

# Synthesis, characterisation and catalytic performance of boron substituted SBA-15 molecular sieves

I. Eswaramoorthi, A.K. Dalai \*

*Catalysis and Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, University of Saskatchewan, Saskatoon, SK, Canada S7N 5C9*

Received 5 October 2005; received in revised form 16 December 2005; accepted 25 January 2006  
Available online 13 March 2006

## Abstract

Boron substituted mesoporous SBA-15 molecular sieves with varying boron content were synthesised by hydrothermal method. The effects of incorporation of boron in the framework on the structure, crystal parameters, framework vibrations and textural properties of SBA-15 were discussed based on the results from XRD, FT-IR and nitrogen adsorption studies. The morphology changes due to boron incorporation were monitored by SEM analysis. The coordination environment of boron in the framework was revealed by  $^{11}\text{B}$  MAS NMR and MQMAS NMR techniques. The type of acid sites created by boron incorporation was analysed by DRIFT study of pyridine adsorbed catalysts. All the characterisation results indicate the successful incorporation of boron in the silica framework of SBA-15 in both tetra and tri coordination. Isopropylation of naphthalene with isopropyl alcohol was carried out to test the acidity of the synthesised materials. The effects of reaction temperature, feed ratio and feed space velocity on naphthalene conversion and products selectivity were discussed. The higher activity in naphthalene conversion and selectivity of di-isopropylated naphthalenes were accounted in terms of the increased acid sites due to boron incorporation in the framework.

© 2006 Elsevier Inc. All rights reserved.

*Keywords:* SBA-15; Boron;  $^{11}\text{B}$  MAS NMR; Naphthalene; Isopropylation

## 1. Introduction

Since the discovery of silica based and metal-substituted mesoporous materials M41S (MCM-41, MCM-48, MCM-50), an extensive research progress has been made in the synthesis and characterisation of ordered mesoporous materials due to their high surface area, large and uniform pore size distribution and potential applications in the field of catalysis, separation and adsorption [1–4]. Among these materials, SBA-15, which is polymer-templated silica with hexagonally ordered mesopores, has attracted much attention recently. Its popularity is due to the larger pore size, thicker pore walls and higher hydrothermal stability compared to the well-known MCM-41, which is surfactant-

templated ordered mesoporous material [5]. Further, the polymer template employed to obtain SBA-15, poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), is biodegradable and cheaper than the surfactants used in the synthesis of MCM-41. Another attractive feature of SBA-15 is the existence of micropores interconnecting hexagonally ordered mesopores, which make it more suitable for catalysis because these interconnections facilitate diffusion inside the entire porous structure [6].

Reports are available on the usage of SBA-15 as a rigid template for the synthesis of mesoporous inorganic oxides and mesoporous carbons because its inverse replicas retain 3D structures after silica removal due to the existing micropores [7–9]. The improved hydrothermal and thermal stability of SBA-15 make them some of the most promising catalytic materials. However, the materials consisting of pure silica frameworks are of limited use for various catalytic applications because of the lack of acid sites and

\* Corresponding author. Tel.: +1 306 966 4771; fax: +1 306 966 4777.  
E-mail address: [ajay.dalai@usask.ca](mailto:ajay.dalai@usask.ca) (A.K. Dalai).

ion-exchange capacity. Generally, incorporation of heteroatom such as Al, Ti, Cu and V within the silica framework of mesoporous materials such as MCM-41 and MCM-48 has been implemented in order to create catalytically active sites, ion-exchange capacity and hence their catalytic activity [10–12]. However, it is very difficult to introduce the metal ions in the silica framework of SBA-15 directly due to the facile dissociation of metal–O–Si bonds under strong acidic hydrothermal conditions. The isomorphous substitution of heteroatom in all silica mesoporous SBA-15 could lead to a useful catalyst for the reactions involving bulkier molecules. Thus, number of direct synthesis and postsynthesis attempts have been made to incorporate Al, V, Zr and Ti in SBA-15 framework [13–17]. Because of the strong acidic media involved during the synthesis, the postsynthesis route found to be more effective over direct synthesis. However, such an approach has been found to reduce the textural properties of the mesoporous framework as well as irregularly distributed active sites. Yue et al. [13] reported the direct synthesis of Al-SBA-15 and found that catalytic activity in cumene cracking is higher as compared to Al-MCM-41. However, the resulting materials have many extraframework aluminium species. The ion-exchange, catalytic and adsorptive properties of aluminosilicate molecular sieves originate from acidic sites which arises from the presence of accessible hydroxyl groups associated with tetrahedral aluminum in the silica matrix. The difficulties for the direct synthesis of Al-substituted mesoporous materials under acidic conditions are due to the too easy dissociation of Al–O–Si bond under acidic hydrothermal condition and the remarkable difference between the hydrolysis rates of silicon and aluminium alkoxides. It can be observed that all the heteroatom incorporated SBA-15 showed enhanced activity in various chemical reactions compared to siliceous SBA-15 due to the acid sites created by metal incorporation. Among the various metallosilicates studied, synthesis of borosilicates is considered as important one because they could be useful in synthesising other metallosilicate analogues, which are sometimes difficult to synthesize by direct hydrothermal method [18,19].

Many efforts have been made to incorporate boron in the framework of zeolites as well as mesoporous materials such as MCM-41 [20–22]. Oberhagemann et al. [23] first hydrothermally synthesised highly ordered B-MCM-41 by using different synthesis procedures and found that regularity of the MCM-41 structure depends mainly on the synthesis conditions such as type of base, molarity of amphiphilic molecules, silica source and thermal treatment. Further, they reported from  $^{11}\text{B}$  MAS NMR studies that the as-synthesised samples show the presence of boron in tetrahedral coordination, whereas in calcined samples, fraction of tetrahedral boron is converted to trigonal and extraframework species [24,25]. Trong On et al. [26] synthesised B-MCM-41 hydrothermally and found that adding boron to the synthesis gel increases the long-range ordering of the materials compared to that of the pure silica analogue. Similar to

MCM-41, incorporation of boron in SBA-15 framework is expected to create acid sites in the neutral framework, which can be used for various chemical reactions.

So far no attempt is made to incorporate boron in the siliceous SBA-15 framework, either by direct synthesis or by postsynthesis method. Hence, in this paper, the direct synthesis of B-SBA-15 and their detailed characterisation related to coordination environment of boron in the framework, crystalline nature, textural properties and acid sites are reported. Isopropylation of naphthalene with isopropyl alcohol was carried out as test reaction. The isopropylation of naphthalene is an important reaction as the products particularly, 2,6-di-isopropyl naphthalene can be used as a new raw material for the production of advanced aromatic polymeric materials such as naphthalene 2,6-dicarboxylate, films and thermotropic liquid crystalline polymers and speciality polyesters [27–29].

## 2. Experimental

### 2.1. Synthesis of B-SBA-15 catalysts

The B-SBA-15 was synthesised by conventional hydrothermal method using poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (P123, average molecular weight 5800,  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , Aldrich), tetraethyl orthosilicate (TEOS, Aldrich) and boric acid (BDH) as template, silicon source and boron source, respectively. The composition of the gel is  $\text{TEOS}:x\text{B}_2\text{O}_3: 0.16\text{P123}: 0.46\text{HCl}$ . In a typical synthesis, 8 g of P123 was finely dispersed in 60 ml of water by stirring for 4 h at room temperature. Then, 240 ml of 2 N HCl solution was added with stirring, which was continued for an hour. After getting a homogeneous solution, the temperature was raised to 40 °C and the silica source TEOS (9.6 ml) was added slowly with stirring. Calculated amount of  $\text{H}_3\text{BO}_3$  in order to get the gel with  $\text{SiO}_2/\text{B}_2\text{O}_3$  ratio of 50, 27, 20 and 10, was added as boron source. The gel mixture thus obtained was continuously stirred for another 24 h at 40 °C. Finally, the gel was transferred to Teflon cup and autoclaved at 120 °C for 72 h. After cooling to room temperature, the solid product was filtered, washed and dried at 100 °C. For comparison purposes, siliceous SBA-15 was synthesised using the same gel composition without boron at 100 °C for 48 h. The calcination of the as-synthesised materials was carried out at 500 °C with heating rate of 3 °C/min in air for 6 h to remove the template molecules. The  $\text{SiO}_2/\text{B}_2\text{O}_3$  ratio in gel of B-SBA-15 catalysts is given between parentheses.

### 2.2. Characterisation of catalysts

The powder X-ray diffraction patterns of the calcined SBA-15 and B-SBA-15 were collected on a X'Pert PRO-XRD diffractometer using  $\text{Cu K}\alpha$  ( $\lambda = 0.1541$  nm) radiation with Ni filter. The diffractograms were recorded in the range of 0.5–10° with a step size of 0.01 and a step time of 10 s.

Download English Version:

<https://daneshyari.com/en/article/76845>

Download Persian Version:

<https://daneshyari.com/article/76845>

[Daneshyari.com](https://daneshyari.com)