Preparation of SBA-15 and Zr-SBA-15 materials by direct-synthesis and pH-adjustment methods

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Abstract

SBA-15 mesoporous silica materials with zirconium atoms incorporated into its structure were prepared by two methods: direct-synthesis and pH-adjustment. Two nominal ratios of Zr/Si=0 and 0.10 were evaluated. N_2-physisorption and X-ray powder diffraction (XRPD) revealed that the morphology and structural order of the SBA-15 materials were greatly affected by the incorporation of zirconium into the SBA-15 structure as well as by the synthesis method. High-resolution transmission electron microscopy (HRTEM) of the materials prepared by pH-adjustment (SBA-15-2 and Zr-SBA-15-2 samples) revealed a more perfectly defined mesoporous structure with long-range ordering when compared with the materials obtained by direct-synthesis (SBA-15-1 and Zr-SBA-15-1 samples). The results by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Energy-Dispersion X-ray Spectroscopy (EDX) to evaluate the elemental composition of the materials indicated a better correlation using the pH adjustment method.

Keywords: mesoporous, structure, silica, SBA-15, zirconium, incorporation

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1. Introduction

The synthesis of well-ordered hexagonal mesoporous silica (SBA-15) has attracted much interest due to its high specific surface area, large pore size, and controllable morphology. A previous work **[1]** reported that SBA-15 with highly ordered and uniform hexagonal mesostructured and silica walls (*p*6*mm*) were synthesized under aqueous acidic conditions in presence of a dilute triblock copolymer. SBA-15 properties can be improved and modified by the incorporation of heteroatoms into its mesoporous structure **[2]**. The introduction of a heteroatom into the walls of the SBA-15 can not only modify its textural characteristic but also enhance its original hydrothermal stability **[3]**. Different heteroatoms can be introduced in the silica framework such as Al^{3+} and Ti^{4+} which will deliver acidic and redox properties to SBA-15 **[4]**.

Direct-synthesis and pH-adjustment are two common methods used for the incorporation of heteroatoms in the silica mesoporous structure **[2, 3]**. The direct-synthesis method entails the co-assembly of a surfactant to form the micellar framework and the condensation of the silicon and heteroatomic species that are added together into the reaction mixture, generating an inorganic structure after a hydrothermal treatment **[5]**. Similarly, in the pH-adjustment method, a modification is carried out with two additional steps consisting of pH regulation of the reaction medium from acid to neutral and further hydrothermal treatment. The efficiency of heteroatomic incorporation in the direct-synthesis method is usually low since only a partial fraction of heteroatom can be introduced into the SBA-15 structure **[2]**. In contrast, it is reported that the pH-adjustment method can incorporate a larger amount of heteroatom into the SBA-15 structure. The materials prepared by this method exhibited a highly ordered mesoporous structure with a large specific surface area and uniform mesopore size distribution **[2]**.

Here, we report the preparation of SBA-15 and the incorporation of zirconium atoms into the SBA-15 structure by direct-synthesis and pH-adjustment methods. Two Zr/Si ratios were evaluated. The effect of the synthesis method on the SBA-15 structure was accessed by different characterization techniques.

2. Materials and Methods

2.1. Synthesis of SBA-15 and Zr-SBA-15 materials

The synthesis of the SBA-15-type materials was carried out following the procedure reported by Kruk *et al*. **[6]** with modifications. $ZrO(NO_3)_2{\cdot}xH_2O$ (99%, Sigma-Aldrich) was dissolved at 45 °C in 100 mL of water. After, 10 mL of a concentrated HNO_3 (65 wt.%, Merck) solution was added. Then, triblock copolymer P-123 (Sigma-Aldrich) was added to the prior solution and stirred for 2 h. Next, $SiC_8H_{20}O_4$ (TEOS, 98%, Sigma-Aldrich) was added dropwise, and stirring continued for 24 h. The mixture molar composition was Y $ZrO(NO_3)_2{\cdot}xH_2O$: (0.0410-Y) TEOS: $6.9x10^{-4}$ P-123: 0.1454 HNO_3: 5.8292 H_2O, taking Y values of 0 and 0.0037 to get nominal ratios of Zr/Si=0 and 0.10, respectively. Subsequently, the mixture was hydrothermally treated in a glass reactor at 60 °C for 48 h. The resulting solids were recovered by filtration, washed with water until neutral pH, and with 100 mL of a 1:1 volumetric mixture of water and methanol (99.6 %, Sigma-Aldrich). Finally, the solids were dried in an oven at 100 °C for 24 h and heated in a muffle from room temperature to 500 °C (2 °C/min) for 5 h. These synthesized solids were coded as SBA-15-1 and Zr-SBA-15-1. The suffix 1 refers to the direct-synthesis method.

Another pair of samples was prepared using the pH-adjustment method **[2]**. Here, the same procedure described above was followed until the hydrothermal treatment. Then, the pH of the resulting mixture was regulated to 7.50 with the dropwise addition of an ammonia solution (25 wt.%, Merck) and a further hydrothermal treatment was carried out at 60 °C for 48 h. Recovery, drying, and calcination processes were the same as those described above. The resulting solids were coded as SBA-15-2 and Zr-SBA-15-2. The suffix 2 refers to the pH-adjustment method.

2.2. Characterization

N_2-physisorption was performed in a Tristar II series Micromeritics apparatus. BET and BJH methods were applied to determine the textural parameters. XRD patterns were recorded on a Siemens D5000 diffractometer using CuK_α radiation (1.5406 Å) at small-angles (2θ range=1-5°, step size=0.01°/s, step time=15s) and wide-angles (2θ range=5-90°, step size=0.05°/s, step time=3s). HRTEM images were obtained at 200 kV using an FEI Tecnai F20 microscope equipped with a field emission source and an energy-dispersive X-ray spectrometer (EDX), with a point-to-point resolution of 0.19 nm. Samples were prepared by depositing a drop of a suspension of the sample in methanol on a holey carbon-coated copper grid and allowed to dry. A Thermo Fisher Scientific iCAP RQ ICP-MS system was used

to determine the elemental composition of the samples. Before the analysis, the samples were digested in a mixture of acids HF-HCl (3:7) in Mileston microwave equipment for 15 min at 120 °C.

3. Results and discussion

The elemental composition analysis of silicon and zirconium to determine the molar ratio of Zr/Si in the Zr-SBA-15-1 and Zr-SBA-15-2 samples indicated that the incorporation of zirconium was more efficient in the material obtained by the pH-adjustment method (i.e., Zr-SBA-15-2) because the ratio determined by ICP and EDX techniques better matches with the nominal value (Table 1).

Table 1. Compositional, textural, and structural properties of the SBA-15-type materials.

Method	Sample	Zr/Si ratio			S_{BET}	V_{pore}	D_{pore}
		Nominal	ICP	EDX	(m^2/g)	(cm^3/g)	(nm)
Direct-synthesis	SBA-15-1	0	-	-	816	0.72	3.8
	Zr-SBA-15-1	0.10	0.07	0.09	633	0.43	3.5
pH-adjustment	SBA-15-2	0	-	-	636	1.41	9.2
	Zr-SBA-15-2	0.10	0.10	0.10	649	0.70	3.9

Figure 1 shows the N_2-physisorption isotherms of the synthesized materials. All isotherms show a type-IV behavior, which is characteristic of mesoporous materials **[7]**. However, various types of hysteresis loops are observed implying a change in the pore morphologies. The materials obtained by the direct-synthesis method (SBA-15-1 and Zr-SBA-15-1) present an H2(a) hysteresis loop. This hysteresis loop can be attributed to the presence of ink-bottle-shaped pores **[7]**. On the other hand, the sample SBA-15-2 showed an H1 hysteresis loop that describes behaviors in its two branches as almost vertical and almost parallel for a range of approximately 0.7 to 0.8 in relative pressure which makes infer a narrow pore distribution, while the Zr-SBA-15-2 sample displayed an H2(b) hysteresis loop. Table 1 shows the surface area (S_{BET}), pore volume (V_{pore}), and pore diameter (D_{pore}) values that agree with mesoporous materials. Generally, a decreasing trend of the textural parameters is observed with the incorporation of zirconium in both methods, except in the case of the specific surface area in the

samples obtained by the pH-adjustment, where preservation of this property is observed. These partial results show that the change in pH to 7.5 in the synthetic treatment generates different porous characteristics in the materials prepared both in the absence and in the presence of zirconium.

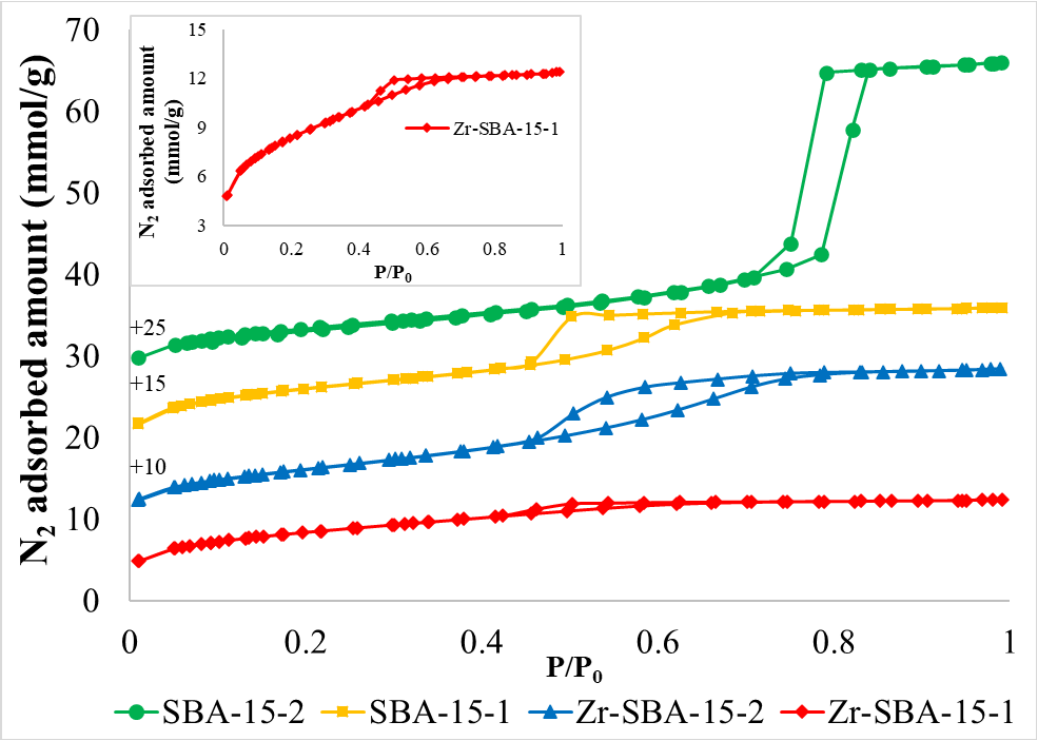

Fig. 1. N_2-physisorption isotherms of the synthesized materials.

Fig. 2(a) shows the small-angle diffraction patterns of the prepared samples. The SBA-15-1 and SBA-15-2 materials present a high-intensity peak at 2θ=1.12 and 0.92°. This peak is associated with the interplanar distance in accordance with the (100) plane, characteristic of highly ordered hexagonal structures with a *p6mm* symmetry **[2]**. Zirconium incorporation into the SBA-15 structure makes the (110) diffraction peak broader and with less intensity. This may indicate that the Zr incorporation rendered a less ordered mesoporous structure. Besides, a pair of extra peaks of less intensity is observed in the SBA-15-2 sample located at 2θ=1.54 and 1.77° related to the d_{110} and d_{200} planes, respectively, which are absent in the other materials. These peaks indicate information on the order level in porous networks **[3]** suggesting that this order is more affected in materials obtained by direct-synthesis. Diffraction patterns at wide-angles of all the samples (Fig. 2b) exhibited a broadened and

centered signal at approximately 2θ=22.5°, which is attributed to the amorphous silica walls **[3]**. This amorphous behavior also suggests a proper dispersion of the Zr species in the materials.

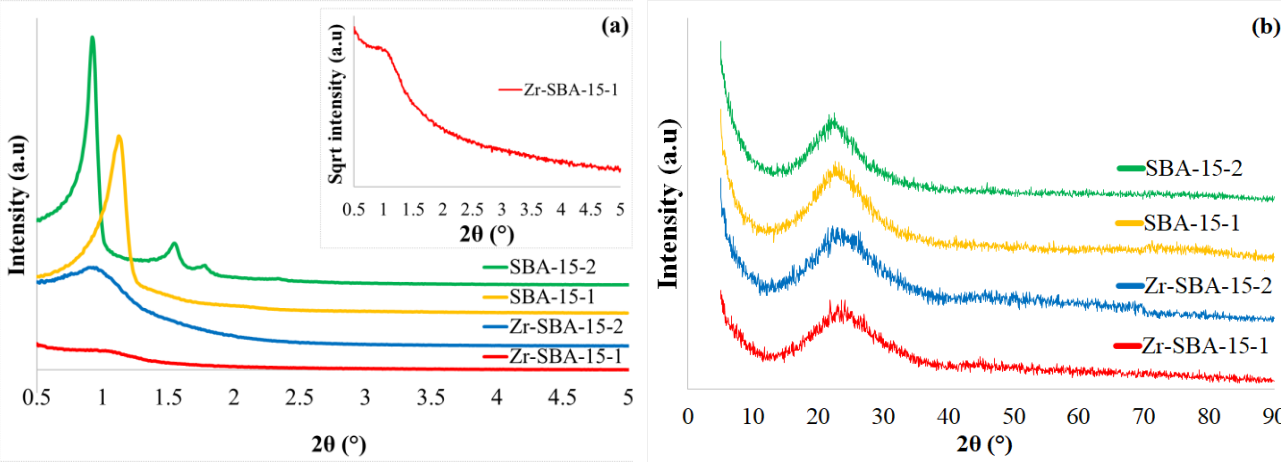

Fig. 2. Diffraction patterns of the synthesized materials at **(a)** small- and **(b)** wide-angles.

Fig. 3 presents the HRTEM images. The morphology of the SBA-15-1 and Zr-SBA-15-1 samples shows a short-range mesoporosity describing a structural order in several domains in the same particle (Fig. 3a and b). EDX of SBA-15-1 (Fig. 3a) exhibits the presence of Si and O signals. EDX of Zr-SBA-15-1 (Fig. 3b) indicates a Zr/Si ratio of 0.09. In contrast, SBA-15-2 and Zr-SBA-15-2 exhibited a more defined mesoporous structure with long-range ordering (Fig. 3c and d). The EDX spectrum in Fig. 3c shows Si and O signals for SBA-15-2, whereas the EDX for Zr-SBA-15-2 (Fig. 3d) a Zr/Si ratio of 0.10 was noticed. Regardless of the preparation method, a decrease in order is evidenced with the incorporation of zirconium in the materials. All characterization results are summarized in Table 1.

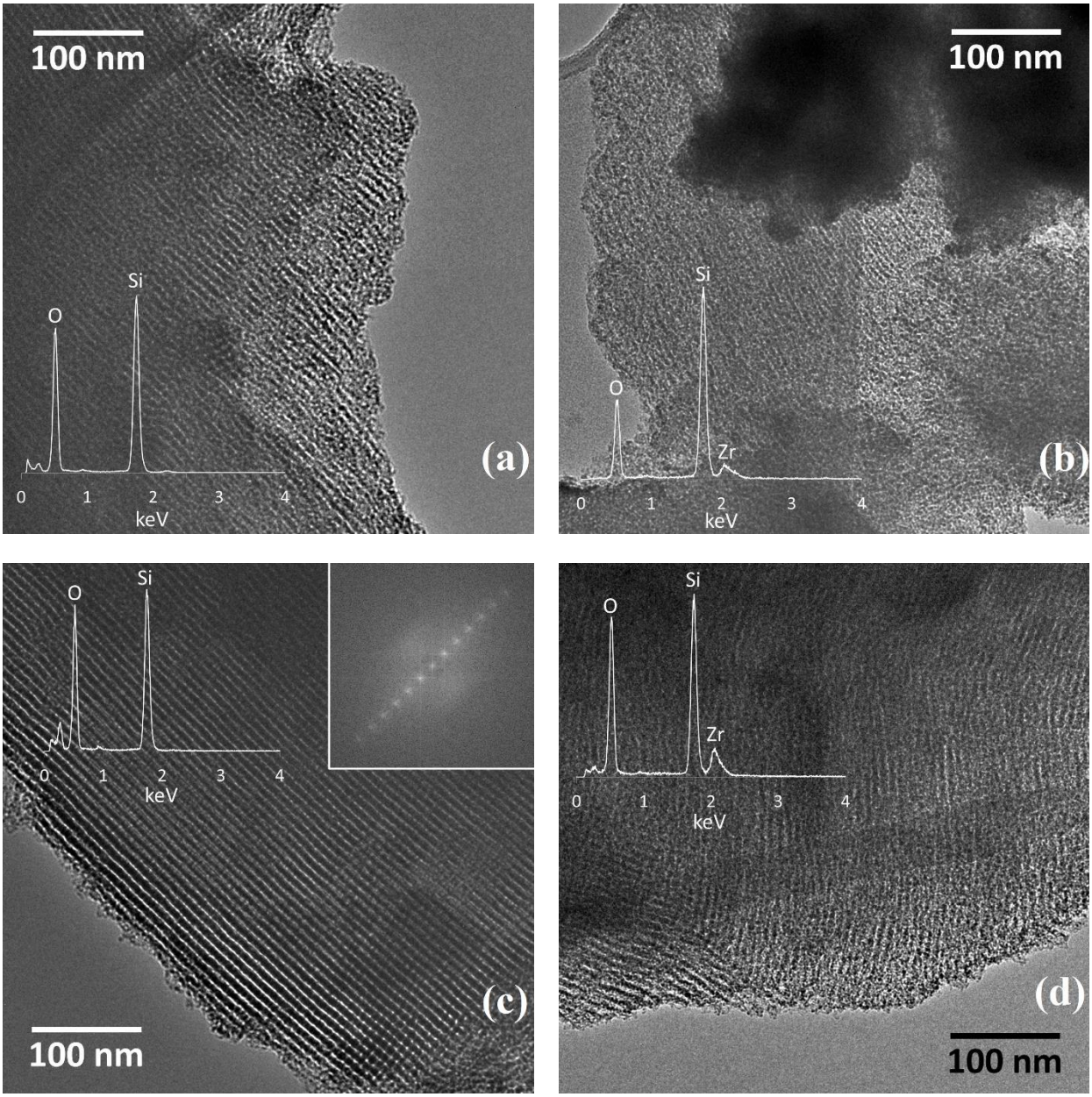

Fig. 3. HRTEM images: **(a)** SBA-15-1, **(b)** Zr-SBA-15-1, **(c)** SBA-15-2, and **(d)** Zr-SBA-15-2.

4. Conclusions

In summary, it can be highlighted that the pH-adjustment method positively influenced the long-range mesoporosity of the samples. Besides, it appears that the incorporation of zirconium atoms by the pH-adjustment method is more efficient as demonstrated by elemental composition. It can be concluded that the synthesis method has a strong influence on the morphology and structure of the silica samples.

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