials [3]. MCM-41 is formed by a surfactant-assisted reaction pathway as a result of the attractive electrostatic interaction between a ceramic precursor and an ionic amphiphile. One of the limitations of calcined MCM-41 materials prepared by using cationic surfactants without additional treatment with TEOS is their instability in water [4]. An alternative approach to mesoporous molecular sieves is the exploitation of nonionic surfactants at low concentrations, which affords

structural material similar to MCM-41. Pinnavaia et al.[5,6] used nonionic surfactants in aqueous solutions to synthesize wormlike disordered mesoporous silica and alumina in neutral media assembled by hydrogen-bonding interactions. Most of the ordered mesoporous silica materials organized with nonionic surfactant species have been made under acidic conditions. Only several studies have been reported to synthesize ordered mesoporous materials under neutral or basic conditions in the presence of fluoride anions [7,10]. Stucky et al. showed that under the conditions where the hydrolysis proceeded rapidly, TMOS was a preferable silica precursor to TEOS for producing ordered mesostructures. They synthesized ordered hexagonal mesoporous silica materials over a wide range of pH by controlling the rate of hydrolysis relative to that of condensation of silica species by use of fluoride and TMOS [9]. It is well-known that triblock copolymers of PEO- PPO-PEO in water form micelles in which the core and shell are composed of PPO blocks and PEO blocks, respectively [11]. At low pH, protonated PEO chains are associated with cationic silica species through weak electrostatic interactions mediated by the negatively charged chloride ions. Before the aqueous isoelectric point of silica in acidic media, cationic silica species will be present as precursors, and the assembly might be expected to proceed through an intermediate form of $(S^{\circ}H^+)(X^-I^+)$. Non-ionic block copolymers are an interesting class of structure-directing agents whose self-assembly characteristics lead to kinetically quenched structures. Block copolymers have the advantage that they provide sacrificial templates whose microstructures can be turned by adjusting solvent compositions molecular weight, or copolymer architecture [12]. Moreover, larger structural features are possible than that of low molecular weight surfactants and these are achieved at low solution concentrations. Also, various template structures such as bicontinuous cubic, hexagonal, or lamellar mesophases can be produced by adding a small amount of a hydrophobic swelling agent, such as butanol or xylene [13]. In the sol-gel route synthesis, a stepwise reaction scheme has been undertaken to control the ratio of hydrolysis to condensation rates [14]. In general, the rate of hydrolysis is fast compared to that of condensation in strong acidic conditions. Therefore, a well-ordered hexagonal arrangement of mesoporous silica is formed at low pH in acidic conditions.

Meanwhile, in neutral or basic conditions ranging from pH 7 – pH 9, the rate of condensation is faster than that of hydrolysis, and eventually, the materials prepared by a single-step reaction at high pH display gel-like structure without mesoporous. It is hence an interesting attempt to synthesize ordered mesoporous materials by a two- step sol-gel route at a lower acidic pH followed by a higher basic pH. In this work, mesoporous silica was synthesized by using triblock copolymer template(F127), investigating pH changing during synthesis.

2. Experimental Synthesis

The triblock copolymer (EO106PO70EO106) (Pluronic F127), was from Aldrich and used as received. Tetraethylorthosilicate (TEOS), was from Aldrich and used as received, was used as a silica source to prepare the silica mesoporous, HCl (from Adwic) and NH₄OH (from Adwic) were used as a synthesis catalyst. Refluxing 4 g of F127 with 100 g of (H₂O/HCl pH = 1.5) under stirring for 1h. Then 8 g of TEOS was added to the resulting clear solution under vigorous stirring for 4h. The resulting mixture was stored at 337 k for 1 day under stirring for synthesis of mesoporous silics. Ammonium hydroxide was used as co-catalyst to induce stepwise pH change in the two- step sol-gel reaction about 2h after the addition of TEOS. The mixture was aged at 373 K for 4h. The solid product was filtered without washing and dried. Template removal by solvent extraction (using EtOH and HCl), then calcination at 723 K for 8h. The sample prepared by single-step sol-gel method was coded sample 1, and the other 2 samples prepared in two-step sol-gel method at pH 4 and pH 9 were coded samples 2 and 3, respectively.

Characterization

Transmission electron microscopy (TEM) was used to examine the microstructure and grain size. To observe the individual grains, the aggregated powder were dispersed in ethanol (0.5% Wt) and sonicated for 20min. The ultra-microtome method was used to observe the pore structure. Nitrogen adsorption-desorption measurements

at 77 K were performed on a volumetric adsorption analyzer. Before the measurement, the samples were outgassed for 6h at 473 K. The pore sizes, surface areas, and pore volumes were estimated using BET and BJH desorption methods

3. Materials and Methods

Transmission Electron Microscopy

As shown in the TEM image of Figure 1, belongs to sample 1 at pH 1.5 (single-step synthesis), the cylindrical-shaped pores with size (4 - 6 nm). A well-ordered 2D-hexagonal array ($p6mm$) of mesoporous silica is observed for calcined sample when the electron beam is parallel to the major axis of the cylinder. Figure 2 shows sample 2 image, where well-ordered hexagonal array of mesoporous silica in many areas also observed, but a little disordered appears as the pH increases from 1.5 to 4 through adding ammonium NH_4OH . The pore structure was transformed from an order to disorder state, but the structural regularity still present in the major. The pore size was ranged from 4– 9 nm. Figure 3 shows sample 3 image, where disordering arises with increasing pH to 9 through more increasing the amount of NH_4OH added, where no ordering observed. These results indicate that the well-ordered hexagonal array was formed as the first step reaction time increased, because the hexagonal structure was already formed during the hydrolysis of TEOS before pH change. The pore size was ranged from 7 – 26 nm.

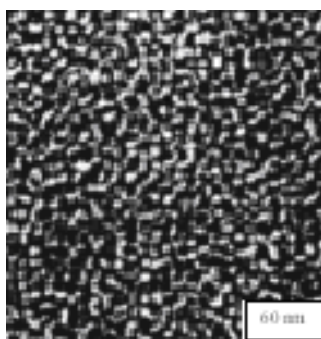


Figure 1. Sample 1 with single-step synthesis at pH = 1.5

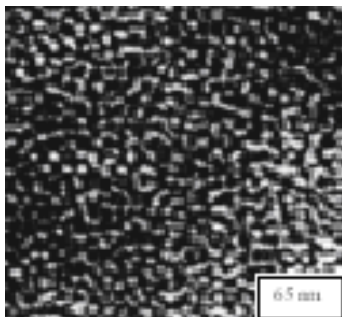


Figure 2. Sample 2 with two-step synthesis at pH= 4

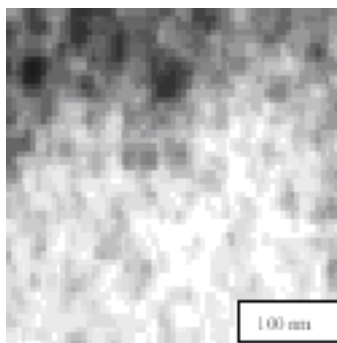


Figure 3. Sample 3 with two-step synthesis at pH= 9

Adsorption isotherm

Figures 4 and 5 show nitrogen adsorption-desorption isotherms and the corresponding pore size distributions for the 3 samples. Pore size distributions (PSD), were analyzed by using the BJH method. Sample 1 has *type-IV* isotherm with H1-type hysteresis that is a typical of mesoporous materials with 1D cylindrical channels. A narrow pore size distribution with a mean value of 55 Å is obtained from BJH desorption method. This sample has a BET surface area of 780 m²/g and a pore volume of 0.62 cc/g. The sample 2 prepared with a low content of ammonium hydroxide and over isoelectric point showed similar isotherm and exhibited pore size of 70 Å, BET surface area of 710 m²/g, and pore volume of 0.58 cc/g. the adsorption isotherm was shifted toward higher values relative to those for sample 1. However, when the pH was above 7, as in sample 3, different isotherm appeared. The pore size increased up to 280 Å, and the BET surface area decreased to 110 m²/g. Sample 3 adsorption-desorption isotherm showed a narrow difference between the adsorption and desorption isotherm and had a relatively broad

pore size distribution. The large pore size and disordered structure of sample 3 referred to rapid condensation rate compared to hydrolysis one at pH over 7. Thus, silica nano particles contain organic moieties (ethyl groups) due to incomplete hydrolysis. The residual ethyl groups lead to weaker interactions between F127 and silica nanoparticles, resulting in poorly ordered silica structures. Also an unreacted silica precursors are able to penetrate the PPO core parts because of weaker hydrophobicity, which lead to large pore size.

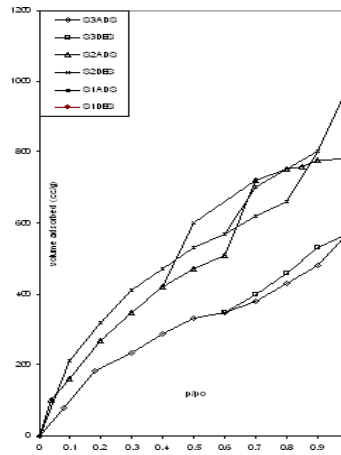


Figure 4. Nitrogen adsorption-desorption isotherm of sample 1 (1,2), sample 2 (3,4), and sample 3(5,6)

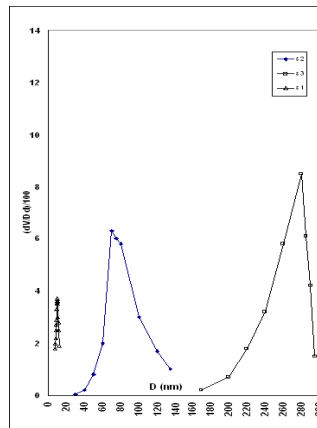


Figure 5. Pore size distribution of samples 1, 2, and 3 respectively

4. Conclusion

Mesoporous silica tailoring by using diluted triblock copolymer F127, 3D- hexagonal arrangement of 5-30 nm pore sizes obtained. The pore sizes and ordering were affected by pH change in synthesis mixture. Although well- ordered hexagonal arrangement of mesoporous was dominant in acidic conditions, the mesoporous silica synthesized in neutral or basic conditions indicates gel-like structures with no mesoporous. The presence of low pH sol-gel reaction, followed by high pH reaction through addition of alkaline during synthesis, not only produced mesoporous materials, but also provided pore size controlling.

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