Journal of Metals, Materials and Minerals, Vol.19 No.2 pp.61-65, 2009

Utilization of Rice Husk Ash Silica in Controlled Releasing Application

Piyawan PRAWINGWONG[1] , Chaiyan CHAIYA[2], Prasert REUBROYCHAROEN[3] and Chanatip SAMART[1]

[1]Department of Chemistry, Thammasat University, Klongluang, Pathumtani, 12121, Thailand
[2]Chemical Engineering Division, Rajamangala University of Technology Krungtep, Sathorn, Bangkok, 10120, Thailand
[3]Department of Chemical Technology, Chulalongkorn University, Pathumwan, Bangkok,10330, Thailand

Abstract

Mesoporous silica was produced by sol-gel technique using rice husk ash as a silica source which was applied in the drug delivery system. The drug releasing behavior was studied in phosphate buffer using indigo carmine as a drug model. The textural properties of mesoporous silica were characterized and considered with the result of the releasing study. The pore volume and silanol group on the surface of mesoporous silica affected the releasing behavior. The larger pore volume could contain the larger amount of drug which showed fast release. The effect of the silanol group presented an interaction between the drug molecule and silanol group resulting in slower releasing.

Introduction

Mesoporous silica materials have been discovered more than ten years ago. There were various textural properties which depended on the synthesis conditions.(11) Mesoporous silica had challenging properties which can be applied in the delivery system. These properties could be adjusted to specific releasing molecule.(7) There were many research articles on mesoporous silica in delivery application. The mesoporous silica was tested in encapsulation and releasing of direct blue dye.(9) There were some types of mesoporous silica which can encapsulate the dye. Porous hollow silica was used as drug carrier.(3, 5) It collected the drug in the cavity in the core and released it back through the shell pore. Pore and morphology of mesoporous silica could be regulated and it had effect on the releasing behavior.(8) Mesoporous silica was functionalized which was selective releasing.(6) The hybrid organic and inorganic system improved the functional surface of silica and biocompatibility.(4) However, the mesoporous silica still have the problem of high production cost before becoming silica precursor from chemical substance. Research reported on the preparation of mesoporous silica from rice husk ash.(2, 10) The rice husk ash is waste from agriculture which can reduce production cost of mesoporous silica. The present research work applied mesoporous silica from rice husk ash in controlled releasing application. The relation between physical properties of mesoporous silica from various synthesis conditions and releasing behavior was studied.

Materials and Experimental Procedures

Material

The experiment used pluronic P123 (Aldrich, USA) and indigo carmine (Himedia, India). as structure directing agent and drug model, respectively. Rice husk was obtained from Pathumtani, Thailand.

Preparation of Rice Husk Ash

Rice husk was treated by 4 M hydrochloric acid for 3 hours under reflux condition. The treated rice husk was washed by distilled water for acid removal and dried at 100°C for 3 hours. The rice husk was combusted at 600°C for 1 hour.(1) Sodium hydroxide, deionized water and rice husk ash were mixed in the the weight ratio of 0.295: 7.38: 1. The mixture was heated at 100°C and vigorously stirred for 2 hours.

E-mail: chanatip@tu.ac.th

Synthesis of Mesoporous Silica and Characterization

The mechanism of mesoporous silica synthesis was generated via supramolecular templating and sol-gel method (Figure 1). Two grams of pluronic P123 were dissolved in 72 ml of 2 M HCl and stirred for 4 hours. Pluronic P123 in mixture of rice husk ash and sodium hydroxide at the ratio of 3:1 has poured into the previous solution and stirred for specified reaction time (20, 30 and 63 hours). Hydrothermal treatment was applied after the end of the reaction time. The mixture was filtered, dried at 100°C for 6 hours and calcined at 600°C for 3 hours to obtain the mesoporous silica. The mesoporous silica was analyzed the textural properties by nitrogen adsorption desorption technique. The microstructure of mesoporous silica was studied by transmission electron microscope, TEM (JSM2010, JEOL). The amount of functional group of surface was quantified by fourier transform infrared spectrometer.

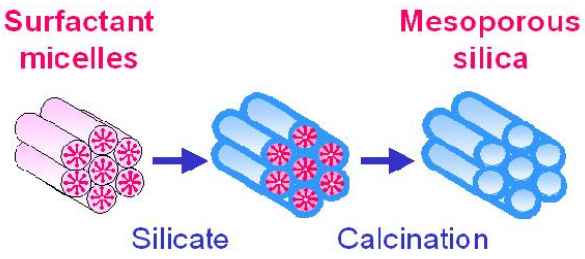


Figure 1. Mechanism of mesoporous silica synthesis

Study of Indigo Carmine Loading and Releasing

The mesoporous silica was dried at 100°C for 6 hours and soaked in 0.5% wt of indigo carmine for 48 hours under vacuum condition, respectively. It was filtered and dried at a temperature of 60°C for 6 hours. The amount of drug loading was calculated by the weight difference before and after drug loading. In the releasing study, five hundred milligrams of drug loaded mesoporous silica were placed in 100 ml phosphate buffer (pH=7) as a simulated body fluid. The releasing of indigo carmine was measured by UV-vis spectrophotometer (CECIL, CE1010) at λ= 610.2 nm. One milliliter of simulated fluid was taken every minute for the first thirty minutes, and after that one time in every thirty minutes.

Results and discussion

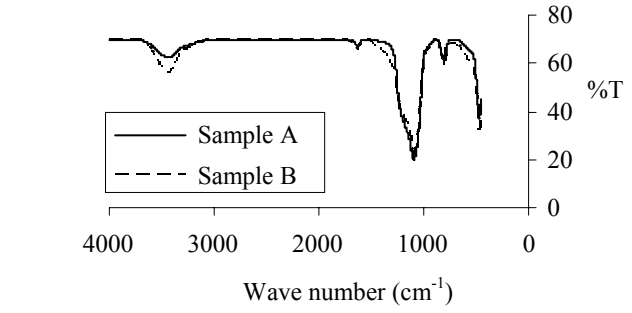
Characterization of Mesoporous Silica

Table 1 presents the textural properties of mesoporous silica at various synthesis conditions. Two synthesis temperatures were studied at 30°C and 60°C. The synthesis temperature affected the surface area and pore volume. The surface area and pore volume decreased from 251.0m^2/g and 1.085cm^3/g to 182.8m^2/g and 0.797cm^3/g while increasing synthesis temperature from 30°C to 60°C. High temperature reduced surface area and pore volume because the micelle was not stable at high temperature. The longer reaction time enhanced pore volume and pore diameter due to a higher degree of condensation. Hydrothermal treatment increased the pore diameter and pore volume because hydrothermal treatment which operates at high temperature and pressure expands the silica framework.

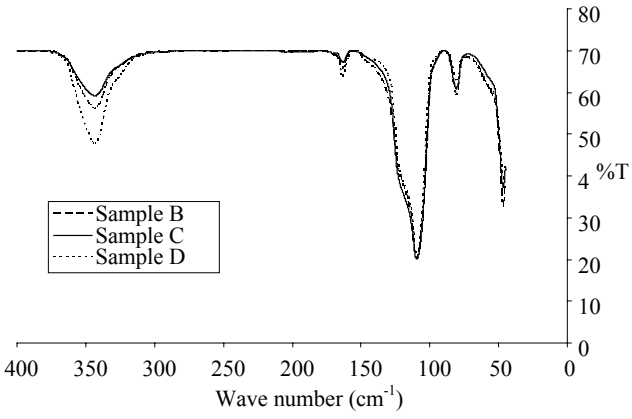
Table 1. Textural properties of mesoporous silica (various synthesis conditions)

Sample	Temperature (°C)	Reaction time (h)	Hydrothermal time (h)	Surface area (BET) (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
A	30	20	24	251.0	1.085	17.29
B	60	20	24	182.8	0.797	17.43
C	60	30	24	257.3	1.286	19.99
D	60	63	24	246.9	1.631	30.08
E	60	30	0	94.79	0.372	15.70
F	60	30	48	227.8	1.195	20.98

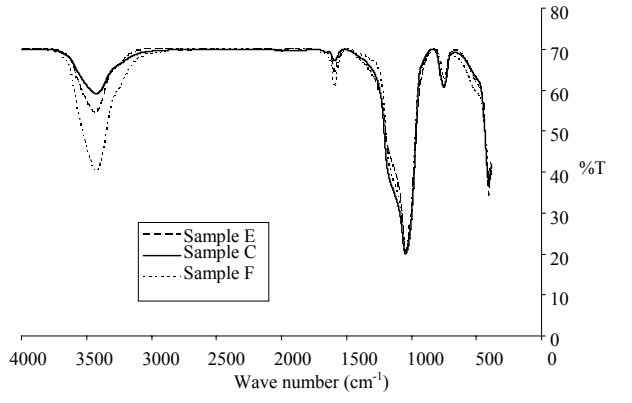
The relative amount of the silanol group was studied by comparison of the FT-IR peak intensity at wave number 3400-3600 cm^{-1} as shown in Figure 2. The effect of the higher reaction temperature was a large amount of silanol group (Figure 2(a)) because higher temperature induced more silica networks with a larger amount of silanol group. The amount of silanol group was also enhanced by longer reaction time and hydrothermal time, which is presented in Figure 2(b) and 2(c), respectively.



(a)



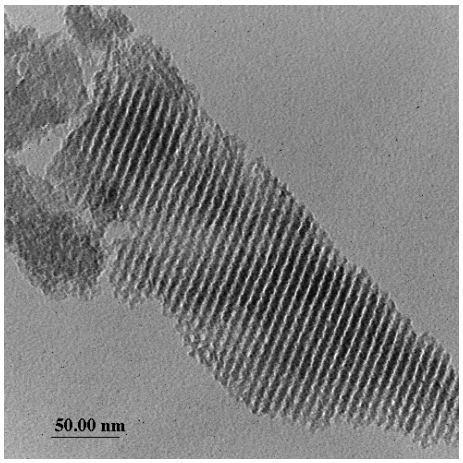
(b)



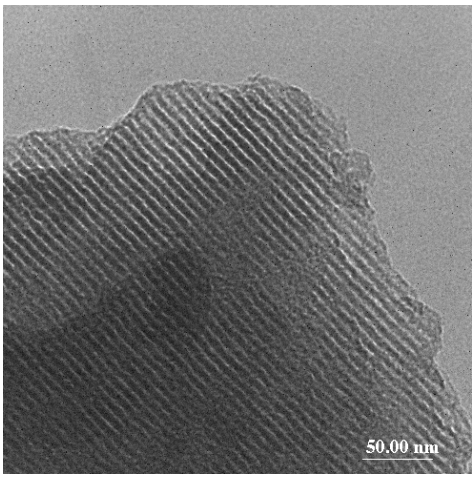
(c)

Figure 2. FT-IR Spectra of mesoporous silica from variation of each parameter; (a) reaction temperature, (b) reaction time, (c) hydrothermal time

The microstructure of mesoporous silica from rice husk ash was ordered long range tubular structure which is presented in TEM micrograph (Figure 3(a)). After loading of indigo carmine, TEM micrograph presented mesoporous silica tube contained indigo carmine molecule as shown in Figure 3(b).



(a)



(b)

Figure 3. TEM micrograph of mesoporous silica from rice husk ash (a) mesoporous silica (b) indigocarmine loaded mesoporous silica

Loading and Releasing Study

The percentages of indigo carmine loading are shown in Table 2. The textural properties and amounts of the silanol group affected the indigo carmine loading. The larger pore volume can contain a larger amount of indigo carmine as shown in samples A, C and F. The sample E showed very low indigo carmine loading due to small pore volume. Comparing samples B and C,

sample B had lower pore volume than sample C, but the sample B and C presented nearly percentage of indigo carmine loading due to the effect of the silanol group. The silanol group can attract molecules of indigo carmine via hydrogen bonding to increase the efficiency of indigo carmine collecting as shown in Figure 3. Sample D had low indigo carmine loading (3.87%) which was the largest pore diameter (30.08 nm). The large pore diameter permitted the free movement of indigo carmine through the pore of mesoporous silica due to absent steric diffusion resistance.[8] Therefore, mesoporous silica collected only a small amount of indigo carmine.

Table 2. Loading percentage of indigo carmine from mesoporous silica from rice husk ash

Sample	Temperature (°C)	Reaction time (h)	Hydrothermal time (h)	Loading percentage of indigo carmine
A	30	20	24	16.9
B	60	20	24	13.5
C	60	30	24	12.2
D	60	63	24	3.87
E	60	30	0	1.14
F	60	30	48	16.5

The releasing behavior of indigo carmine consisted of two stages as shown in Figures 4-6. The first stage was fast releasing from adsorbed indigo carmine in external surface. Secondly, the indigo carmine from porous of silica was released slowly which was mainly affected by the textural properties and the silanol group. The releasing rate depended on the amount of indigo carmine loading. The mesoporous silica sample B gave higher percentage loading than sample A (Table 2) which also released faster as shown in Figure 4.

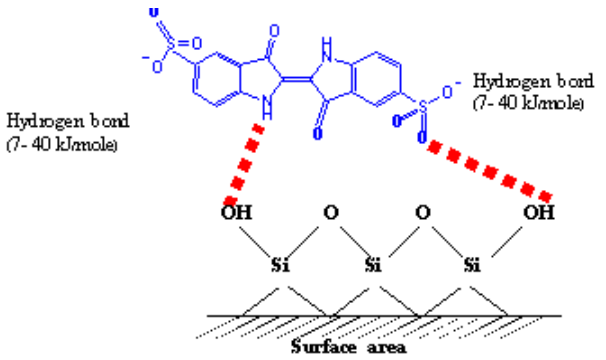


Figure 4. Interaction between silanol group and indigo carmine molecule

The releasing behavior of indigo carmine in Figure 5 shows the effect of the silanol group which is presented in sample C. Sample C contained nearly the same indigo carmine as sample B, but sample C showed faster releasing than sample B. From Figure 2(b), sample C had a lower silanol group than sample C. Silanol group played the interaction force with indigo carmine molecule (Figure 3).

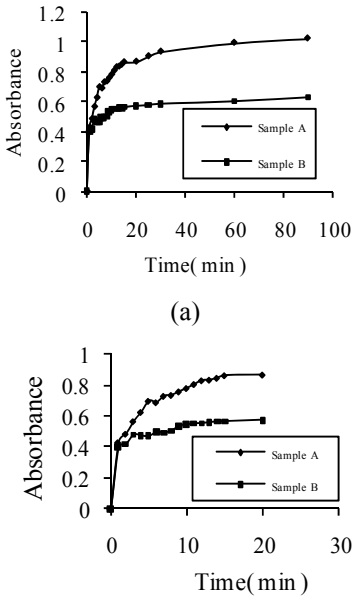
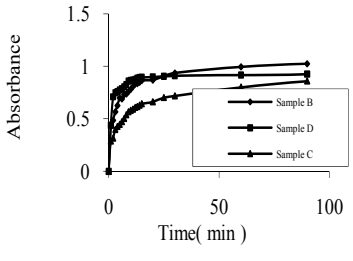
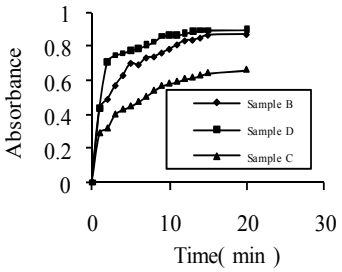


Figure 5. Releasing profiles of indigo carmine from mesoporous silica synthesized from rice husk ash at various reaction temperatures (a) releasing time 90 min (b) releasing time 20 min

The hydrothermal effect is presented in Figure 6. The highest amount of loading indigo carmine was released within five minutes because loaded indigo carmine was adsorbed by silanol group in theexternal surface. Hydrothemal treatment can enhance the silanol group in the external surface. This is corroborated by the fact that the longest hydrothermal time showed the largest amount of silanol group as shown in Figure 2(c).



(a)



(b)

Figure 6. Releasing profiles of indigo carmine from mesoporous silica synthesized from rice husk ash at various reaction times (a) releasing time 90 min (b) releasing time 20 min

Conclusions

The variation of synthesis conditions provided different physical properties of mesoporous silica from rice husk ash as pore volume, pore diameter and the amount of silanol group. These properties influenced indigo carmine releasing behavior. The pore volume had the major effect on indigo carmine loading which affects the driving force of the concentration between silica particle and buffer solution. The silanol group also affected loading and releasing behavior because the hydroxyl group interacts with indigo carmine molecule by hydrogen bonding.

Acknowledgements

This research was granted by Thammasat University Research Fund.

References

1. Chareonpanich, M., Namto T., Kongkachuichay P. and Limtrakul, J. 2004. Synthesis of ZSM-5 zeolite from lignite fly ash and rice husk ash. *Fuel Process. Technol.* **85(15)**: 1623– 1634.

2. Chareonpanich, M., Nanta-ngern, A. and Limtrakul, J. 2007. Short-period synthesis of ordered mesoporous silica SBA-15 using ultrasonic technique. *Mater. Lett.* **61(29)**: 5153–5156.

3. Chen, J. F., Ding, H. M., Wang, J. X. and Shao, L. 2004. Preparation and characterization of porous hollow silica nanoparticles for drug delivery application. *Biomaterials* **25(4)**: 723-727.

4. Fagundes, L. B., Sousa, T. G. F., Sousa, A., Silva, V. V. and Sousa, E. M. B. 2006. SBA-15-collagen hybrid material for drug delivery applications. *J. Non-Cryst. Solids* **352(32)**: 3496–3501.

5. Li, Z. Z., Wen, L. X., Shao, L. and Chen, J. F. 2004. Fabrication of porous hollow silica nanoparticles and their applications in drug release control. *J. Controlled Release* **98(2)**: 245-254.

6. Marini, M., Pourabbas, B., Pilati, F. and Fabbri, P. 2008. Functionally modified core-shell silica nanoparticles by One-pot synthesis, *Colloids Surf., A.* **317(3)**: 473-481.

7. Nandiyanto , A.B. D., Kim, S.G., Iskandar, F. and Okuyama, K. 2009. Synthesis of spherical mesoporous silica nanoparticles with nanometer-size controllable pores and outer diameters. *Microporous Mesoporous Mater*. **120(3)**: 447-453.

8. Qu, F., Zhu, G., Huang, S., Li, S., Sun, J., Zhang, D. and Qiu, S. 2006. Controlled release of captopril by regulating the pore size and morphology of ordered mesoporous silica. *Microporous and Mesoporous Mater*. **92(1-3)**: 1-9.

9. Ren, T. Z., Yuan, Z. Y. and Su B. L. 2007. Encapsulation of direct blue dye into mesoporous silica-based materials. Colloids *Surf., A.* **300(1-2)**: 79–87.

10. Witoon, T., Chareonpanich, M. and Limtrakul, J. 2008. Synthesis of bimodal porous silica from rice husk ash via sol–gel process using chitosan as template. *Mater. Lett*. **62(10-11)**: 1476–1479.

11. Zhao,D., Feng, J., Huo, Q., Melosh, N., Fredrickson, G. H., Chmelka, B. F. and Stucky, G. D. 1998. Triblock copolymer syntheses of mesoporous Silica with Periodic 50 to 300 Angstrom Pores. *Science* **279(5350)**: 548-552.