Direct and Postsynthetic Functionalization of Mesoporous B-SBA-15-SO₃H Acid Catalyst and Application to Methyl Propionate Esterification

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Organic functionality can be added to mesoporous silicates in two ways: either by covalent grafting (postsynthetic) of various functional groups onto the channel walls or by incorporating functionalities directly during the synthesis (one-pot). If the grafted catalytically active groups experience similar environments and are isolated from each other, catalysis process is greatly facilitated. For this purpose, boric acid, as boron source, was added into the initial reaction mixture and then acid functionalization was performed by post and direct method. The obtained acid catalysts were tested in the esterification of propionic acid with methanol and the activity of these new materials was compared to that of SBA-15-SO₃H. Boron addition has facilitated the methyl propionate esterification for both postsynthetic and direct functionalized acid catalyst. Boron incorporated and postsynthetic functionalized mesoporous acid catalyst has highly enhanced the esterification reaction, compared to direct functionalized acid catalyst. The post functionalization method seems to be superior to one-pot functionalization method for preparation of mesoporous acid catalysts.

1. Introduction

Acid or base incorporated mesoporous silicas attract attention in organic synthesis, green chemistry and industry because of their high selectivity and high yields and have distinct advantages, such as heterogeneity and reusability. These hybrid materials, having various properties, can be designed by incorporating specific organic moieties on, or within, the pore walls of their mesostructure [1]. SBA-15 seems to be a good candidate for a support, because of its high surface area and uniform pore size distribution. The polymeric silicate framework of SBA-15 provides structural, thermal, and mechanical stability, whereas the incorporated organic species permit flexible control of interfacial and bulk material properties. Mesoporous materials are generally hydrophilic because of the surface silanol groups. Organofunctionalization converts the surface properties from hydrophilic to hydrophobic [2]. Thus, the hydrophobic nature of the active site environment can be utilized to perform reactions, which are outside the reach of the other inorganic solid acid catalysts. As an organofunctionalization agent, 3-mercaptopropyl trimethoxysilane (MPTMS), containing a SH group, a stable propyl spacer and a hydrolizable Si(OMe)₃ moiety, is the key precursor in the synthesis of sulfonic acid functionalized mesoporous materials [3].

Organic functionality can be added to mesoporous silicates by either, covalent grafting of various functional groups onto the channel walls or by incorporating functionalities directly during the synthesis, named as post-functionalizing and one-pot functionalizing, respectively. The postsynthetic method has been widely applied to anchor organic moieties through condensation on the surface silanol groups of the mesoporous silicate framework. However, it is difficult to control the concentration and distribution of functional groups on the silicate surface due to non-uniform existence of silanol groups and also there are more silanol groups present on the external surface accessible for functionalization. This grafting on the external surface, however, can be minimized by passivating the external silanol groups before functionalization of those internal. The one-pot method is based on the co-condensation of one tetraalkoxysilane with trialkoxyorganosilane precursors in a templating environment. This procedure can produce mesoporous silicates with high loading and homogeneous surface functionality. The negative side of this approach is that organic functional groups may be damaged or destroyed during the template removal process [2].

It has been reported that addition of elements, such as sulfur, boron, and phosphorus into carbon affects physicochemical properties of mesoporous carbon support [4]. Due to promising, cheap and environmentally benign properties, boron element that imparts activity to mesoporous materials is preferrable [5]. According to literature [6], 63% of the world's total boron reserves are located in Turkey. Inspired by these studies, we prepared sulfonic acid functionalized mesoporous boron silicate, B-SBA-15-SO₃H, in two different ways: in the first approach, boric acid was added into the initial reaction

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mixture in strongly acidic media. When the B-SBA-15 mesostructure was formed, after hydrothermal treatment and calcination, 3-mercaptopropyltrimethoxysilane as organoalkoxysilane precursor was grafted to the mesoporous B-SBA-15 (post functionalizing). In the second approach, after boric acid was added into the initial reaction mixture, TEOS as silica source, 3-mercaptopropyltrimethoxysilane as organoalkoxysilane precursor and H_2O_2 as an oxidation agent were mixed in just the same way as during direct functionalizing. The sulfonic acid functionalized catalysts, obtained by different methods, were tested in the esterification of propionic acid with methanol and the activity of this new material was compared to that of SBA-15-SO₃H.

2. Experimental

2.1. Synthesis of post-functionalized B-SBA-15-SO₃H

In a typical synthesis, 4 g of non-ionic surfactant (Pluronic P123) was dissolved in 125 g of 1.9 M HCl. After rising its temperature to 40 °C, 8.5 g of tetraethoxysilane (TEOS) and $B(OH)_3$ (SiO_2/B_2O_3 mole ratio: 60) were added to the solution, followed by stirring for 24 h at 40 °C and by keeping stable another 24 h at 90 °C. The gel was filtrated and dried at 60 °C over one night and then calcined at 500 °C for 6 hours. Sample of 2 g was refluxed in 100 ml of toluen with 2.1 ml of MPTMS during 20 h. After being filtrated, the solid was subjected to Soxhlet extraction with dichloromethane, for three times. The resulting material was oxidized with 21.5 ml of 30% H_2O_2 for 24 h, filtrated and dried at 60 °C. Post functionalized SBA-15-SO₃H was denoted as p-SBA-15-SO₃H, boron incorporated sample is also denoted as p-B-SBA-15-SO₃H. Analogously, sulfonic acid functionalized B-SBA-15 from direct syntheses (one-pot functionalization) samples were labeled as o-B-SBA-15-SO₃H.

2.2. Synthesis of one-pot functionalized B-SBA-15-SO₃H

Unlike in the post functionalization method mentioned above, the mercapto groups were directly incorporated in the boron added surfactant environment by co-condensation of TEOS and MPTMS. To prevent the loss of mercapto groups, non-ionic surfactant was removed by extraction with ethanol/HCl at 78 °C for 24 h.

3. Results and discussion

Figure 1 shows that XRD patterns of post functionalized samples display a sharp peak at 2θ value of 0.9, that matches well with the reported pattern for mesoporous materials. This peak is indexed to the (100) reflection of the 2D hexagonal mesostructure with space group *p6mm* [5]. Presence of this peak confirms that the hexagonal structure is also maintained after boron incorporation [7]. The p-B-SBA-15-SO₃H sample yielded a higher quality XRD pattern compared to p-SBA-15-SO₃H, suggesting that using $B(OH)_3$ in the synthesis gel increases the long-range ordering of the material [8]. In

contrast, the XRD patterns of the one-pot functionalized samples have no evidence of hexagonal arrangement. This tendency can be attributed to different interactions between the non-ionic surfactant molecules and the silica or MPTMS precursors during the hydrothermal reaction [9]. The surfactant-silicate interface becomes an electrostatically neutral region depending on the $S^0(IX)^0$ interaction between the organic and inorganic parts of the material [10]. The fact that MPTMS organic precursor and $B(OH)_3$ are introduced simultaneously, causes the decrease of the density of silanol groups at the interface, so that the fewer surfactant molecules are needed for charge balance. This trend can result in the contraction of the cylindrical micelle and hence also the hexagonal arrangement of o-B-SBA-15-SO₃H.
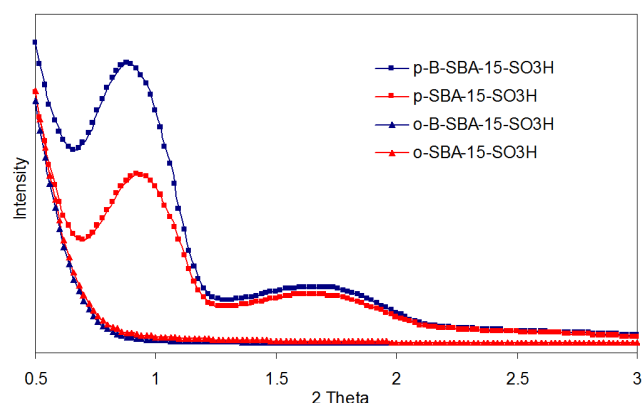

Fig. 1. XRD spectra for post and one-pot functionalized samples.
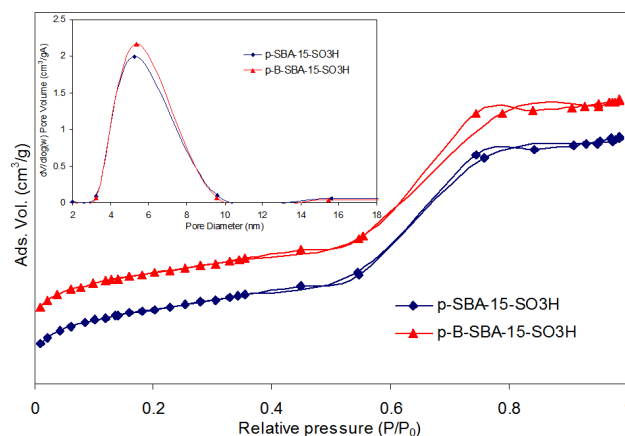

Fig. 2. N₂ adsorption/desorption isotherms of p-SBA-15-SO₃H and p-B-SBA-15-SO₃H samples (pore size distribution in inset).

As shown in Fig. 2, both of the samples show type IV isotherms with a sharp capillary condensation step in the relative pressure p/p_0 range of $0.4 - 0.8$, indicating the mesoporous structures and narrow pore size distribution (inset of Fig. 2). The isotherms of p-SBA-15-SO₃H and boron incorporated sample show slight hysteresis loops, which may resulted from the instability of the

liquid nitrogen meniscus inside the narrow channels [9]. The textural characteristics of the samples functionalized with post and one-pot methods are compiled in Table I. All of the results refer that mesoporous structures of p-B-SBA-15-SO$_3$H were maintained. The specific surface areas of boron incorporated samples, calculated by the BET method and the pore sizes and volumes, obtained using the BJH method, are lower than those of naked SBA-15-SO$_3$H. The fall in the surface area of B-SBA-15-SO$_3$H samples may be due to deboration during calcination or extraction, which blocks the mesopores [7].

TABLE I

Some textural and acid properties of the catalyst samples functionalized by post and one-pot methods.

Samples	Surface area [m^2/g]	Pore volume [cm^3/g]	Pore size [nm]	Acid capacity^a [meq/g]
p-SBA-15-SO$_3$H	412.4	0.61	5.47	0.688
p-B-SBA-15-SO$_3$H	437.6	0.61	5.57	1.173
o-SBA-15-SO$_3$H	384.8	0.07	3.30	1.755
o-B-SBA-15-SO$_3$H	379.0	0.08	3.50	1.995

^{a}The acid exchange capacities were measured by means of titration, using sodium chloride as exchange agent. The standard deviation is ±0.042.
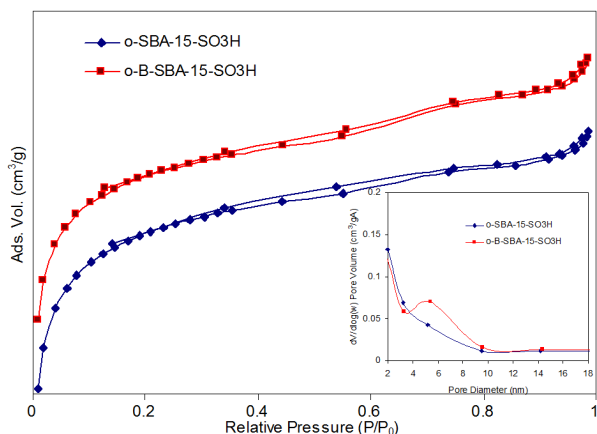

Fig. 3. N$_2$ adsorption/desorption isotherms of o-SBA-15-SO$_3$H and o-B-SBA-15-SO$_3$H samples (pore size distribution in inset).

In the one-pot functionalization (Fig. 3), the condensation step was not well developed, as in the case of post-functionalization. Although o-SBA-15-SO$_3$H samples have narrower channels and smaller hysteresis loops, compared to p-SBA-15-SO$_3$H, they have also mesoporous character. In the o-B-SBA-15-SO$_3$H samples, mercapto groups are filling the space between the boron and the silica surface, making it less accessible to nitrogen molecules. Thus, the surface area available to nitrogen decreases. This provides strong evidence that mercapto groups are located inside the channel surfaces and this result is in accordance with the literature [9].
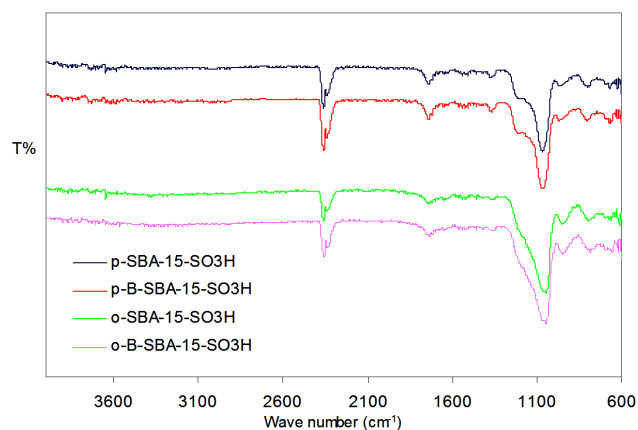

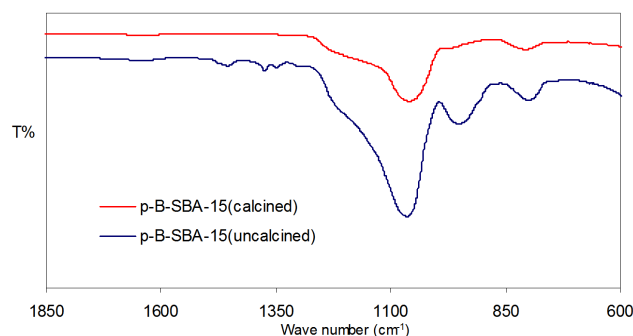Fig. 4. FT-IR spectra for o,p-SBA-15-SO$_3$H and o,p-B-SBA-15-SO$_3$H samples.

Fig. 5. FT-IR spectra for calcined and uncalcined p-B-SBA-15 samples.

All FT-IR spectra are characterized by the typical bands related with the Si–O bonds at $1120 - 1020$ cm^{-1}, and Si–O–Si bonds at $840 - 790$ cm^{-1}. Absorption at $950 - 920$ cm^{-1} (Si–OH) and at 1620 cm^{-1} (H–O–H) suggest the presence of terminal hydroxyl groups, as well as adsorbed water. The presence of boron gives rise to peaks at $1500 - 1300$ cm^{-1} (B–O) and at 1195 cm^{-1} (B–OH) (Fig. 4) [11]. Because of three-coordinate boron's electron-deficient nature, it is easily attacked by nucleophilic molecules like water. Therefore, boron parts of the material quickly hydrolyze rather than condense to form borosiloxane. During heat treatment, some of the boron source had condensed with the siloxy-network to form borosiloxane, and some was lost due to evaporation at high calcination temperature (500 °C) [12]. This change for calcined and uncalcined p-B-SBA-15-SO$_3$H is proven in Fig. 5. It was concluded from Fig. 5 that all of the bands between $1500 - 1300$ cm^{-1} have disappeared after calcination. According to the work of Soraru et al. [11], during the sol-gel process, to obtain SiO$_2$-B$_2$O$_3$, borosiloxane bridges are initially formed in solution through the reaction:

$$\equiv\text{Si–OH} + \text{HO–B}= \quad \rightarrow \quad \equiv\text{Si–O–B}= + \ H_2O. \quad (1)$$
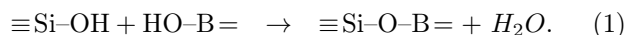
Then, the condensation reactions lead to an increase of the water concentration that can hydrolyze back the borosiloxane bonds, so no B–O–Si bonds are found in the final gel.

It is well known that propionic acid-methanol esterification reaction is a consecutive reaction. As can be seen from Fig. 6, both of the B-SBA-15-SO₃H catalysts show enhanced activity compared to SBA-15-SO₃H, indicating that the acid sites created by boron incorporation are responsible for the catalytic activity [7]. This result can be proven with the acid capacity values shown in Table I. The difference in acid capacity values of the catalysts is not as high as reaction conversions, especially in post functionalization method. In our opinion, the boron, which is being added during synthesis, acts as a second structure agent material besides non-ionic surfactant. After calcination, the template molecules are removed from the substrates to leave pores and the cavities in the monolayer coating. The size and the shape of the cavities could be varied by the second template, i.e, boron.
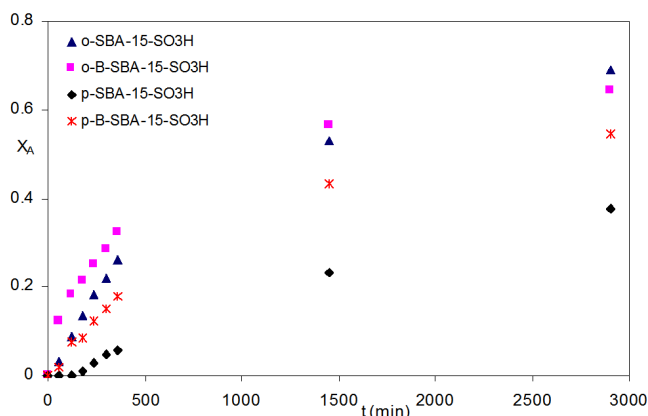

Fig. 6. Propionic acid conversion for post and one-pot functionalized samples (60 °C, 500 rpm, 0.5 g/100 ml catalyst, methanol:propionic acid molar ratio: 1/1).

4. Conclusions

On the basis of the XRD and N_2 adsorption/desorption experiments and the kinetic results, boron source in the post functionalized catalyst is located on the external surface and after calcination a large part of it is removed, which leads to formation of ordered cavities. When MPTMS is anchored to the framework, active sites are isolated from each other and p-B-SBA-15-SO₃H catalyst increases the reaction activity more than o-B-SBA-15-SO₃H. However, in one-pot functionalized catalyst, the boron source is located on the internal surface and when MPTMS is introduced during the synthesis, it is tightly bound to the internal surface, resulting in narrow channels and collapsed mesostructure.

p-B-SBA-15-SO₃H catalyst is structurally better defined and increases the catalytic activity better than o-B-SBA-15-SO₃H. In summary, the post functionalization approach seems to be superior to one-pot functionalization one for preparation of the B-SBA-15-SO₃H catalyst.

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