

## Synthesis and Characterization of Functionalized SBA-15 Mesoporous Silica by N, N'-Bis(salicylidene)ethylenediamine Schiff-Base

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### Abstract

In this work, BSEA-SBA-15 was prepared for the first time, which was prepared by covalently anchoring Schiff-base compound (N,N'-bis(salicylidene)ethylenediamine (BSEA) on SBA-15 by hydrothermal method. The structure and physicochemical properties were determined by elemental analysis, XRD, nitrogen adsorption-desorption, thermogravimetric analysis and FTIR spectroscopy, SEM, BET surface area and BJH pore size. The average pore diameter after the modification is 69 Å. It is expected that BSEA-SBA-15 can be used as an effective adsorbent for the removal of metal ions due to having porous structure and active functional groups.

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## 1. Introduction

Many research efforts have focused on the modification of mesoporous materials with organic functional groups such as ordered mesoporous silicas, for applications in separation, adsorption, catalysis, drug delivery, and nanotechnology [1]. Mesoporous silicas can be functionalized with different organic groups such as 5-nitro-2-furaldehyde [1], salicylaldehyde [2] and several another functional groups. MCM-41 [4] and SBA-15 [5] were widely used as supports due to their tunable pore size and narrow pore size distribution. In comparison with other mesostructured materials, SBA-15 is better because of having larger pores

(5–30 nm) and thicker pore walls (3.1 – 6.4 nm), which cause high hydrothermal stability [6]. In particular, mesoporous SBA-15 has been prepared by hydrothermal method in the presence of non-ionic surfactant (P123) [7]. In this work, we successfully synthesized BSEA-SBA-15 for the first time. It is expected that this compound can be used as an effective adsorbent for the removal of metal ions due to having porous structure and active functional groups as the other similar works [8-10]. The incorporation of the functional group has been showed by FT-IR spectroscopy and amount of this group got by elemental analysis.

## 2. Experimental procedure

### 2.1. Materials

All of the used chemicals were purchased from Merck and Aldrich Co. and used without further purification.

### 2.2. Synthesis method

#### 2.2.1. SBA-15

This material was synthesized by hydrothermal method using tetraethylortosilicate (TEOS), Pluronic P123 as template, and HCl to cause the media acidic [5, 11]. 4 g Pluronic (P123, Mn = 5800, EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, (Aldrich Co.)), 90 mL of 2 M hydrochloric acid and 21 mL deionized water were stirred at room temperature. Then, 6.4 g (6.8 mL) TEOS (Merck Co.) was added to solution with stirring at 40°C for 24 h. The mixture was aged in autoclave at 100°C for 24 h. The obtained compound, filtered, washed and dried at room temperature. Then, the result white solid was calcined at 600°C for 6 h.

#### 2.2.2. Cl-SBA-15

5 g of activated SBA-15 was stirred in dry toluene (50mL) for 1 h. Then, 5 mL (20.76 mmol) of chloropropyltriethoxy silane (CPTES) (Merck Co.) was added and refluxed at 122°C for 24 h under nitrogen atmosphere. The resulting compound was filtered, washed and dried at 110°C for 4 h in a vacuum oven [12].

#### 2.2.3. SA-SBA-15

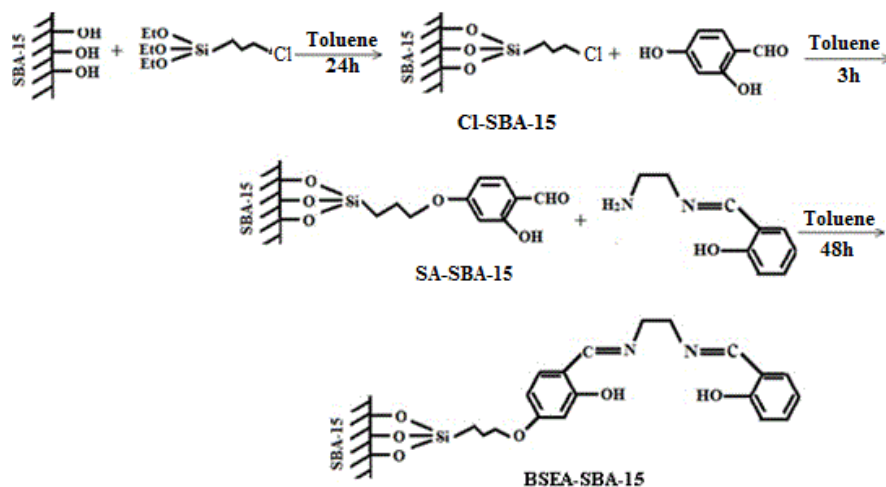
2, 4-dihydroxy benzaldehyde (Aldrich Co.) (2.83g), Cl-SBA-15 (2g) and triethylamine (Merck Co.) (2 g) in toluene (50 mL) were refluxed for 3 h. Then, the obtained solid was filtered, rinsed with ethanol and dried in a vacuum oven at 80°C for 10 h.

#### 2.2.4. BSEA-SBA-15

Salicylic acid (Merck Co.) (10.62 mL) and ethylene diamine (Merck Co.) (67.6 mL) in ethanol (50 mL) were refluxed for 2 h. The resulting compound was filtered, washed and air-dried. 1 g of this compound and 1 g of SA-SBA-15 in toluene (50 mL) were refluxed for 48 h under nitrogen atmosphere. The obtained solid was centrifuged, washed with 50 mL of the mixed solvents (ethanol, diethyl ether, distilled water) and dried in vacuum for 10 h at 90°C. Finally, any residual impurities (surfactant and organosilane) were removed by Soxhlet extraction over the mixture of diethylether and dichloromethane (1:1) at 100 °C for 24 h and heated for 10 h at 40°C under vacuum. Synthesis steps are displayed in Scheme 1. The characterization of mesoporous was carried out by XRD, SEM, FT-IR, BET, BJH, FESEM, TGA and elemental analysis.

### 2.3. Characterization

Low-angle XRD pattern was recorded on a Bruker diffractometer using Cu K $\alpha$  radiation (wavelength,  $\lambda = 1.5418 \text{ \AA}$ ). Fourier transform infrared (FT-IR) spectrum was recorded on a Shimadzu-8400S spectrometer in the range of 400-4000 cm<sup>-1</sup> using KBr pellets. The surface area of the product was determined by using Brunauer-Emmett-Teller (BET) technique with Micromeritics (Gemini) in the range of relative pressures from 0.0 to 1.0. Before employing, the sample was degassed at 200 °C for 2 h. In addition, the pore size distribution was obtained from the desorption branch of the isotherm curve using the Barrett-Joyner-Halenda (BJH) model. Thermogravimetric analysis (TGA) was carried out on PerkinElmer Pyris Diamond from room temperature to 800°C by a ramp rate of 10°C/min in air.



**Scheme 1.** The synthesis steps of BSEA-SBA-15

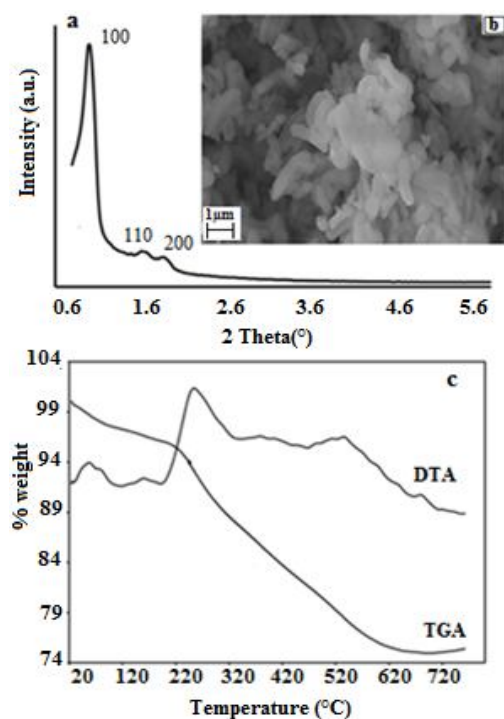
Elemental analysis (CHN) was evaluated by combustion on Perkin Elmer CHNS/O Elemental Analyzer model 2400 II apparatus. FESEM images were taken by Hitachi S4160 Japan.

### 3. Results and discussion

The low-angle XRD pattern of BSEA-SBA-15 has been exhibited two weak lines (110, 200) and a single strong peak (100), which can be confirmed on hexagonal and order lattice (Fig 1a) [5]. The morphology of the BSEA-SBA-15 was studied by a scanning electron microscopy. A regular and ordered structure with relatively uniform size approximately 1 $\mu$ m, which is in good agreement with SBA-15, can be observed in FESEM image (Fig 1b). Thermogravimetric analysis (TGA) and the enthalpy changes (DTA) have been showed significant thermal stability for BSEA-SBA-15. The results have been given in Fig 1c. The TGA analysis shows the loss of mass (about 3%) between room temperature and 200°C that is related to physically adsorbed water molecules, which is an endothermic process according to DTA curve. The largest weight loss (22%) from 200 to 600°C is due

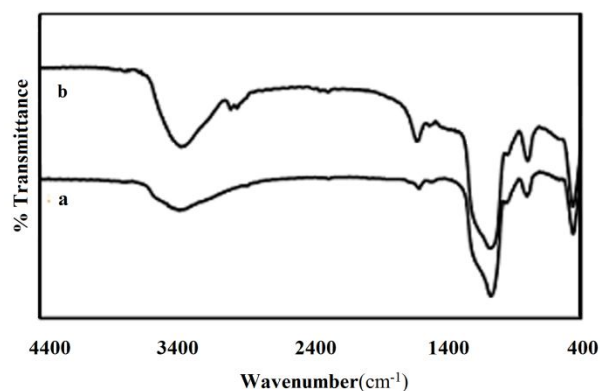
to the degradation process of the grafted Schiff base ligand on SBA-15, which is an exothermic process as shown on TGA and TDA curves in Fig 1c [13].

The FT-IR spectra of SBA-15 and BSEA-SBA-15 are shown in Fig 2. The FT-IR spectrum of SBA-15 (Fig 2a) displays a large broad band at 3435  $\text{cm}^{-1}$ , which related to the O-H stretching vibration of the surface silanol groups [10]. The appeared peaks around 1000-1100  $\text{cm}^{-1}$  can be attributed to Si-O-Si and Si-O-H asymmetric stretching vibrations and indicates the presence of silica in the prepared nanomaterials. There are two new bands at 2931 and 1630  $\text{cm}^{-1}$ , which belong to the stretching vibrations of C-H in propyl group and C=N bond, respectively (Fig 2b) and confirm the presence of anchored propyl groups. The relative broad peak about 3400  $\text{cm}^{-1}$  for BSEA-SBA-15 is sharper than one for SBA-15, which is related to stretching vibration of hydroxyl groups in Schiff base ligand [14].



**Fig. 1.** (a) Low angle XRD pattern, (b) SEM image (c) TGA and DTA diagrams of BSEA- SBA-15.

Therefore, these results indicate successful grafting of (N, N'-bis (salicylidene)ethylenediamine). Textural and physicochemical properties of BSEA-SBA-15 such as the pore diameter ( $D_{BJH}$ ), the BET surface area ( $S_{BET}$ ), the total pore volume ( $V_{total}$ ) and N content are given in Table 1. According to Table 1, the decrease of the BET surface area, the mesoporous volume and average pore diameter after the modification, indicates the ligand grafting (N content also confirms the loading of the Schiff- base). Fig 3 displays a type IV nitrogen sorption isotherm in accordance to the defined behavior of SBA-15[15].



**Fig.2.** (a) FT-IR spectra of SBA-15 (b) BSEA-SBA-15

**Table 1.** Textural and physicochemical properties of BSEA-SBA-15

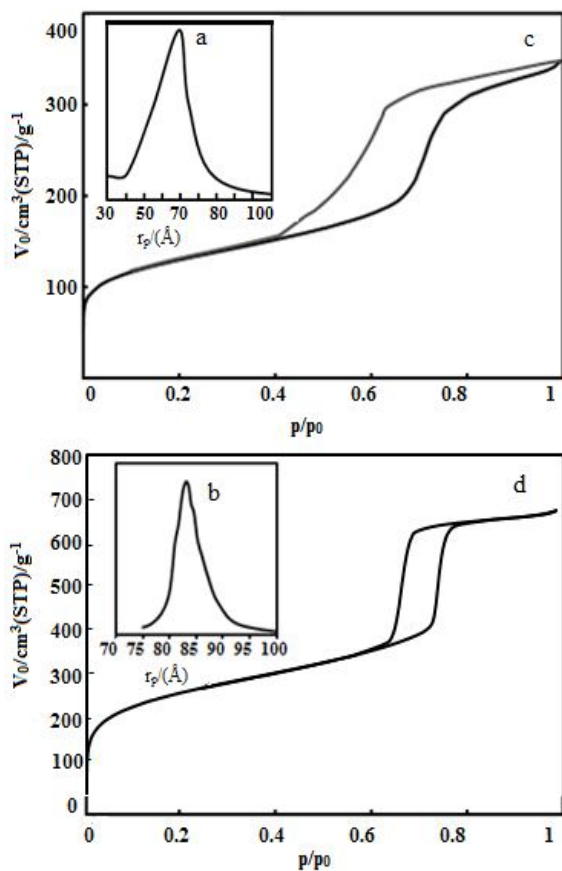
| Sample      | BET surface area<br>( $m^2/g$ ) | Pore diameter <sup>a</sup><br>(BJH)( $\text{\AA}$ ) | Total pore volume<br>( $m^3/g$ ) | N content <sup>b</sup><br>(mmol/g) |
|-------------|---------------------------------|---|----------------------------------|------------------------------------|
| SBA-15      | 869                             | 85  | 1.034                            | –                                  |
| BSEA-SBA-15 | 285                             | 69  | 0.399                            | 0.43                               |

<sup>a</sup> The average pore size was calculated by BJH model from the adsorption branches

<sup>b</sup> N content was obtained from the elemental analysis

**Table 2.** The grafting of various ligands on SBA-15

| Mesoporous Support | Ligand                                 | $D_{(BJH)}$ (nm) | Reference |
|--------------------|--|------------------|-----------|
| SBA-15             | aminobenzenesulfonamide                | 5.1              | [16]      |
| SBA-15             | ethylenediamine                        | 2.7              | [17]      |
| SBA-15             | 1-furoyl thiourea                      | 0.8              | [10]      |
| SBA-15             | N, N'-bis(salicylidene)ethylenediamine | 6.9              | This work |



**Figure.3.** The diagram of pore size distribution (a) BSEA-SBA-15 (b) SBA-15 and  $N_2$  adsorption-desorption isotherms (c) BSEA-SBA-15 (d) SBA-15

The grafting of various ligands on SBA-15 has been showed in Table 2. As seen in Table 3, the ligand BSEA has a large pore diameter and in comparison with the previous reports, it is a Schiff base ligand.

#### 4. Conclusion

In this work, the functionalization of SBA-15 with (N, N'-bis(salicylidene)-ethylenediamine Schiff-base as ligand has been successfully carried and the structure ordering of SBA-15 was protected during the chemical modifications. The modified SBA-15 materials show hexagonal mesoscopic order, excellent thermal and hydrothermal stabilities. The pore diameter and the surface area of BSEA-SBA-15

have been obtained  $69\text{\AA}$ ,  $285\text{m}^2/\text{g}$  by BET. According to the other reports, BSEA-SBA-15 can be used as an effective adsorbent for the removal of metal ions due to having porous structure and active functional groups.

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