

## Activity of B(OEt)<sub>3</sub>-MCM-41 catalyst in the MPV reduction of crotonaldehyde

BURCU UYSAL

Department of Chemistry, Akdeniz University, 07058 Antalya, Turkey

e-mail: buysal@akdeniz.edu.tr

MS received 13 May 2013; revised 10 September 2013; accepted 11 September 2013

**Abstract.** Mesoporous silica material MCM-41 was functionalized with boron tri-ethoxide (B(OEt)<sub>3</sub>) groups by the grafting method and denoted as 'B(OEt)<sub>3</sub>-MCM-41'. With the use of TEM, X-ray diffraction, high-resolution thermogravimetry (TGA) and N<sub>2</sub> adsorption-desorption isotherms, it was shown that the initial hexagonal structure, the high specific surface area, and porosity are retained in the functionalized material. <sup>29</sup>Si NMR- and <sup>11</sup>B NMR- spectroscopies revealed that the surface of MCM-41 consists of boron alkoxide species. The Meerwein-Ponndorf-Verley (MPV) reduction of crotonaldehyde to but-2-en-1-ol was conducted in the presence of B(OEt)<sub>3</sub>-MCM-41 catalyst. MPV reduction of crotonaldehyde also showed that functionalization leads to the creation of Lewis acidic sites. A combination of mesoporous structure with Lewis acidic properties makes the MCM-41 functionalized with boron tri-ethoxide groups, useful as solid Lewis acid catalysts.

**Keywords.** MCM-41; B(OEt)<sub>3</sub>-MCM-41; boron tri-ethoxide; Meerwein-Ponndorf-Verley reduction; chemoselective crotonaldehyde reduction.

### 1. Introduction

MCM-41, and other ordered silica-based molecular sieve materials, have an organized structure, determined by the orientation of the extended pores: high surface area and narrow pore size distribution.<sup>1</sup> Purely siliceous materials have poor catalytic activity, if any. There have been continuous efforts to confer to these materials catalytic activity by introduction of active sites. Thus, inclusion of Al<sup>3+</sup> ions usually results in an increase in the acidity of the materials, making it similar to that of acidic zeolites.<sup>2</sup> Titanium (IV) ions in siliceous materials can provide active oxidation and photooxidation catalysts.<sup>3</sup> Introduction of Ti<sup>4+</sup> can be achieved either by their incorporation into the siliceous framework or functionalization of the surface.

Functionalization of the MCM-41 surface with metal alkoxides can be regarded as an optional method for the creation of active Lewis acid sites. Functionalization of the MCM-41 surface with metal alkoxides is usually achieved by grafting methods. Several 'Meerwein-Ponndorf-Verley (MPV)' reduction catalysts such as Al-alkoxides, B-alkoxides, Zr-alkoxides as well as Hf and Zr alkyl complexes have been anchored on MCM-41 or on amorphous SiO<sub>2</sub> in order to generate potential catalytic activity.<sup>4-9</sup> Thus, grafting of MCM-41 materials with MPV reduction catalysts yields active Lewis acid sites on MCM-41 materials.<sup>4,5,10</sup>

Reduction of carbonyl compounds by hydrogen transfer from an alcohol is known as the 'Meerwein-Ponndorf-Verley reaction' or 'MPV reaction' in organic chemistry and can be performed under mild conditions using Lewis acids as catalyst.<sup>11,12</sup> The MPV reduction of carbonyl compounds is a highly selective reaction since only the carbonyl group coordinates with the Lewis acid centre, while the double bond remains unreacted.<sup>13</sup> Therefore, the MPV reduction offers a facile access to unsaturated alcohols, many of which are important starting materials for the production of fine chemicals.<sup>14</sup> Traditionally, the MPV reaction can be catalysed using homogeneous catalysts such as metal alkoxides. Heterogeneous catalysts for the MPV reactions include zeolites,<sup>15-17</sup> grafted alkoxides,<sup>8,18</sup> metal oxides such as magnesium oxide, zirconia, silica, alumina,<sup>19</sup> etc. A major advantage of heterogeneous catalysis over homogeneously catalysed MPV reactions is that the catalysts can easily be separated from the liquid reaction mixture.<sup>7,15</sup>

In the literature, boron (B) has been incorporated into the catalyst structure in order to generate potential catalytic activity.<sup>20-22</sup> There are different studies which used B-modified MCM-41 for catalyst systems. Jiamwijitkul and coworkers investigated the effect of B-modification on the MCM-41-supported dMMAO/zirconocene catalyst during ethylene/1-octene copolymerization.<sup>23</sup> Also, catalytic performance of Al,B-MCM-41 materials for

the cyclohexanone oxime rearrangement was studied by Conesa and coworkers.<sup>24</sup> MCM-41 mesoporous materials [Si/(Al + B) molar ratio of 20], with Al/B ratio in the range of 2–0.5, were prepared by direct synthesis using tetraethyl orthosilicate (TEOS), boric acid ( $\text{H}_3\text{BO}_3$ ) and  $\text{Cl}_3\text{Al} \cdot 6\text{H}_2\text{O}$  as silica, boron and aluminum sources, respectively, and cetyltrimethylammonium bromide (CTABr) as the template, following the procedure described by Grün *et al.*<sup>25</sup> with some variations.

In the present article, we demonstrate how functionalization via grafting with boron tri-ethoxide groups influences the structural characteristics and produces Lewis acidic sites on MCM-41 material. In the previous study, we used this procedure to functionalize MCM-41 with boron tri-isopropoxide groups in order to develop new solid Lewis acid catalyst ' $\text{B}(\text{O}^i\text{Pr})_3$ -MCM-41'. The results were found encouraging for reduction of a variety of  $\alpha,\beta$ -unsaturated aldehydes and ketones.<sup>4,10</sup> Up to the present time, there has not been any literature report the preparation of boron tri-ethoxide grafted MCM-41 catalyst and comparison with MCM-41 material. To test catalytic activity of the new  $\text{B}(\text{OEt})_3$ -MCM-41 catalyst, MPV reduction reaction of crotonaldehyde was studied.

## 2. Experimental

### 2.1 Preparation of mesoporous silica material MCM-41

Pure siliceous MCM-41 was synthesized following a previously reported procedure.<sup>10</sup> In a typical synthesis, MCM-41 was prepared by dissolving 19.43 g (26.4 mmol) of tetraethylammonium hydroxide (TEAOH, 20%) and 16.16 g (12.6 mmol) cetyl trimethylammonium chloride (CTMACl, 25%) in 20 mL of deionized water with stirring (1000 rpm) until a clear solution was obtained. A measure of 19.27 g (128.3 mmol) of LUDOX AS-40 (Dupont) was added to the solution with stirring. After 15 min an additional amount of 32.33 g (25.3 mmol) CTMACl and 20 mL  $\text{H}_2\text{O}$  were added. The resulting mixture was vigorously stirred (1000 rpm) for another 1 h. Molar composition of the final gel mixture was  $\text{SiO}_2$ : 0.3CTMACl: 0.2TEAOH: 46.3 $\text{H}_2\text{O}$ .

The gel mixture was placed in a Teflon-lined stainless-steel autoclave (BERGHOF BR-200 pressure reactor). The rotating autoclave was heated at 110°C for 48 h. The product was washed and calcined as suggested by Uysal and Oksal.<sup>4</sup>

### 2.2 Grafting of boron tri-ethoxide

Boron alkoxide-containing ordered mesoporous silica material was prepared by the grafting method.<sup>4,5</sup> Prior

to grafting, the support (MCM-41) (2.0 g) was dried at 250°C for 2 h. It was then added to a solution of (1.5 mL; 5.8 mmol)  $\text{B}(\text{OEt})_3$  (as a 70 wt% solution in ethanol) in dry hexane (25 mL). The suspension was stirred (750 rpm) for 4 h at room temperature. The product was filtered under  $\text{N}_2$  atmosphere, washed thrice with 10 mL of hexane and finally dried under the same inert gas flow. The material containing the grafted alkoxide contains 2.6 mmol B per g final material and is denoted as  $\text{B}(\text{OEt})_3$ -MCM-41.

### 2.3 Characterization

The surface area, average pore diameter and pore size distribution of MCM-41 support and prepared  $\text{B}(\text{OEt})_3$ -MCM-41 were determined by nitrogen adsorption using a Micromeritics Gemini III 2375 Surface Area Analyser. Prior to measurements, the samples were degassed at 300°C and 0.15 mbar at least for 6 h. The surface area was calculated by the method of Brunauer, Emmett and Teller (BET). Pore size distribution curves were obtained from the analysis of desorption branch of the nitrogen adsorption–desorption isotherm by the BJH (Barrett–Joyner–Halenda) method. The bulk crystalline phases of the samples was determined by powder X-ray diffraction (XRD). This was conducted using a X'Pert Pro MPD Diffractometer from PANalytical, with a  $\text{CuK}\alpha 1$  radiation wavelength 0.154 nm.

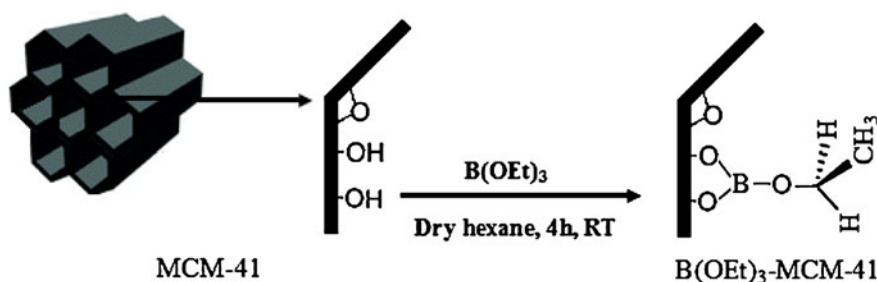
Thermogravimetric analysis was carried out in nitrogen atmosphere using a high-resolution SII EXSTAR 6000 thermal analyser.

Transmission electron microscopy (TEM) images were recorded on a Tecnai G<sup>2</sup> 20 S-TWIN with an energy dispersive X-ray spectrometer (EDAX, r-TEM SUTW) located at the ZELMI, TU Berlin.

Boron content of the grafted catalyst was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The mesoporous material  $\text{B}(\text{OEt})_3$ -MCM-41 was dissolved in a mixture solution of HCl and HF. An aqueous HCl and HF solution containing boron was used as standard reference. ICP-OES was performed using Perkin Elmer Optima 4300DV.

The anchoring of boron tri-ethoxide species on MCM-41 was followed by  $^{29}\text{Si}$  MAS NMR spectroscopy.

$^{29}\text{Si}$  MAS NMR and  $^{11}\text{B}$  MAS NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer with a resonance frequency of 79.46 and 128.3 MHz for  $^{29}\text{Si}$  and  $^{11}\text{B}$  using a Bruker 4 mm double-resonance probe head operating at a spinning rate of 12 kHz for  $^{29}\text{Si}$  and  $^{11}\text{B}$ .  $^{29}\text{Si}$  spectra were collected with 70° rf pulses, 30 s delay with ~ 6000 scans.  $^{11}\text{B}$  MAS NMR



**Scheme 1.** Schematic representation of MCM-41 and as-synthesized material ( $\text{B(OEt)}_3\text{-MCM-41}$ ).

spectra were accumulated for 1024–4096 scans with  $\pi/4$  pulse width of 1.1  $\mu\text{s}$  and 2 s recycle delay.

#### 2.4 Catalytic activity of $\text{B(OEt)}_3\text{-MCM-41}$

The  $\text{B(OEt)}_3\text{-MCM-41}$  catalyst was tested during MPV reduction of crotonaldehyde. The reaction mixture containing 30 mmol of the crotonaldehyde, 200 mmol (9.214 g; 11.7 mL) ethanol and 500 mg of dried catalyst were placed in a 50 mL two-mouthed flask with a side stopcock equipped with a 100 cm condenser. The flask was immersed in an oil bath. The rigorously stirred reaction mixture was gently heated to reflux at  $80^\circ\text{C}$ . During the reduction reaction time, a slow stream of dry nitrogen was passed just over the surface of reaction mixture. By this way, the formed acetaldehyde was removed by nitrogen flow. Thus, the equilibrium shifts more towards product side. Aliquots were removed at different reaction times and analysed by gas chromatography–mass spectrometry (GC–MS).

The reduction products were identified on the basis of their retention times by comparing with authentic samples and their mass spectral fragmentation patterns with those stored in the data bank (Wiley/NIST library). Analyses were performed on a Varian CP 3800 gas-chromatograph equipped with a Varian Saturn 2200 MS detector (Walnut Creek, CA, USA) and a VF-5 ms capillary column (30 m length and 0.25 mm I.D., 0.25  $\mu\text{m}$  film thickness) (Palo Alto, CA, USA).

Selectivity towards the but-2-en-1-ol ( $S_{\text{UOL}}$ ) at variable conversion levels was calculated from the following expression:<sup>16</sup>

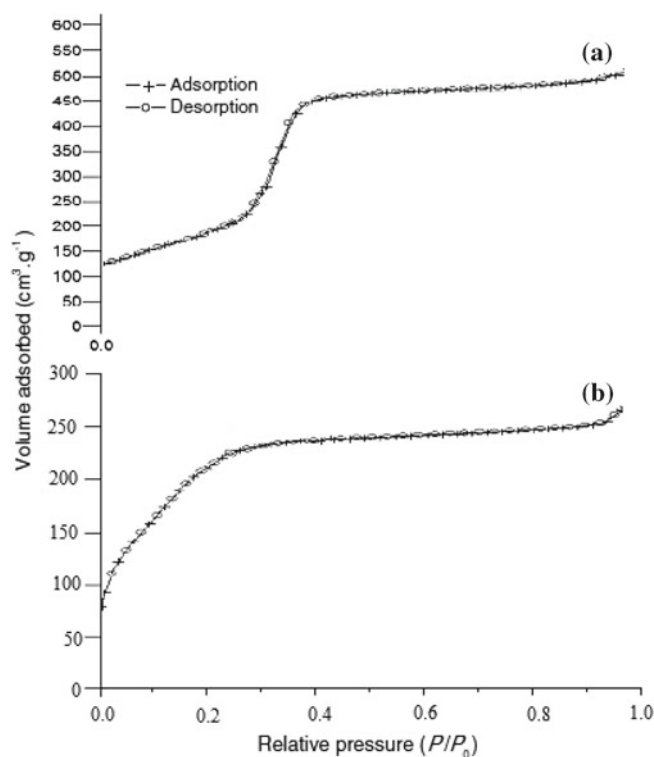
$$S_{\text{UOL}} = \left( \frac{\text{mmol of but-2-en-1-ol formed}}{\text{mmol of crotonaldehyde converted}} \right) \times 100.$$

To test for any leaching, about 500 mg of the grafted catalyst was refluxed in 200 mmol of ethanol at  $80^\circ\text{C}$  for 6 h. The solution was filtered and the filtrate was tested for activity in the MPV reduction of crotonaldehyde. The filtrate and quenched solutions of the catalyst did

not show any catalytic activity. This confirms that the activity observed is only due to the solid catalyst and not partly due to the leached active species.

### 3. Results and discussion

Schematic representations of the MCM-41 and as-synthesized material ( $\text{B(OEt)}_3\text{-MCM-41}$ ) are given in scheme 1. The synthetic procedure adopted for obtaining material  $\text{B(OEt)}_3\text{-MCM-41}$  catalyst is also given in scheme 1. Similar synthetic procedure and structural formulation for MCM-41 are represented in one of the earlier studies.<sup>26</sup> Removal of the template (CTMACl) from as-synthesized MCM-41 may open mesopores as well as easily cause structure shrinkage.<sup>27</sup> Most of the



**Figure 1.**  $\text{N}_2$  adsorption/desorption isotherms of (a) MCM-41 and (b)  $\text{B(OEt)}_3\text{-MCM-41}$ .

**Table 1.** Surface properties of MCM-41 and B(OEt)<sub>3</sub>-MCM-41.

Sample	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (Å)
MCM-41	1100	0.38	25.1
B(OEt) <sub>3</sub> -MCM-41	762	0.12	20.8

high molecular weight surfactant is removed from as-synthesized MCM-41 via calcination. So, the preparation of MCM-41 materials usually includes a high temperature calcination for destroying the surfactant template.

### 3.1 Characterization of materials

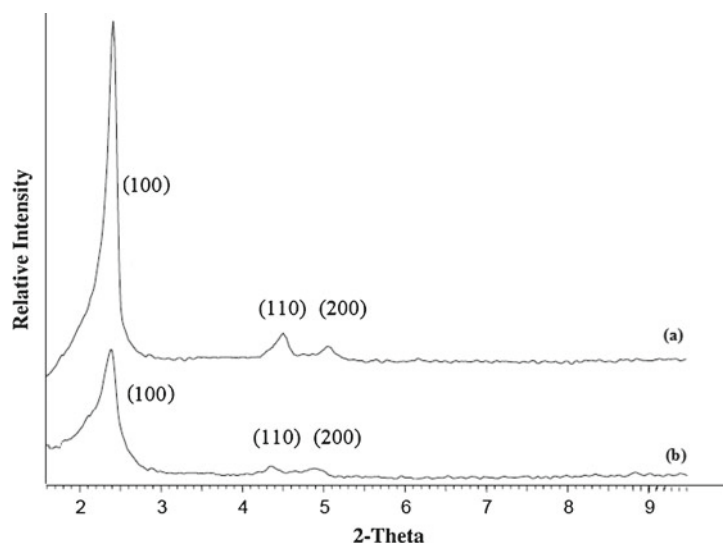
The as-obtained MCM-41 and B(OEt)<sub>3</sub>-MCM-41 samples were investigated with various analytical methods including N<sub>2</sub> adsorption/desorption measurements (Brunauer–Emmett–Teller method), high-resolution thermogravimetry (TGA), XRD and TEM techniques, <sup>29</sup>Si MAS NMR and <sup>11</sup>B MAS NMR spectroscopies.

The N<sub>2</sub> adsorption–desorption isotherms for the MCM-41 and B(OEt)<sub>3</sub>-MCM-41 samples are shown in figure 1. The N<sub>2</sub> isotherm for the MCM-41 sample is shown in figure 1 (a). It is a typical type IV adsorption isotherm as defined by IUPAC nomenclature without any hysteresis, and shows a sharp capillary condensation step at a relative pressure between 0.2 and 0.4.<sup>28–31</sup> A sharp inflection between relative pressure  $P/P_0 = 0.2$  and 0.4 corresponds to capillary condensation within uniform mesopores. The sharpness of

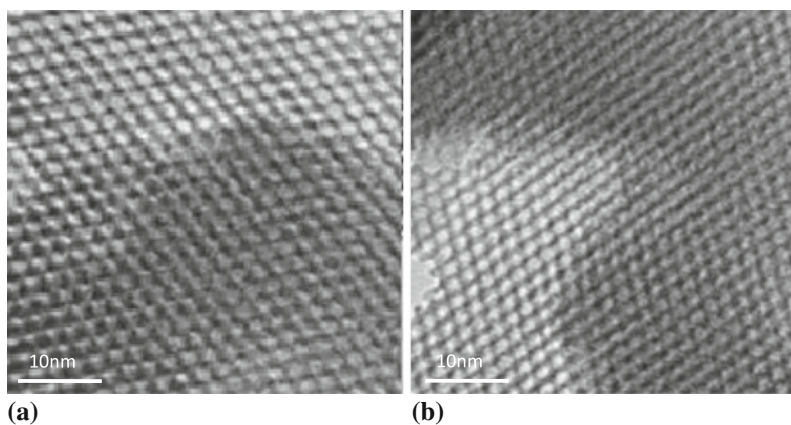
this step reflects the uniform pore size.<sup>32</sup> Compared to the untreated MCM-41 sample, the sharp capillary condensation step in the case of incorporated MCM-41 samples shifts toward lower  $P/P_0$  region. This suggests that the introduction of B(OEt)<sub>3</sub> into the channel causes changes in the pore structure of the support during the incorporation process. Also, B(OEt)<sub>3</sub>-MCM-41 still displays a type IV adsorption isotherm according to IUPAC without any hysteresis between the adsorption and the desorption curves (figure 1 (b)).

As seen in table 1 before functionalization with B(OEt)<sub>3</sub>, the calcined MCM-41 has a surface area of 1100 m<sup>2</sup>/g, with an average pore diameter of 25.1 Å as deduced using the Barrett–Joyner–Halenda method. Specific surface decreases to 762 m<sup>2</sup>/g, with an average pore diameter of 20.8 Å. This implies that the surface functionalization to some extent decreases the available pore volume and diameter, but the material still has all the characteristics of an ordered, mesoporous support.

The low-angle XRD patterns of MCM-41 and B(OEt)<sub>3</sub>-MCM-41 are shown in figure 2 (a) and (b), respectively. X-ray diffractograms of the MCM-41 and B(OEt)<sub>3</sub>-MCM-41 materials were characterized by three distinct Bragg reflexes at low angles indexed to (100), (110) and (200) representatives of ordered

**Figure 2.** Low-angle XRD patterns of (a) unmodified and (b) B(OEt)<sub>3</sub> modified MCM-41 supports.





**Figure 3.** TEM of (a) MCM-41 and (b) B(OEt)<sub>3</sub>-MCM-41.

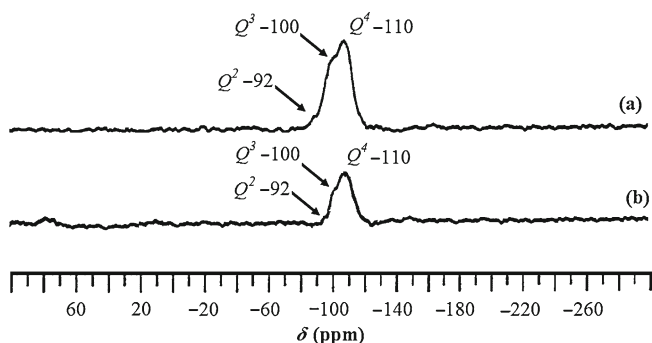
materials with hexagonal arrangement of mesopores (figure 2 (a) and (b)). The XRD pattern of the untreated MCM-41 exhibits a high intensity (100) and two low intensity reflections (110) and (200), which are characteristic of the hexagonal mesoporous MCM-41.<sup>33</sup> After the incorporation of boron alkoxide complex into the framework, the main peak intensity decreases. This result indicates that the incorporation of boron alkoxide complexes in the channel of MCM-41 leads to a substantial loss in the scattering contrast between the channel and the wall, and reduces the intensity of the scattered X-ray in the powder diffraction experiment.<sup>34</sup> Furthermore, intensity of the two less intense reflections (110) and (200) decreases much more. This observation is supported by a drop in the pore volume and the surface area (table 1).

ICP-OES analysis showed 2.81 wt% of boron content in the catalyst. To determine boron content, B(OEt)<sub>3</sub>-MCM-41 was dissolved in a mixture solution of HCl and HF. An aqueous HCl and HF solution containing boron was used as standard reference; 2.6 mmol B was found per g of B(OEt)<sub>3</sub>-MCM-41.

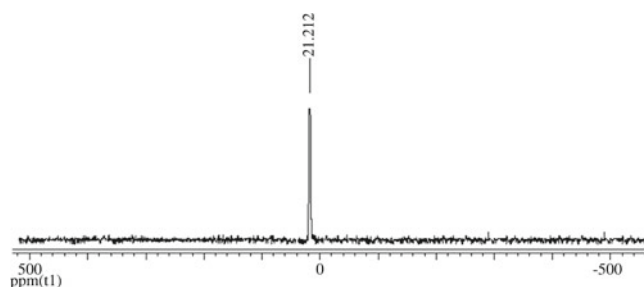
Figure 3 shows the representative TEM images of MCM-41 and B(OEt)<sub>3</sub>-MCM-41. The highly ordered

hexagonal arrays of mesoporous channels confirm the existence of a hexagonal mesostructure for B(OEt)<sub>3</sub>-MCM-41. These images reveal that the hexagonally ordered mesostructure of the MCM-41 host material was unaffected by grafting of boron tri-ethoxide.

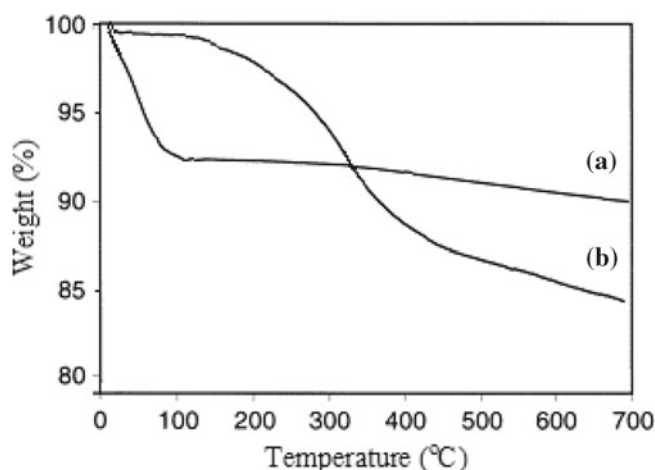
Grafting of B(OEt)<sub>3</sub> on the calcined MCM-41 material was followed by <sup>29</sup>Si solid state NMR. <sup>29</sup>Si MAS NMR spectra of calcined mesoporous MCM-41 and B(OEt)<sub>3</sub>-MCM-41 samples are shown in figure 4. Presence of broad resonance peaks from −90 to −110 ppm, indicative for a range of Si–O–Si bond angles and the formation of more tetrahedral silicon environments. The <sup>29</sup>Si MAS NMR spectrum of the calcined MCM-41 shows signals of *Q*<sup>4</sup> species (Si(4OSi)) at −110 ppm, *Q*<sup>3</sup> species (Si(3OSi,1OH)) at −100 ppm, and *Q*<sup>2</sup> species (Si(2OSi,2OH)) at −92 ppm. Compared to MCM-41, the spectrum of B(OEt)<sub>3</sub>-MCM-41 shows a marked decrease in the intensity of the *Q*<sup>3</sup> and *Q*<sup>2</sup> signals, due to the substitution of hydroxyl groups belonging to *Q*<sup>2</sup> or *Q*<sup>3</sup> with boron alkoxide-complex during the incorporation process. In addition, the <sup>11</sup>B NMR of the B(OEt)<sub>3</sub>-MCM-41 reveals the presence of 3-fold coordinated boron with a very characteristic peak around 21 ppm as shown in figure 5 indicating the successful modification of MCM-41 by boron ethoxide.



**Figure 4.** <sup>29</sup>Si solid-state MAS NMR spectra of (a) pure MCM-41 and (b) B(OEt)<sub>3</sub>-MCM-41.



**Figure 5.** <sup>11</sup>B NMR spectra of B(OEt)<sub>3</sub>-MCM-41.



**Figure 6.** Weight loss curves for (a) unmodified MCM-41 and (b)  $\text{B(OEt)}_3$ -MCM-41.

Thermogravimetric weight loss curves for MCM-41 and  $\text{B(OEt)}_3$ -MCM-41 are shown in figure 6. It can be seen that unmodified MCM-41 exhibited a major weight loss at temperatures up to ca. 100°C, which can be attributed to the release of physically adsorbed water<sup>35,36</sup> and therefore indicates a relatively hydrophilic character of its surface. At higher temperatures, the TGA curve was very flat, especially up to ca. 600°C, showing that there is no remarkable condensation of silanol groups on the surface of the material.<sup>35,36</sup> Weight loss profile of the MCM-41 material was significantly altered as a result of the modification. In the case of samples with boron alkoxides bonded ligands (see figure 1), weight loss up to 100°C was very small. At higher temperatures, the TGA curves were initially flat and then exhibited a rapid decline in the temperature range from ca. 383 to 600 K, followed by a more gradual weight loss. Prominent steps on the TGA curves can be attributed to the decomposition of bonded boron alkoxide moieties, and their height is roughly proportional to carbon contents in the samples.

### 3.2 Activity of $\text{B(OEt)}_3$ -MCM-41 material

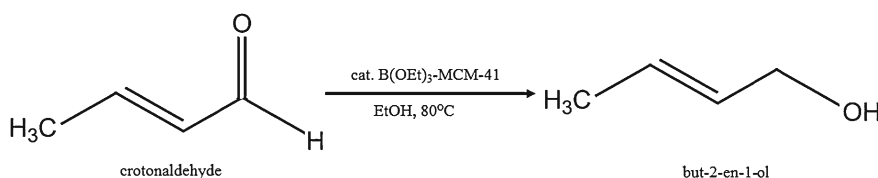
The MPV reaction have been catalysed by various metal alkoxides such as aluminum 2-propoxide, zirconium 1-propoxide, etc.<sup>37</sup> Also, different boron alkoxides

such as boron 2-propoxide, boron tri-ethoxide, etc., have been used in the MPV reductions.<sup>38,39</sup> In this study, we first aimed to prepare the new material MCM-41 functionalized with boron tri-ethoxide and compare the surface properties with pure MCM-41. Second, we wanted to show the applicability of the new material as heterogenous catalyst in the MPV reduction.

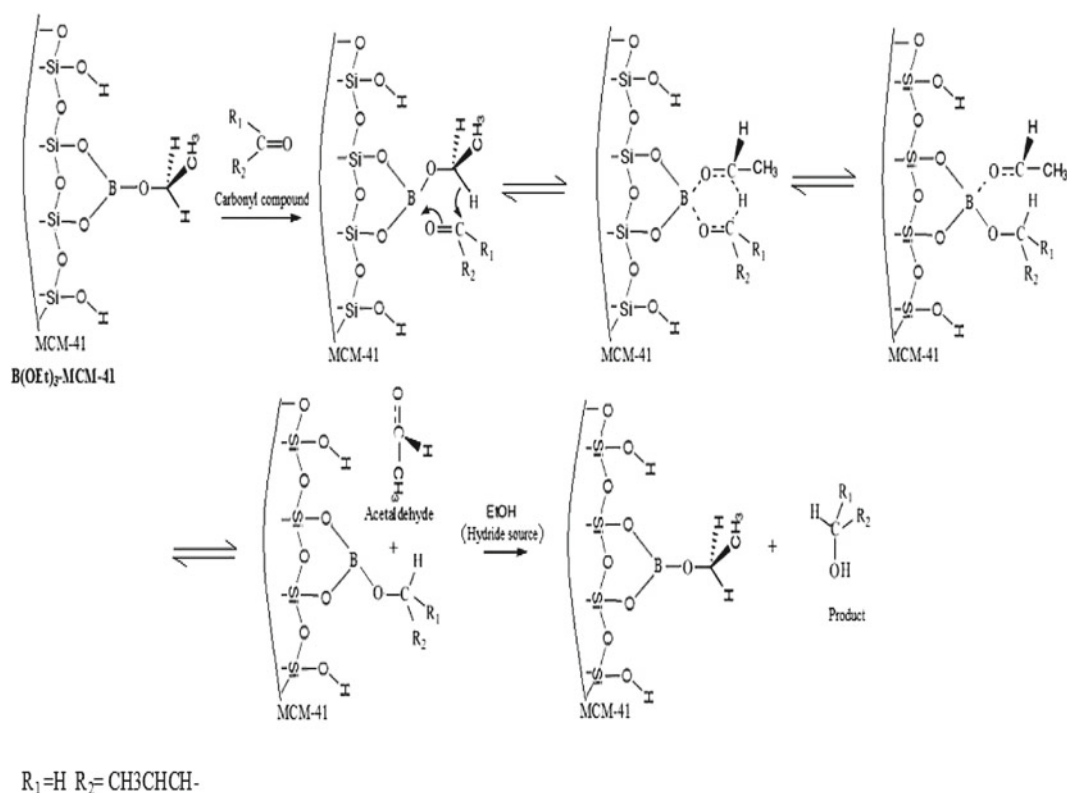
High surface area mesoporous material such MCM-41 provides useful support for the heterogenization of boron alkoxides.<sup>4,10</sup> Surface hydroxyl groups are involved in the grafting reaction, probably allowing boron tri-ethoxide to build up to a monolayer. Therefore, MCM-41 with hexagonal pore structure will favour easy access of the reactants to the B centres. And thus, MCM-41 will increase the reaction rate.<sup>4</sup> This is consistent with the tendency of B-alkoxides to form aggregates in homogeneous reaction medium. So, compared with homogeneous catalysts, heterogeneous boron alkoxide catalysts which are dispersed over the siliceous surface by reaction with the surface silanol groups, have more available B centres for MPV reaction.<sup>40</sup>

Herein, we reported that our preliminary results on the development of  $\text{B(OEt)}_3$ -MCM-41 catalyst can be employed for the chemoselective catalytic MPV reduction of various aldehydes and ketones under mild reaction conditions. For this purpose,  $\text{B(OEt)}_3$ -MCM-41 was tested for chemoselective reduction of crotonaldehyde to but-2-en-1-ol (scheme 2).

Reaction mechanism for the homogeneous MPV reaction involves a cyclic six-membered transition state.<sup>41–43</sup> Recent studies by Creighton *et al.*<sup>13</sup> proposed that over heterogeneous catalysts such as zeolite beta, the MPV mechanism also involves a six-membered transition state, where both the alcohol and the ketone coordinate to the same Lewis acid site.<sup>40</sup> In this regard, the reaction mechanism for the reduction reaction of crotonaldehyde can be presumed to be similar to the classical MPV reduction of carbonyls reported for aluminium isopropoxide and boron tri-isopropoxide.<sup>4,8,39</sup> Scheme 3 shows the proposed mechanism for the MPV reduction of crotonaldehyde in the presence of  $\text{B(OEt)}_3$ -MCM-41. First, the carbonyl compound is coordinated to the boron of the boron alkoxide. The reaction proceeds by hydride-transfer to the carbonyl compound



**Scheme 2.** MPV reduction of crotonaldehyde using  $\text{B(OEt)}_3$ -MCM-41 catalyst.



**Scheme 3.** Proposed mechanism for the MPV reduction of crotonaldehyde in the presence of  $B(OEt)_3$ -MCM-41.

from the alcohol, which is bound to the boron centre as an alkoxide. Since the reduction is reversible, the acetaldehyde was removed from the medium by a slow stream of nitrogen. Removal of acetaldehyde from the reaction solution leads to the progress of the reaction to the right hand side.<sup>42</sup>  $B(O^iPr)_3$ -MCM-41 also reduces carbonyl compounds with a similar mechanism; the acetone produced was removed by the same procedure.<sup>4</sup> Removal of acetone (bp 81°C) is more difficult than acetaldehyde (bp 56°C). Therefore, the yield of the alcohol products from reduction will be greater than those using  $B(O^iPr)_3$ -MCM-41.

It is found that  $B(OEt)_3$ -MCM-41 is an active catalyst in the MPV reduction of crotonaldehyde. Yield

of the reduction product, reaction time and chemoselectivity to but-2-en-1-ol in the presence of heterogeneous catalyst were summarized in table 2. As seen in table 2, in the presence of  $B(OEt)_3$ -MCM-41, the desired but-2-en-1-ol was obtained with high selectivity at high crotonaldehyde conversion (table 2). The important carbonyl compound possesses conjugated C=C and C=O bonds. The C=C bonds are more readily hydrogenated than the C=O bonds in most usual techniques.<sup>44</sup> Although reduction of the C=O bonds without affecting the C=C bonds is very difficult, C=O bond of this compound was reduced using  $B(OEt)_3$ -MCM-41 catalyst. An interesting result was that the selectivity towards the reduced product was 99% in the

**Table 2.** Reduction of crotonaldehyde to but-2-en-1-ol under different reaction conditions: reduction time, product alcohol yields, chemoselectivity to but-2-en-1-ol: comparison with Zr (100) catalyst.

System	Yield (%)	Selectivity (%)	t(h)	System (ref. 45)	Yield (%)	t(h)	Selectivity (%)
$B(OEt)_3$ -MCM-41	89.8 <sup>[a]</sup>	99	5	Zr (100)	95.2 <sup>[a]</sup>	6	100
No catalyst	— <sup>[b]</sup>						
Filtrate	— <sup>[b]</sup>						
Quenched solution	— <sup>[b]</sup>						
$B(OEt)_3$ free MCM-41	— <sup>[b]</sup>						

Reaction condition: Crotonaldehyde (30 mmol), catalyst (500 mg) in ethanol (200 mmol, 15.4 mL) refluxed at 353 K for 6 h

<sup>[a]</sup>Yield on single experiment

<sup>[b]</sup>No reaction

presence of heterogeneous catalyst, showing that the supported boron alkoxide catalyst is highly selective.

To show catalytic efficiency of  $\text{B}(\text{OEt})_3$ -MCM-41 catalyst according to different MPV catalysts, heterogeneous boron tri-ethoxide catalyst compared with Zr (100) (Si/Zr ratio of 100) MPV catalyst in table 2.<sup>45</sup> In the literature, it was found that Zr-zeolite beta is a very efficient catalyst for the reduction of alkyl- and aryl-saturated ketones.<sup>46</sup> Lewis acid sites resulting from the incorporation of Zr into the zeolite framework were considered as active centres of the zeolite. Zhu and coworkers investigated the use of Zr-zeolite beta in the MPV reduction of  $\alpha,\beta$ -unsaturated aldehydes.<sup>45</sup> In comparison with heterogeneous Zr(100) catalyst, for crotonaldehyde, the  $\text{B}(\text{OEt})_3$ -MCM-41 heterogeneous catalyst shows similar activity (yield) and selectivity.<sup>46</sup> As shown in table 2, but-2-en-1-ol yield is 95.2% for Zr(100) and 89.8% for  $\text{B}(\text{OEt})_3$ -MCM-41 catalysts. Also, comparing  $\text{B}(\text{OEt})_3$ -MCM-41 catalyst with Zr (100) catalyst, it was found that in the presence of  $\text{B}(\text{OEt})_3$ -MCM-41 catalyst, crotonaldehyde was reduced with reduced reaction time (table 2). Therefore,  $\text{B}(\text{OEt})_3$ -MCM-41 catalyst is as good as Zr(100) catalyst with respect to MPV reduction of crotonaldehyde.<sup>45</sup>

#### 4. Conclusion

Modification with boron-tri-ethoxide groups of MCM-41 material creates new Lewis acid sites (of moderate and stronger Lewis acidity, according to the  $\text{B}(\text{O}^i\text{Pr})_3$ -MCM-41 results) while, to a certain degree, the initial structural characteristics (high surface area, narrow pore size distribution, and crystalline hexagonal structure) are preserved.

In conclusion, we have devised an essentially new boron alkoxide based heterogeneous ' $\text{B}(\text{OEt})_3$ -MCM-41' catalyst. The  $\text{B}(\text{OEt})_3$ -MCM-41 catalyst was tested in MPV reduction of crotonaldehyde. The catalyst prepared in this study possess sufficient catalytic activity in the MPV reduction of crotonaldehyde. It is useful for high catalytic activity with EtOH as a hydride donor in the MPV reduction of various  $\alpha,\beta$ -unsaturated carbonyl groups. It has a remarkable potential for practical use since heterogeneous  $\text{B}(\text{OEt})_3$ -MCM-41 catalyst offers the advantage of ease of separation.

#### Acknowledgement

The authors thank Scientific Research Projects Unit of Akdeniz University for financial support.

#### References

1. Kresge C T, Leonowicz M E, Roth W J, Vartuli J C and Beck J S 1992 *Nature* **359** 710
2. Yue Y, Gedeon A, Bonardet J L, Melosh N, d'Espinose J B and Fraissard J 1999 *Chem. Commun.* **19** 1967
3. Berlini C, Guidotti M, Moretti G, Psaro R and Ravasio N 2000 *Catal. Today* **60** 219
4. Uysal B and Oksal B S 2012 *Appl. Catal. A-Gen* **435** 204
5. De bruyn M, De Vos D E and Jacobs P A 2002 *Adv. Synth. Catal.* **344** 1120
6. Quignard F, Graziani O and Choplin A 1999 *Appl. Catal. A* **182** 29
7. Leyrit P, Mc Gill C, Quignard F and Choplin A 1996 *J. Mol. Catal. A: Chem.* **112** 395
8. Anwender R, Palm C, Gerstberger G, Groeger O and Engelhardt G 1998 *Chem. Commun.* 1811
9. Inada K, Shibagaki M, Nakanishi Y and Matsushita H 1993 *Chem Lett.* **22** 1795
10. Uysal B, Aksu Y and Oksal B S 2013 *J. Porous Mat.* **20** 115
11. Minambres J F, Aramendia M A, Marinas A, Marinas J M and Urbano F J 2011 *J. Mol. Catal. A: Chem.* **338** 121
12. Urbano F J, Aramendia M A, Marinas A and Marinas J M 2009 *J. Catal.* **268** 79
13. Creighton E J, Ganeshie S D, Downing R S and van Bekkum H 1997 *J. Mol. Catal. A* **115** 457
14. Creighton E J and Downing R S 1998 *J. Mol. Catal. A: Chem* **134** 47
15. Creighton E J, Huskens J, van der Waal J C and van Bekkum H 1997 In *Heterogeneous catalysis and fine chemicals IV* (eds) H U Blaser, A Baiker and R Prins (Amsterdam: Elsevier) p. 531
16. Kunkeler P J, Zuurdeeg B J, van der Waal J C, van Bokhoven J A, Koningsberger D C and van Bekkum H 1998 *J. Catal.* **180** 234
17. Corma A, Domine M E and Valencia S 2003 *J. Catal.* **215** 294
18. Anwender R and Palm C 1999 *Stud. Surf. Sci.* **117** 413
19. Ivanov V A, Bachelier J, Audry F and Lavalley J C 1994 *J. Mol. Catal.* **91** 45
20. Sayari A, Danumah C and Moudrakovski I L 1995 *Chem. Mater.* **7** 813
21. On T D, Joshi P N and Kaliaguine S 1996 *J. Phys. Chem.* **100** 6743
22. Charoenchaidet S, Chavadej S and Gulari E 2002 *J. Mol. Catal. A-Chem.* **185** 167
23. Jiamwijitkul S, Jongsomjit B and Praserttham P 2007 *Iran. Polym. J.* **16** 549
24. Conesa T D, Campelo J M, Luna D, Marinas J M and Romero A A 2007 *Appl. Catal. B: Environ.* **70** 567
25. Grün M, Unger K, Matsumoto A and Tsutsumi K 1999 *Micropor. Mesopor. Mater.* **27** 207
26. Maity N, Rajamohanam P R, Ganapathy S, Gopinath C S, Bhaduri S and Lahiri G K 2008 *J. Phys. Chem. C* **112** 9428
27. Chen C Y, Li H X and Davis M E 1993 *Microporous Mater.* **2** 17
28. Vetrive S and Pandurangan A 2005 *Catal. Lett.* **99** 3–4–3–141



29. Ziolk M, Lewandowska A and Grybowska B 2003 *React. Kinet. Catal. Lett.* **80** 2
30. Gao X, Wachs I E, Wong M S and Ying J Y 2001 *J. Catal.* **203** 18
31. Mathew T, Sivaranjani K, Gnanakumar E S, Yamada Y, Kobayashia T and Gopinath C S 2012 *J. Mater. Chem.* **22** 13484
32. Xu J, Luan Z, He H, Zhou W and Kevan L 1998 *Chem. Mater.* **10** 3690
33. Park S E, Kim D S, Chang J S and Kim W Y 1998 *Catal. Today*. **44** 301
34. Kinski I, Gies H and Marlow F 1997 *Zeolite* **19** 375
35. Jaroniec C P, Gilpin R K and Jaroniec M 1997 *J. Phys. Chem. B.* **101** 6861
36. Iler R K 1979 *The chemistry of silica* (Wiley: New York)
37. Namy J L, Soupe J and Collin Kagan J H B 1984 *J. Org. Chem.* **49** 2045
38. Uysal B and Buyuktas B S 2007 *Arkivoc* **14** 134
39. Uysal B and Oksal B S 2011 *J. Chem. Sci.* **123** 681
40. Bruyn M D, Limbourg M, Denayer J, Baron G V, Parvulescu V, Grobet P J, De Vos D E and Jacobs P A 2003 *Appl. Catal. A.* **254** 189
41. De Graauw C F, Peters J A, van Bekkum H and Huskens J 1994 *Synthesis.* **10** 1007
42. Uysal B and Buyuktas B S 2012 *Chem. Pap.* **64** 123
43. Zhu Y, Liu S, Jaenicke S and Chuah G 2004 *Catal. Today* **97** 249
44. Narayanan S 2003 *Bull. Catal. Soc. India* **2** 107
45. Zhu Y, Chuah G K and Jaenicke S 2006 *J. Catal.* **241** 25
46. Zhu Y Z, Chuah G K and Jaenicke S 2004 *J. Catal.* **227** 1