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Synthesis and characterization of mesoporous silica: laboratory exercises for students

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Synthesis and characterization of SBA-15 were proposed as a laboratory course: linked series of exercises for graduate students. The standard preparation method was modified to fit a typical schedule of students' classes, that is, 3-hours units every second week. The properties of materials obtained by different students' groups were compared with the properties of materials obtained by means of a standard method.

1. INTRODUCTION

SBA-15 is an unique mesoporous silica material, which has obtained much attention due to its high specific suface area, uniform particle size, regular array of pores, thermal stability, and low toxicity, and an early paper [1] on its synthesis and characterization obtained over 7000 citations in WoS®. Original and modified SBA-15-materials have been considered as adsorbents, catalyst supports, and components of medicines (controlled drugs release), and several studies of these materials have also been performed by the members of Professor Stanisław Chibowski's research group [2–4].

Relatively simple synthesis of SBA-15 inspired us to propose a laboratory course: linked series of exercises for graduate students. The students synthesize SBA-15 themselves and then characterize their

material by means of low-temperature nitrogen adsorption and by microelectrophoresis. The main challenge in designing such a course is the framework of the academic year, namely the entire synthesis must fit several relatively short and equal (3 h or so) units which repeat regularly every week or every second week. Such a framework makes this necessary to modify a standard preparation method.

2. ORGANIZATION OF CLASSES

The present modified synthesis was adjusted to the following conditions. The students work in small groups, 3-5 students each. Each group is responsible for synthesis and characterization of one batch of SBA-15. The course consists of 8 units (one unit every second week): one unit 2×45 min. and 7 units, 4×45 min. each. In principle the break between consecutive units is 2 weeks, but due to national and religious holidays it can be longer (3 or even 4 weeks). The present modified recipe is flexible and it can be adjusted to other frameworks, e.g., 10 units, 3×45 min. each, etc.

3. SYNTHESIS

The present synthesis is based on the recipe described by Milonjic [5], which is one of many recipes described in [1]. The amounts of components were scaled down by a factor of 2 in order to adjust the volume of the entire batch to the size of a commercial thermostated reactor (capacity of 150 cm^3). We only describe in detail those elements, which are directly related to synthesis of SBA-15, and skip less important details.

Unit 1. The students received workplace health and safety (WHS) training, which is obligatory before every laboratory course. They also prepared 2 M HCl, to be used in unit 2.

Unit 2. About 2 g of Pluronic P123 was put into a glass, thermostated reactor. The temperature was set to 35°C. Due to the gel-like consistency of P-123 this is very difficult to get exactly 2 g. This is why it is more convenient to use an approximate amount, and re-calculate the amounts of all other reagents. P-123 was dissolved in 15 cm^3 of water and 60 g of 2 M HCl. The above amounts refer to 2 g of Pluronic P123, and they have to be re-calculated when the mass of Pluronic is different. Both water and

2 M HCl are added on volume basis, and the specific density of 2 M HCl is taken from chemical tables. The mixture was stirred at 35°C, and the students observed gradual dissolution of P123. Once the dissolution was completed (this takes 1 h or so), the mixture was stirred for 10 more minutes, and 4.25 g of TEOS were added manually dropwise within about 1.5 h. TEOS was added on volume basis (with the stirrer still on), and its specific density was taken from chemical tables. The above amount of TEOS refers to 2 g of Pluronic P123, and it has to be re-calculated when the mass of Pluronic is different. The above steps take together about 4×45 min. The students leave the thermostat and the stirrer on and the class is complete. The teacher stops the stirrer on the next day, 20 h after the addition of TEOS was completed (the students are absent) and transfers the mixture into an air tight plastic bottle, which is kept at room temperature until unit 3.

Unit 3. The students observe the reaction mixture and record its properties (odor, structure of the particles and their stability). They put the bottle with the mixture into a laboratory forced air oven. The temperature is set to 80°C, and the time is set to 48 h. After this time the temperature drops automatically to room temperature, so the presence of the teacher or of students is not necessary to terminate the heating at 80°C. The activities of the students during unit 3 are not particularly extensive. The rest of the time can be used for another exercise (unrelated to SBA-synthesis).

Unit 4. The students observe the reaction mixture and record its properties (odor, structure of the particles and their stability). They wash the particles in a series of centrifugation-decantation cycles. They transfer approximately equal amounts of the dispersion into two centrifuge tubes, of capacity of 250 cm^3 each, add water to a total volume of about 180 mL in each tube, and bring them to equal mass using distilled water. The centrifugation at 3000 rpm takes 30 min. The clear liquid is removed after the first centrifugation, and fresh water is added to a total volume of about 180 mL in each tube. Such a centrifugation-decantation cycle is repeated 3 times. The last centrifugation cycle is longer (45 min.) and at higher speed (4000 rpm). The centrifuge tubes are transferred into a laboratory forced air oven. The temperature is set to 60°C, and the particles were dried for 1 d. After this time the temperature drops automatically to room temperature, so the presence of the teacher or of students is not necessary to terminate the heating at 60°C.

Unit 5. The students observe the dry particles and record their properties. The particles were transferred into an oven, and calcined in a

stream of air. The temperature was raised to 500°C within 8 h and then maintained at 500°C for 6 more hours. After this time the temperature drops automatically to room temperature, so the presence of the teacher or of students is not necessary to terminate the calcination at 500°C. The activities of the students during unit 5 are not particularly extensive. The rest of the time can be used for another exercise (unrelated to SBA-synthesis). They also prepare the following solutions: 1 mM NaCl, 0.1 M NaOH, and 0.1 M HCl, which will be used in the next units.

Unit 6. The students observe the calcined particles and record their properties. Then they perform a measurement of low temperature nitrogen adsorption by means of Gemini 2365 from Micromeritics. The amount of SBA-15 used in this analysis is about 10 mg. The students record the mass of SBA-15 before and after drying (300°C, 30 min.) and estimate the amount of adsorbed water as the difference. This should be emphasized that the uptake of water by SBA-15 severely depends on the level of ambient humidity, and it cannot be used to characterize the material. Then 9 to 14 data points were recorded by means of Gemini, and the program automatically calculated the BET specific surface area (p/p_0 up to 0.3), the total pore volume (single point, p/p_0 of about 0.98), and average pore width (4 V/A(BET)).

Unit 7. The students prepare a dispersion of 100 mg of SBA-15 in 0.5 dm^3 of 1 mM NaCl, ultrasonify it within 15 min, and pour 50 cm^3 portions of this dispersion into each of 10 plastic test tubes. Than the pH is adjusted to different values by addition of small amounts of 0.1 M NaOH of HCl. The ζ potential was measured by means of Malvern Zetasizer Nano using disposable transparent cells, and the pH was measured just after the electrophoretic measurement.

Unit 8 was used to discuss the written reports prepared by the students (one report per a group of 3 to 5 students).

Our recipe is different from the standard recipe in the following points:

- long delay between heating at 35°C (unit 2) and heating at 80°C,
- long delay between heating at 80°C (unit 3) and washing,
- different washing procedure,
- scaling the amounts of reagents up or down may also matter.

The above points might substantially affect the properties of SBA-15. The other differences, e.g., delay between drying at 60°C (unit 4) and calcination (unit 5) are rather unlikely to affect the properties of SBA-15.

4. RESULTS AND DISCUSSION

The results obtained by Gemini are summarized in Table 1.

Table 1. BET specific surface area, total pore volume, and average pore width reported in the literature and obtained by 5 student groups.

Group	Surface area [m^2/g]	Pore volume [cm^3/g]	Pore size [nm]
H	844	0.93	4.4
A	1020	1.12	4.4
D	819	0.91	4.4
V	700	0.65	3.7
P	1090	–	–
[1]	780	0.8	6
same recipe	820	1.03	7.7
[1] various recipes	630–1040	0.7–1.23	4.6–10
[5]	710	–	2.9*

* peak

All materials prepared by the students had high specific surface area, high pore volume, and average pore size about 4 nm. The minor differences in particular materials were probably due to the steps which are difficult to control, e.g., manual dropwise addition of TEOS (unit 2), uncontrolled evaporation of solvent during long storage periods, and scaling the amounts of reagents up and down (the amount of Pluronic used by particular groups ranged from 1.8 to 2.1 g). Yet the modification of the recipe to adjust it to the organization of classes did not induce any major difference with respect to materials obtained by means of standard method (Table 1). Table 1 shows only two examples taken from literature, but in fact similar results for the standard recipe were obtained by many research groups.

The results obtained by means of Malvern Zetasizer are summarized in Fig. 1.

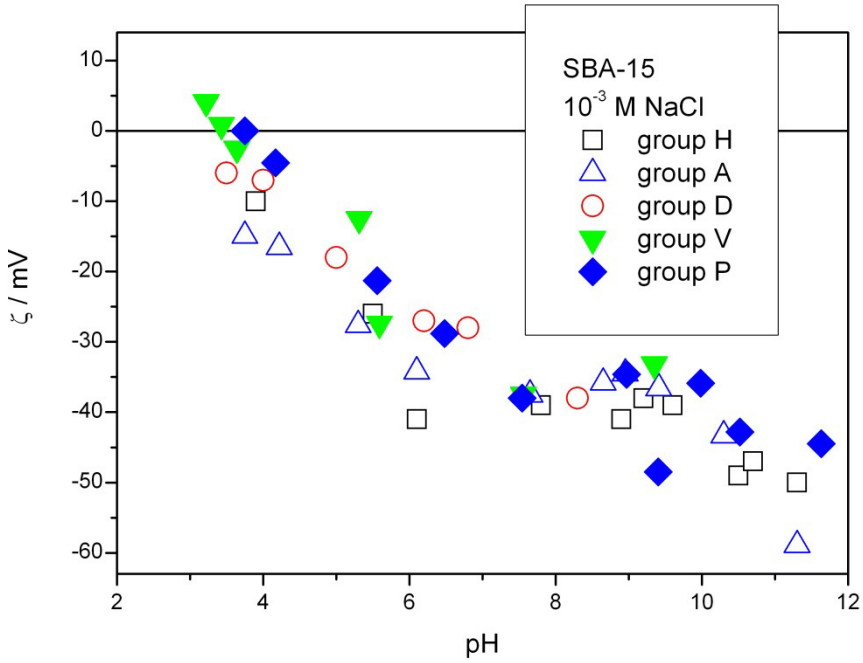

Fig. 1. Electrokinetic potential of SBA-15.

The results presented in Fig. 1 show some scatter, but they are all consistent with one master curve, and with IEP at pH 3.3. Similar IEP for the standard recipe was reported in the literature [5]. The studies reporting the electrokinetic properties of SBA-15 are less numerous than the studies reporting its specific surface area. Rosenholm and Linden [6] found an IEP at pH 2.5. Perez et al. [7] found an IEP between pH 3.5 and 6 (no data points in between). Nieto et al. [8] found an IEP at pH 4. Relatively high IEP reported by Nieto et al. may be due to the fact, that they used KCl as the supporting electrolyte. Namely KCl is known to shift the IEP of silica to high pH. Bui [9] found a CIP of charging curves of SBA-15 at pH 4. Their result is rather unusual, namely charging curves of silica reported in most studies merge at low pH, and they do not show a sharp CIP. The present results confirm the general trend found in silicas made of organic precursors. They have relatively high IEP (>3 with a few exceptions) as compared with natural quartz, which often shows only negative ζ potentials, even at very low pH.

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REFERENCES

[1] D.Y. Zhao, J.L. Feng, Q.S. Huo, N.Melosh, G.H. Fredrickson, B.F. Chmelka, and G.D. Stucky, *Science*, **279,** 548, (1998).
[2] M. Barczak, E. Skwarek, W. Janusz, A. Dąbrowski, and S. Pikus, *Appl. Surf. Sci.*, **256,** 5370, (2010).
[3] A.W. Marczewski, A. Deryło-Marczewska, I. Skrzypek, S. Pikus, and M. Kozak, *Adsorption*, **15,** 300, (2009).
[4] A. Deryło-Marczewska, A.W. Marczewski, I. Skrzypek, S. Pikus, and M. Kozak, *Appl.Surf.Sci.*, **255,** 2851, (2008).
[5] M. Kokunesoski, J. Gulicovski, B. Matovic, M. Logar, S.K. Milonjic, and B. Babic, *Mater.Chem.Phys.*, **124,** 1248, (2010).
[6] J.M. Rosenholm, M. Linden, Chem. Mater. **19,** 5023, (2007).
[7] H. Perez, P. Navarro, M. Montes, *Chem. Eng. J.* **158,** 325, (2010).
[8] A. Nieto, F. Balas, M. Colilla, M. Manzano, M. Vallet-Regi, *Microp. Mesop. Materials*, **116**, 4 (2008).
[9] T.X. Bui, H.C.Choi, *J.Hazard.Mat.* **168,** 602, (2009).