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# Synthesis, characterization and catalytic application of a novel ethyl and boron sulfonic acid based bifunctional periodic mesoporous organosilica

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## ABSTRACT

A novel ethyl and boron sulfonic acid based bifunctional periodic mesoporous organosilica [BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub>] with dual Lewis-protic acidic sites was prepared, characterized and applied as efficient nanocatalyst for the synthesis of tetrahydrobenzo[b]pyrans. The BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub> was prepared by the chemical attachment of boric acid [B(OH)<sub>3</sub>] on an ethyl-based periodic mesoporous organosilica (PMO-Et) followed by treatment with chlorosulfonic acid (ClSO<sub>3</sub>H) at room temperature. This nanocatalyst was characterized using Fourier transform infrared (FTIR) spectroscopy, thermal gravimetric analysis (TGA), low-angle powder X-ray diffraction (LAPXRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis and transmission electron microscopy (TEM). The BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub> was shown to be a highly efficient nanocatalyst for three-component synthesis of tetrahydrobenzo[b]pyran derivatives at room temperature under solvent-free conditions. Moreover, the BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub> was recovered and reused at least 8 times without significant decrease in its activity.

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## 1. Introduction

Periodic mesoporous organosilicas (PMOs) are a noble class of hybrid organic–inorganic nanomaterials in which organic groups are well incorporated and distributed into their wall [1–4]. The incorporation of bridged organosilica into the pore wall increases lipophilicity of the materials and also can produce active species for different chemical applications [5]. Due to advantages of high surface area, high loading and uniform distribution of organic functional groups in the framework, superior thermal stability, non-toxicity, reusability as well as stability against air and moisture, PMOs play key role in the fields of electronic, support, adsorption chemistry, separation, chromatography and sensing [1,3,6–8]. These noble mesoporous materials also opened a unique and new way for modification of mesostructures in catalytic processes [9–13]. Especially, bifunctional PMOs (BPMOs) involving functional moieties both in wall and mesopores are very attracted in catalytic processes due to their excellent benefits such as high flexibility and availability of active catalytic sites, easy diffusion of organic substrates in their channels and tunable of their physiochemical properties by changing mole ratio of precursors during synthesis process. One effective method for the preparation of BPMOs with

catalytic properties is chemical grafting of a suitable functional group on a pre-prepared PMO nanomaterial [14–16]. To date several catalysts have been successfully immobilized into/onto PMO materials and their applications have been studied in different organic transformations. Some of recently developed BPMOs including catalytic centers are BPMO-Pr-SO<sub>3</sub>H [17], PMO-Pr-NH<sub>2</sub> [18], PMO-SO<sub>3</sub>H-NH<sub>2</sub> [19], BPBMO [20], thiophene-isocyanurate PMOs [21] and BPMO-IL-KCO<sub>3</sub> [22].

One of well-known catalyst with dual Lewis-protic acidic sites is boron sulfonic acid that has been excellently applied in different organic processes [23]. In special, the use of supported boron sulfonic acid is very attracted due to easy recoverability and stability [24,25]. Although several studies have been reported on the application of supported boron sulfonic acid in organic reactions, however, according to our knowledge, there is no report on the PMO supported boron sulfonic acid in the literature. Therefore, design and creation of bifunctional PMO containing boron sulfonic acid is very interesting and appealing subject in the catalytic world.

On the other hand, tetrahydrobenzo[b]pyrans are very attractive and significant compounds in organic chemistry due to their pharmacological and therapeutic properties such as anticancer, spasmolytic, anticoagulant and anti-anaphylactagants [26–28]. Also, they have a broad range of applications as cognitive enhancers for the treatment of neurodegenerative illnesses such as Huntington and Parkinson, amyotrophic lateral sclerosis,

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AIDS-associated dementia, Alzheimer's disease and Down's syndrome as well as for the treatment of myoclonus and schizophrenia [29]. Tetrahydrobenzo[b]pyrans have been traditionally synthesized using different catalysts under homogeneous conditions such as tetrabutylammonium bromide [30], (S)-proline [31], hexadecyltrimethylammonium bromide (HTMAB) [32], tetramethylammonium hydroxide (TMAH) [33], Zn(Phen)<sub>2</sub>Cl<sub>2</sub> [34] and 1-methylimidazolium tricyanomethanide [HMIM]C(CN)<sub>3</sub> [35]. However, due to problems associated with these systems such as catalyst and product separation, several recoverable heterogeneous catalysts including Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@TiO<sub>2</sub> [36], SO<sub>4</sub><sup>2-</sup>@MCM-41 [37], Fe<sub>3</sub>O<sub>4</sub>@MWCNTs [38], Mn(III)-pentadentate Schiff-base complex@MWCNTs [39] have been successfully applied in this regard. Although the latter catalytic systems removed problems of recoverability and reusability, however, the most of these have disadvantages of volatile organic solvents and high reaction temperature. Therefore, design and preparation of efficient catalytic systems are important for the synthesis of tetrahydrobenzo[b]pyrane under better conditions than before.

According to the abovementioned notes as well as the importance of both bifunctional PMO and chemical immobilization of boron sulfonic acid, herein, in continuation of our recent studies on the preparation of supported catalytic systems [22,40–42], a novel ethyl and boron sulfonic acid based BPMO with dual Lewis and protic acidic sites [BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub>] is prepared and characterized using several techniques such as FT-IR, TGA, SEM, TEM, EDX and low angle PXRD. This novel nanocatalyst was successfully applied in the synthesis of tetrahydrobenzo[b]pyrans at room temperature under solvent free media (Scheme 1).

## 2. Experimental section

### 2.1. General

All chemicals and reagents such as boric acid, chlorosulfonic acid, tetramethoxysilane (TMOS), 1,2-bis(triethoxysilyl)ethane (BTEE), pluronic P123, KCl, HCl, malononitrile, dimedone and all applied aldehydes were purchased from Merck and Fluka companies. Solvents were dried and purified before use according to standard procedures. The purity of the products and the reaction monitoring were carried out using TLC on silica gel polygram SILG/UV 254 plates. Transmission electron microscopy (TEM) images were taken on a FEI TECNAI 12 BioTWIN microscope operated at 120 kV. Scanning electron microscopy (SEM) analysis was performed on a Philips, XL30 emission electron microscope. The thermal gravimetric analysis (TGA) was measured from room temperature to 800 °C by a NETZSCH STA 409 PC/PG apparatus. Fourier transform infrared (FT-IR) spectroscopy was recorded on a Bruker-Vector 22 spectrometer. NMR spectra were recorded in CDCl<sub>3</sub> as solvent on a Bruker Advanced DMX-400 MHz spectrometer. Melting points were determined using a KSB1N, Kruss apparatus in open capillary tubes.

### 2.2. Preparation of ethyl based PMO nanomaterial (PMO-Et)

Periodic mesoporous organosilica with ethyl framework (PMO-Et) was prepared *via* hydrolysis and co-condensation of tetramethoxysilane (TMOS) and 1,2-bis(triethoxysilyl)ethane (BTEE) in the presence of pluronic P123 surfactant under acidic conditions [43,44]. Typically, pluronic P123 surfactant (1 g) was added to a flask containing deionized water (5.85 g), HCl (2 M, 25 g) and potassium chloride (6.25 g), and then the resulting solution was stirred for 1.5 h at 40 °C. After complete dissolution of surfactant, a mixture of tetramethoxysilane (5 mmol) and 1,2-bis(trimethoxysilyl)ethane (5 mmol) was added to reaction vessel and stirred at the same temperature for 24 h. Then, the obtained

mixture was aged for 72 h at 100 °C. Finally, the solid material was separated by filtration, washed with deionized water and dried at room temperature. The P123 template was removed from the as-synthesized material by a Soxhlet apparatus using acidic ethanol for 48 h. The final PMO material was dried at 75 °C for 24 h and denoted as PMO-Et.

### 2.3. Preparation of ethyl and boric acid based bifunctional PMO [BPMO-Et-B(OH)<sub>2</sub>]

The BPMO-Et-B(OH)<sub>2</sub> nanomaterial was prepared through a grafting approach. Typically, PMO-Et (1 g) was added into a flask containing dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) in an ice bath. After complete dispersion of PMO-Et in CH<sub>2</sub>Cl<sub>2</sub>, thionyl chloride (1.5 mL) was added very slowly and the mixture was stirred for 1 h. The solvent was removed under reduced pressure and the resulting material was denoted as PMO-Et-Cl. Then a saturated solution of boric acid [B(OH)<sub>3</sub>] was added to a suspension of PMO-Et-Cl (1 g) in dry acetone. This mixture was refluxed under argon atmosphere for 12 h. The obtained precipitate was filtered and completely washed 4 times with ethanol and water. The final material was dried for 12 h at 70 °C and gave a white powder denoted as BPMO-Et-B(OH)<sub>2</sub>.

### 2.4. Preparation of ethyl and boron sulfonic acid based bifunctional PMO [BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub>]

For this purpose, BPMO-Et-B(OH)<sub>2</sub> (1 g) was added in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and the resulting mixture was stirred for 20 min under argon atmosphere. Then, chlorosulfonic acid (3 mL) was added drop-wise over a period of 1 h at room temperature while stirring was continued for 2 h. The solvent was removed and the residue was washed several times with CH<sub>2</sub>Cl<sub>2</sub> and water to remove unreacted chlorosulfonic acid. Finally, the obtained material was dried at 70 °C overnight and denoted as BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub>.

### 2.5. Determination of acidity of the BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub> nanocatalyst

Sulfonic acid loading on the solid surface of BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub> nanocatalyst was calculated by ion-exchange pH analysis. For this, 50 mg of BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub> nanocatalyst was added to an aqueous solution of NaCl (1 M, 250 mL) and the resulting mixture was stirred at RT for 44 h. After that, an inverse titration by NaOH (0.05 M) was performed on the obtained mixture. According to this experiment the loading of H<sup>+</sup> on the BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub> nanocatalyst surface was obtained to be 1.71 mmol g<sup>-1</sup>.

### 2.6. Procedure for the preparation of tetrahydrobenzo[b]pyrans using BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub> nanocatalyst

For this, dimedone (1 mmol), malononitrile (1 mmol), aldehyde (1 mmol) and BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub> (0.8 mol%) were added in a reaction vessel and the resulting mixture was stirred at room temperature under solvent-free conditions. The reaction progress was monitored by TLC. After completion of the reaction, the crude product was dissolved in hot ethanol (10 mL) and the catalyst was separated *via* filtration. Then, the pure products were obtained after recrystallization in methanol.

### 2.7. General procedure for the recovery of BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub> nanocatalyst in the synthesis of tetrahydrobenzo[b]pyrans

BPMO-Et-B(OSO<sub>3</sub>H)<sub>2</sub> nanocatalyst (0.8 mol%) was added into a mixture of benzaldehyde (1 mmol), dimedone (1 mmol) and malononitrile (1 mmol) in a test tube and the resulting mixture was stirred under solvent-free conditions at room temperature. Upon

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