The Effect of Pluronic 123 Surfactant concentration on The N$_2$ Adsorption Capacity of Mesoporous Silica SBA-15: Dubinin-Astakhov Adsorption Isotherm Analysis

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Abstract. Mesoporous SBA-15 has been successfully synthesized at various concentration of Pluronic 123 surfactant (7mM, 50 mM, 54 mM, 60 mM and 66 mM) and the effect of these various concentrations on the N$_2$ adsorption capacity has been investigated. The adsorption analysis was conducted using Dubinin-Astakhov isotherm model for multilayer adsorption phenomenon. It was found that at low concentration of Pluronic 123, the system exhibits type I adsorption isotherm while at high concentration, the system exhibits type IV adsorption with H1 hysteresis curve which indicates the existence of pores with cylindrical geometry, relatively uniform pore size and possibility of pore network effects. It also was found that, by using D-A isotherm model fitting, at 60 mM concentration of Pluronic 123, SBA-15 has the highest adsorption capacity which stands at 421 cm$^3$/gram.

1. Introduction

In recent years, mesoporous materials draw the attention due to their applications in many fields such as: catalysis [1], adsorbent [2], drug delivery [3], biosensor [4] and separation [5]. Mesoporous material is a material with pore of diameters in the range of 2-50 nm as defined by IUPAC [6]. This material has highly ordered mesostructure which yields high surface area. This advantage allows diffusion and adsorption of large molecules which are applicable in wide applications. There are compounds of mesoporous materials such as: silica, alumina, carbon and transition metal oxides. Other Micropores such as has limited application to chemical catalysis and separation due to bulky nature of adsorbate [7]. One of the widely used compound is silica due to its abundance, inexpensive, thermally stable, chemically inert and harmless. Zhao et. al [8] successfully produced Santa Barbara Amorphous 15 (SBA-15) which has the larger pores and thicker walls and has exceptional thermal and mechanical stability and chemical resistance which make this SBA-15 a promising material for many applications.

Pure SBA-15 has ordered hexagonal structure with diameter of pores ranging from 4.6 nm to 30 nm and was synthesized using triblock copolymer in acid environment [9]. Surface of pure SBA-15 can be as high as 650 m$^2$/gram although theoretically this kind of structure can only has surface area of 204$^2$ m/gram. Ravikovitch et. al [10] reported that SBA-15 can also have regular cylindrical arranged in hexagonal structure. The synthesis of SBA-15 using triblocce opolymer as template has gained interest due to the ease of process. In this paper we used Pluronic 123 (P123), a triblock copolymer...
due to its capability to form long cylindrical micelles which are specifically suitable to synthesis SBA-15 with precursor TEOS. The suitable concentration of template/surfactant is crucial to synthesis SBA-15 since the pores size and structure are heavily dependent on template structure. The use of SBA-15 as adsorbent is related to its adsorption capacity. Higher adsorption capacity towards selective adsorbate is preferred. In order to study the possibility the use of SBA-15 to adsorb compounds such as inert gases, heavy metals and etc, the isotherm adsorption study is important. In this paper we investigate the effect of P123 on adsorption capacity of SBA-15 using Dubinin- Astakhov (DA) isotherm model. This model was developed to explain the multilayer adsorption and volume filling.

2. Experimental Methods

2.1 Synthesis and Characterization

In this synthesis, the precursor used was Tetraethyl Orthosilicate (TEOS) and the template used was P123. The process is called sol-gel solution and the solution is in acidic condition. First step, 5 ml ethanol was added to 31.25 gram TEOS and stirred for 30 minutes at 25°C. Second, 5 ml ethanol was mixed with 10 ml HCl. This solution then was mixed with ethanol (10 ml) + 50 ml distilled water solution and was stirred for 30 minutes at room temperature. The mixed solution was then refluxed for 2 hours at temperature of 60°C. Next the surfactant template solution was made. 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). This surfactant solution was then added drop wise into TEOS solution and was continuously stirred until the solution turned into gel. The gel then was dried at 100°C for an hour and calcined for 5 hours. The product was then ready for adsorption measurement. The adsorption characterization was conducted using Quantachrome equipment at 77 K. N$_2$ gas was used as adsorbate. The specific surface area was determined by the Brunauer-Emmer-Teller (BET). Small angle X-ray scattering (SAXS) measurements (Shimadzu XRD-6000) was carried out to determine the structure of the synthesized samples.

2.2 Dubinin-Astakhov isotherm model of adsorption

Freundlich [11] has recognized empirical model of an adsorption isotherm which was derived from Langmuir equation [12] and was extended to heterogeneous surfaces. Later, BET equation was derived from a simplification of Langmuir and can explain multilayer adsorption phenomena. Before BET equation was widely used, Dubinin [13] developed adsorption equation based on Weibull distribution of adsorption potential. The BJIH, HK and density functional theory (DFT) were also developed but the calculation was complicated and time consuming. On the other hand, DA model by Dubinin is simpler and can be used to analyze adsorption on mesoporous and can be shown as

$$ C = C_0 \exp \left[ - \left( \frac{A}{\beta E_0} \right)^{\frac{1}{\beta}} \right] $$

where $C$ is the volume of adsorbate filling mesopores, $C_0$ is the maximum capacity of adsorbent to adsorb adsorbate, $A = RT \ln \left( P_0 / P \right)$ is the differential of molar work of adsorption, $\beta$ is the affinity coefficient, $E_0$ is the characteristic energy, $R$ is the Boltzmann constant, $T$ is the equilibrium temperature, $P_0/P$ is relative pressure. Fitting can be done by linearizing eq. (1) which is written as:

$$ \ln C = \ln C_0 - \left[ RT / \beta E_0 \ln \left( P_0 / P \right) \right] $$

DA model is valid over a range of N$_2$ relative partial pressure up to 0.02.
3. Results and Discussion

First, SAXS results are shown in Figure 1. All measured samples show three main peaks (100), (110) and (200). These results are in agreement with the results obtained by Su et. al [14]. These three peaks show that synthesized SBA-15 has 2D hexagonal structure. As concentration of surfactant increases, there is tendency that the peaks shift to the lower angle. This shifting is expected as the increase of surfactant concentration can result in the expansion of lattice parameters thus increasing pore size [15]. In addition, at concentration 60 mM, the (100) peak is much broader than other concentration. This may indicate that more non-uniform mesopores were produced. Second, The N₂ adsorption-desorption isotherm (bold-dash lines) of SBA-15 with various concentration of P123 (7 mM, 50 mM, 54 mM, 60 mM and 66 mM) is shown in figure 2. It can be seen from figure 2 that there are two kinds of adsorption type. At low concentration of P123 (7 mM), the curve exhibits type I isotherm without hysteresis loop. This means that the adsorption is limited to a single monolayer of adsorbate at the surface of SBA-15, which in this case is N₂. This curve indicates that at low concentration of surfactant, SBA-15 has small external surface. The limitation of uptake (maximum filling volume of adsorption) is governed by the accessible pores and not by internal surface area. This indication resonates with the fitting results which show that at concentration 7 mM, the maximum filling capacity is lowest. At high concentration of P123 (50 mM, 54 mM, 60 mM and 66 mM) curves exhibit type 4 isotherm. This translates to an adsorption which proceeds via multilayer adsorption. This is followed by a capillary condensation. Their curves reveal an H2 type hysteresis loops. This which indicates the existence of pores with relatively non uniform pore size.

![Figure 1. SAXS patterns for P123 concentration at (a)7 mM (b)50 mM (c)54 mM (d)60 mM and (e)66 mM.](image)

DA isotherm model fitting is shown in figure 3. All curves were fitted up to relative pressure up to 0.3. The fitting results of maximum filling capacity/maximum adsorption capacity (C₀) are shown in figure 4. The lowest adsorption capacity is at 7 mM which stands at 175 cm³/gram and the highest adsorption capacity is at 60 mM which stands at 421 cm³/gram. The quadratic nature of relation between surfactant concentration and maximum adsorption capacity can be explained as follows. At optimum concentration, the hexagonal template which is formed in self-assembly manner by surfactant reach its maximum surface area. Further addition of surfactant leads to decrease of surface area. At maximum surface area of hexagonal template, the pore size will be optimum thus yields highest adsorption capacity. The behavior of optimum surfactant concentration value for
producing specific geometry (such as hexagonal lamellar) may be attributed to the effort of the system to minimize free energy. The lamellar structure may form branches as concentration is increased. The characteristic energy adsorption for all samples are given in figure 5. At high concentration of P123 (50 mM, 54 mM, 60 mM and 66 mM), the value of their characteristic energy are around 200-250 J mol⁻¹, much lower in comparison with the value of characteristic energy for low concentration of P123 at 7 mM which has value 503.638 J mol⁻¹. The characteristic energy of adsorption is related to the isosteric heat of adsorption. These results show that at high concentration of surfactant, the system needs much lower energy to adsorb gas yielding high uptake. On the other hand, at low concentration of surfactant, the system needs much higher energy to adsorb gas thus yielding low uptake. We suggest that the characteristic energy can be used as a parameter to differentiate between two types of adsorption (type 1 and type 4) as well as two types of pore structure and geometry.

Figure 2. The N₂ adsorption-desorption isotherm (bold-dash lines) of SBA-15 with various concentration of P123.

Figure 3. DA isotherm model fitting for various concentration of P123. All curves were fitted up to relative pressure up to 0.3.

Figure 4. The fitting results of maximum filling capacity/maximum adsorption capacity for various concentration of P123.

Figure 5. Characteristic energy of adsorption for various concentration of P123.
4. Conclusions

SBA-15 has been successfully synthesized with various concentration of P123 (7 mM, 50 mM, 54 mM, 60 mM and 66 mM). DA model was found to be fitted well up to relative pressure of 0.3 and can be used to estimate adsorption capacity of SBA-15. It was found that at concentration 60 mM, SBA-15 has highest adsorption capacity. At this optimum concentration, the hexagonal template which is formed in self-assembly manner by surfactant reaches its maximum surface area, thus yields highest adsorption capacity. In addition it was found that the characteristic energy is strikingly different for low and high concentration. All of this results can be used as guidance for the use of mesopores materials to the applications such as study of adsorption for other gases or heavy metals.

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