

The structure heterogeneity of silica mesopores of Sba-15 in respect to the pluronic 123 template concentration

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Abstract. The analysis of structure heterogeneity factor of silica mesoporous SBA-15 has been conducted. The structure factor has been found to be different for low and high concentration of Pluronic-123 template. The structure heterogeneity of high concentration of Pluronic-123 has been found less than 1 while for low concentration, the structure heterogeneity was found to be larger than 1. This indicates the dissimilarity of the structure and can be used as a probe to detect the formation of large mesopores. It also was found that the system exhibits type IV and H1 adsorption type which indicates the capillary condensation and interconnected pores.

1. Introduction

Silica mesoporous is one of promising nanotechnology materials that has many potential applications in wide area. Recently, it has been used as catalysis [1], drug delivery [2-4], adsorption of biomolecules [5], biosensor [6] and membrane separation [7]. According to IUPAC [8], silica mesoporous material, is a silica based materials with mesoporous with pore of diameters in the range of 2-500 nm. Due to highly ordered mesostructures, this material yields high surface area which is extremely suitable for catalysis and sorption. This advantage allows diffusion and adsorption of larger molecules compared to zeolite or other micropores materials. No wonder that mesoporous silica can be applicable in wide applications.

Silica Mesoporous was invented in 1970 but this went largely unnoticed [9]. However in 1990, Yanagisawa et. al [10], synthesized mesoporous silica and was named as M41S/MCM. Some of typical MCM mesoporous silica are MCM-41, MCM-48 and MCM-50. MCM-41 has hexagonal packed rod-shaped structure, MCM-48 has cubic structure and MCM-50 has lamellar structure. Again in 1998, Zhao et. al [11] successfully synthesized mesoporous silica named as Santa Barbara Amorphous-15/SBA-15 (named after University of California, Santa Barbara). SBA-15 has the larger pores and thicker walls than older mesoporous silica. In addition it has good thermal, mechanical stability and chemical resistance properties which make SBA-15 a promising material for wide applications.

SBA-15 has a ordered hexagonal structure. It has diameter of pores of 4.6 nm to 30 nm and was synthesized using triblock copolymer [12]. Surface area of pure SBA-15 can be as high as 650 m²/gram. The synthesis of SBA-15 using triblock copolymer as template has an advantage which is much easier to synthesize. In this paper we used Pluronic 123, a triblock copolymer surfactant [13]. The pluronic 123 has capability to form long cylindrical micelles which is specifically suitable to synthesis SBA-15 with precursor silica Tetraethyorthosilicate/TEOS. The use of SBA-15 in sorption application is related to its adsorption capacity. The higher adsorption capacity/ adsorbate uptake towards the selective adsorbate is preferred. In order to study the possibility the use of silica mesoporous SBA-15 to be used as adsorbant to adsorb heavy metals, the isotherm adsorption study is important. To guarantee that the adsorption occurs homogeneously in the surface, the structure heterogeneity factor knowledge is important in addition of adsorption capacity. In this paper we calculate of SBA-15 by varying the concentration of surfactant/Pluronic 123. Jaroniec [14] described the structure heterogeneity as a heterogeneity resulted from interconnected pores of different sizes and



shapes. To calculate the structure heterogeneity factor Dubinin- Astakhov (D-A) isotherm model was used. This model actually was developed to explain the multilayer adsorption phenomenon. In the results and discussion subsection, the value of structure homogeneity as a function of the concentration of surfactant/Pluronic 123 will be discussed as a recommendation of the use SBA-15 as adsorbant materials

2. Experiment

2.1 Materials

In order to synthesize silica mesoporous SBA-15, silica precursor Tetraethyorthosilicate/TEOS (Merck) and Surfactant Pluronic 123 (BASF) as template were used. HCl 2 M (Merck), ethanol and distilled water were used as solvent. All of materials were used without further purification.

2.2 Synthesis

To synthesize SBA-15, wet sol-gel process was conducted. The basic ingredients are building block of mesoporous materials which is silica and the wet template. The source of silica is TEOS and the template is surfactant Pluronic 123. The sol gel process should be conditioned in acidic condition to ensure the self-assembly of silica occurs on template. First step, 5 ml et.OH was added to 31.25 gram TEOS and then the mixing was stirred for 30 minutes under room temperature. Then, 5 ml et.OH was mixed again with 10 ml HCl to make acid environment. This solution then was mixed again with et.OH (10 ml) and addition of 50 ml distilled water solution and they were stirred for 30 minutes under room temperature. The mixed solution was then refluxed for 2 hours at temperature of 70 C. The TEOS solution was ready to be used in further step.

Next the surfactant template solution was synthesized. The concentration of surfactant was varied at 7 mM, 50 mM, 55 mM, 60 mM and 66 mM. This surfactant then was added into mixture of HCl (10 ml) and ethanol (25 ml) in acidic condition. This surfactant solution was then added drop wise into already made TEOS solution and was continuously stirred until the solution turned into gel. The gel then was dried at 100oC for an hour and then was calcined for the addition of 5 hours. The product was then ready for adsorption measurement.

2.3 Characterization

In order to measure the structure heterogeneity factor, the adsorption isotherm experiment was conducted using Quantachrome adsorption-desorption equipment at 77 K. N₂ gas was used as adsorbate. The specific surface area was determined by the Brunauer-Emmer-Teller (BET). In order to check the crystallinity of the sample, the addition small angle X-ray scattering (SAXS) measurements (Shimadzu XRD-6000) were carried out.

3. Dubinin-Astakhov isotherm model of adsorption

Dubinin [15] proposed the micropore volume filling theory which is related to the Polanyi characteristic curve. Dubinin acknowledged that heterogeneity of surface solid can affect the adsorption capacity/ gas uptake amounts. This is called as surface and homogeneity factor which can be originated from interconnected pores and crytall irregularities on the surface respectively. In this paper, those two heterogeneities are called structure heterogeneity factor. Dubinin assumed that the surface contains numerous distribution of pore size distributions related to their characteristics energy. This means that the mathematical form of generalized D-A model can be written as follows

$$C = C_0 \sum_{i=1}^m f_i \exp \left[- \left(\frac{A}{E} \right)^n \right] \quad (1)$$

where f_i is the local fraction of adsorption sites, $A = -\Delta G = RT \ln (P_0/P)$ is the adsorption potential of the Polanyi theory which is related to the change of Gibbs free energy ΔG and the change of relative pressure P_0/P , E is the characteristic energy, n is the structural heterogeneity parameter which is linked to the adsorption of structurally heterogeneous surface, $P_s = (T/T_c)^2 P_c$ (for $T > T_c$) is the saturated pressure, P_c and T_c are critical pressure and temperature respectively. This model is suitable to describe adsorption in highly activated carbon [16]. However in silica mesopore system, we assume that only one site homogenous energy which is related to only one distribution of pore size in order to make calculation easier. By taking this assumption, the simplified D-A model reads

$$C = C_0 \exp \left[- \left(\frac{A}{\beta E_0} \right)^n \right] \quad (2)$$

The fitting can be conducted by linearizing equation (1) which can be written as follows:

$$\ln C = \ln C_0 - \left[\frac{RT}{\beta E_0} \ln \left(\frac{P_0}{P} \right) \right]^n \quad (3)$$

D-A model is valid over a range of N_2 relative partial pressure up to 0.03.

4. Results and Discussion

In order to confirm that our sample is in the crystal form, we checked small angle X-ray scattering (SAXS) results which are shown in Figure 1. All of our SBA-15 measured samples show three main peaks (100), (110) and (200). These results are in good agreement with the results obtained by Su et. al [17]. These three peaks show that synthesized SBA-15 has 2D hexagonal structure. As we increase the concentration of surfactant, the peaks shift to the lower angle. This shifting is due to the expansion of lattice parameters. This increase yields the expansion of pore sizes. At concentration 60 mM, the (100) peak is much broader than other concentration which indicates that more non-uniform mesopores were produced.

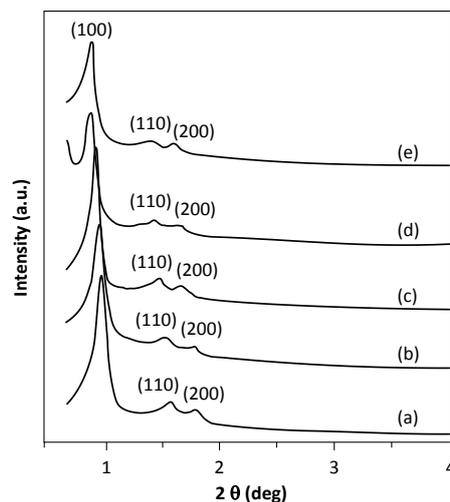


Figure 1. SAXS patterns of SBA-15 with different concentration of Pluronic 123 (a) 7 mM (b) 50 mM (c) 54 mM (d) 60 mM and (e) 66 mM.

The N₂ adsorption-desorption isotherms (bold-dash lines) of SBA-15 with various concentration of Pluronic 123 (7 mM, 50 mM, 54 mM, 60 mM and 66 mM) are shown in figure 2. BET results are given in table 1 including spesific surface area, average pore diameter. Wall size is pedicted using AFM image (which is not shown here) which is around 2-3 nm. In order to fit with the D-A model in equation 3, we took low relative pressure of adsorption isotherms and redrawn the plot. The fitting is shown in figure 3. From figure 2 we can conclude that there are two kinds of adsorption type. At low concentration of Pluronic 123 (7mM), the curve exhibits type I isotherm without hysteresis loop. This curve indicates that at low concentration of surfactant, SBA-15 has small external surface. The uptake is determined only by the accessible pores instead of surface area. At high concentration of Pluronic 123 (50 mM, 54 mM, 60 mM and 66 mM) curves exhibit type 4 isotherm. Their curves reveal a H1 type hysteresis loops. This shows a cillyndrically structure of pores, capillary condensation phenomenon and the possibility of interconneted networks. The relation between the surfactant concentration and adsorption capacity is given in figure 4. The lowest adsorption capacity is at 7 mM concentration of surfactant which stands at 175 cm³/gram and the highest adsorption capacity is at 60 mM which stands at 421 cm³/gram.

Table 1. BET results for various P123 concentrations.

No	P123 concentration (M)	Spesific surface area (m ² /g)	Average pore diameter (nm)
1	7 mM	482.2	3.440
2	50 mM	534.6	3.044
3	54 mM	598.5	3.040
4	60 mM	702.1	3.397
5	66 mM	746.7	3.045

Now let discuss the structure heterogeneity parameter. In this paper we do not differentiate between structure heterogeneity and surface heterogeneity. We just called both heterogeneity in single term called structure heterogeneity. This parameter reflects degree of heterogeneity of surface (pore size) as well as interconnectivity of pores. Take a look figure 5. At low concentration of surfactant, the value of structure heterogeneity is larger than 1 at high concentration of surfactant the value is less than 1. This may indicate the fundamental difference of structure. it can be inferred at low concentration, the pore sizes are much larger and more homogenous. There is minimal interconnectivity effect and no capillary condensation. This is in agreement with figure 3 and 4 results which tell us that at low concentration the type I isotherm adsorption occurs and it has lowest gas uptake/adsorption capacity. On the other hand, at high concentration of surfactant, it can be inferred from the results in figure 5, the pore sizes are smaller and thus more heterogeneous. There is interconnectivity effect and capillari condensation. This argument is reflected from figure 3 and 4 results which tell us that at high concentration the type IV isotherm adsorption (with H1 type of hysteresis) occurs and it has highest gas uptake/adsorption capacity. However, at concentration of surfactant of 66 mM however the *n* value bit higher while for other high concentration much less similar. Our analysis suggests that the structure heterogeneity parameter can be used to figure out indirectly the pore structure of micro/mesopores materials. The heterogeneity of surface information is crucial for mesoporous in order to be applied in adsorption application, heavy metal adsorption for example. This structure may determine the effectivity of adsorption.

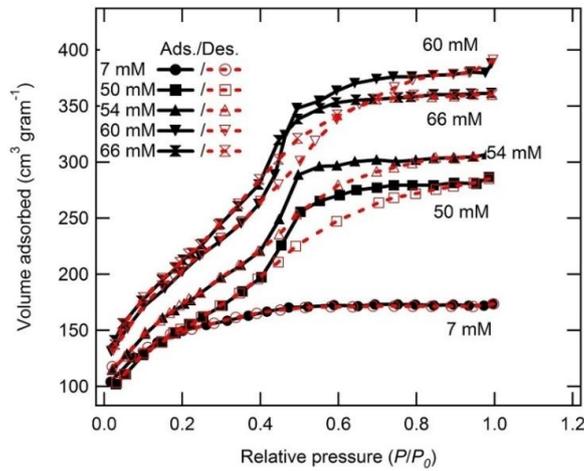


Figure 2 The N₂ adsorption-desorption isotherm (bold-dash lines) of SBA-15 with various concentration of Pluronic 123 (7 mM, 50 mM, 54 mM, 60 mM and 66 mM). The hysteresis curve observed in all samples except at Pluronic 123 concentration of 7 mM.

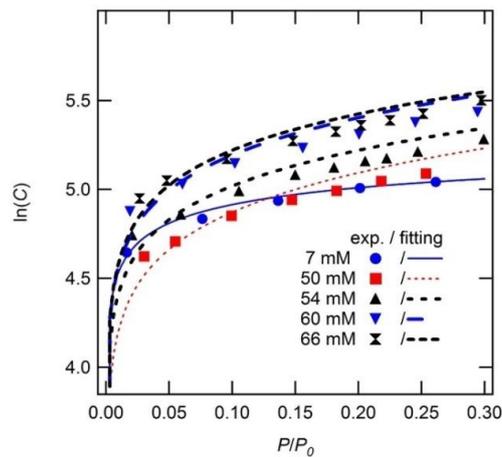


Figure 3 D-A isotherm model fitting for various concentration of Pluronic 123 (7 mM, 50 mM, 54 mM, 60 mM and 66 mM). All curves were fitted up to relative pressure up to 0.3.

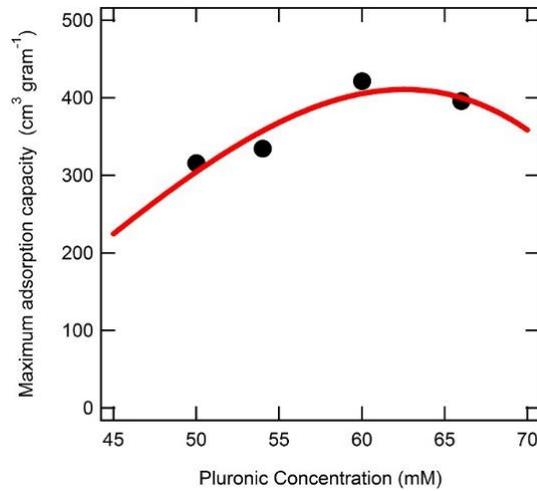


Figure 4 The fitting results of maximum filling capacity/maximum adsorption capacity (C_0) for various concentration of Pluronic 123 (7 mM, 50 mM, 54 mM, 60 mM and 66 mM).

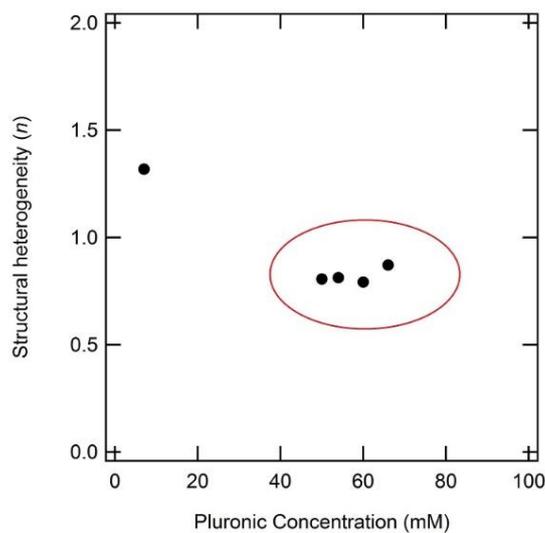


Figure 5. The structure heterogeneity (n) of different Pluronic 123 concentrations. Circled points show lower structural heterogeneity values at high concentration of surfactants.

5. Conclusions

SBA-15 has been successfully synthesized with various concentration of Pluronic 123 (7 mM, 50 mM, 54 mM, 60 mM and 66 mM). D-A model was found to be fitted well up to relative pressure of 0.3 and can be used to estimate the structure heterogeneity factor of mesoporous. It was found that at concentration 60 mM, SBA-15 has highest adsorption capacity. At low concentration of surfactant, the value of structure heterogeneity is larger than 1 at high concentration of surfactant the value is less than 1. This means that at high concentration of surfactant, SBA-15 much more heterogeneous than at low concentration. This results suggest that the structure heterogeneity factor is important to obtain the information of surface of mesoporous. This results can be applied for other applications such as study of adsorption for other gases or adsorption of heavy metals.

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