

New heterogeneous B(OEt)₃-MCM-41 catalyst for preparation of α,β -unsaturated alcohols

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Abstract Grafting of boron tri-ethoxide on mesoporous MCM-41 resulted in a highly active catalyst for the Meerwein–Ponndorf–Verley (MPV) reduction and the catalyst denoted as B(OEt)₃-MCM-41. Chemoselective reduction of α,β -unsaturated aldehydes and ketones to the corresponding α,β -unsaturated alcohols was achieved by MPV reduction reaction using a new B(OEt)₃-MCM-41 catalyst. The prepared new heterogeneous catalyst, B(OEt)₃-MCM-41, was characterized in detail by using XRD, ²⁹Si NMR-, ¹¹B NMR-, ¹³C NMR-, and TEM, N₂ adsorption, and ICP-OES. The results demonstrated the successful homogenous distribution of the B(OEt)₃ on the MCM-41 support. The heterogeneous B(OEt)₃-MCM-41 catalyst, in comparison with the homogeneous B(OⁱPr)₃ and B(OEt)₃ catalysts, displayed similar catalytic activity in the MPV reduction of α,β -unsaturated aldehydes and ketones with alcohols as reductants. Reduced reaction times and very high selectivities for the unsaturated alcohols were obtained with the heterogenous catalyst compared with the homogeneous catalysts. The B(OEt)₃-MCM-41 catalyst was found to be encouraging, as is recyclable up to six cycles without any significant loss in its catalytic activity.

Keywords Mesoporous MCM-41 · Boron tri-ethoxide · Chemoselectivity · α,β -Unsaturated aldehydes and ketones · MPV reduction

Introduction

Allylic alcohols are important intermediates in the production of pharmaceuticals, agrochemicals, and fragrances [1, 2]. They may be produced by oxidation of olefins

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[3], or by alkylation of unsaturated aldehydes [4], but a more general route is the chemoselective reduction of α,β -unsaturated carbonyl compounds to allylic alcohols [3], and this reaction generally proceeds with special catalysts [4]. The stoichiometric $\text{NaBH}_4/\text{CeCl}_3$ system, and most conspicuously the ternary combination of Ru (phosphine) with a chiral diamine and a base, proved to be excellent for chemoselective reductions [5–7]. However, this catalyst requires extra base for its activation; it is not easily recuperated from the reaction mixture and may lose its activity in recycling. Therefore, considerable effort has been done to develop heterogeneous catalysts for this type of reduction [8]. Particularly, the combination of group VIII metals (Pt, Rh, Ru) and some metal additives (Sn, Fe) has been found to be suitable for the selective reduction of unsaturated aldehydes to allylic alcohols [9, 10]. However, when applied to the selective reduction of α,β -unsaturated ketones, these catalysts often show high selectivity for the saturated ketone or the alcohol [11]. As an alternative to metal-catalyzed hydrogenations, hydrogen transfer reactions of the Meerwein–Ponndorf–Verley (MPV) type form an attractive approach [12–14].

The reduction of carbonyl compounds by hydrogen transfer from an alcohol is known as the MPV reaction in organic chemistry and can be performed under mild conditions using Lewis acids as catalyst [15, 16]. The MPV reduction of carbonyl compounds is a highly selective reaction since only the carbonyl group coordinates with the Lewis acid center, while the double bond remains unreacted [17]. Therefore, the MPV reduction offers a facile access to unsaturated alcohols, many of which are important starting materials for the production of fine chemicals [18]. Traditionally, the MPV reaction can be catalyzed using homogeneous catalysts such as metal alkoxides. Heterogeneous catalysts for the MPV reactions include zeolites [19–21], grafted alkoxides [22, 23], and metal oxides such as magnesium oxide, zirconia, silica, alumina [24], etc. A major advantage of heterogeneously over homogeneously catalyzed MPV reactions is that the catalysts can easily be separated from the liquid reaction mixture [19, 25].

The heterogenation of the MPV catalysts also offers the advantage of reusability [26]. In order to heterogenize the metal complexes used in MPV reductions, grafting onto inorganic supports has been carried out. Recently, the mesoporous silicate MCM-41 was explored as a versatile support material for metalorganic moieties [27, 28]. Since its discovery by Mobil in 1992 [29, 30], MCM-41 and related mesoporous molecular sieves have attracted great attention. As is known, MCM-41 possesses unidirectional channel-like pores of rather uniform size which are arranged in a regular hexagonal pattern. The pores diameters are adjustable from 15 to 100 Å depending on the synthesis conditions, such as temperature, and the type and size of the templating detergent cations [31].

Modification of the MCM-41 may provide an alternative strategy to obtain suitable supports to maintain high activity in the heterogeneous catalyst system for the reduction of carbonyl compounds. Several MPV reduction catalysts, such as Al-alkoxides, Zr-alkoxides as well as Hf and Zr alkyl complexes, have been anchored on MCM-41 or on amorphous SiO_2 in order to generate potential catalytic activity [32–35]. Many of these catalysts have been applied in reactions of saturated ketones (e.g., substituted cyclohexanones), which are much easier to reduce than

unsaturated ketones. Only a few heterogeneous catalysts have been applied in the MPV reduction of α,β -unsaturated ketones [26, 33, 36].

In the present study, we reported a new heterogeneous catalyst B(OEt)₃-MCM-41, characterized its structure, and showed the selective reduction of a variety of α,β -unsaturated aldehydes and ketones using heterogenised boron tri-ethoxide catalyst. Heterogeneous MPV catalyst of similar type has just previously applied to the reduction of unsaturated aldehydes and ketones using heterogenized B(OⁱPr)₃-MCM-41, and the results have been very encouraging [37, 38]. Up to the present time, there has not been any literature reporting on the boron tri-ethoxide grafted MCM-41 heterogeneous catalyst for the reduction of α,β -unsaturated ketones and aldehydes to α,β -unsaturated alcohols.

Experimental

Preparation of mesoporous support

Pure siliceous MCM-41 was synthesized following a previously reported procedure [37]. 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 (1,000 rpm) until a clear solution was obtained. Then, 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 H₂O were added. The resulting mixture was vigorously stirred (1,000 rpm) for another 1 h. The molar composition of the final gel mixture was SiO₂:0.3CTMACl:0.2TEAOH:46.3H₂O.

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 in Refs. [37, 38].

Grafting of boron tri-ethoxide, B(OEt)₃

Boron alkoxide-containing ordered mesoporous silica material was prepared by the grafting method [38, 39]. 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) B(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 N₂ atmosphere, washed three times 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 B(OEt)₃-MCM-41.

Characterization

The surface area, average pore diameter, and pore size distribution of the MCM-41 support and the prepared heterogeneous catalyst were determined by nitrogen

adsorption using a Micromeritics Gemini III 2375 Surface Area Analyzer. Prior to measurements, the samples were degassed at 300 °C and 0.15 mbar for at least for 6 h. The surface areas were calculated by the method of Brunauer, Emmett, and Teller (BET). The pore size distribution curves were obtained from the analysis of desorption branch of the nitrogen adsorption–desorption isotherm by the Barrett–Joyner–Halenda (BJH) 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 of 0.154 nm.

Transmission electron microscopy (TEM) images were recorded on a tecnai G² 20 S-TWIN with an energy dispersive X-ray spectrometer (EDAX, r-TEM SUTW) located at the ZELMI, TU Berlin.

The 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 a Perkin Elmer Optima 4300DV.

The anchoring of boron tri-ethoxide species on MCM-41 was followed by ²⁹Si MAS NMR and ¹¹B MAS NMR spectroscopies.

Solid state ¹³C MAS NMR, ²⁹Si MAS NMR, and ¹¹B MAS NMR spectra were recorded on a Bruker Advance 400 NMR spectrometer with a resonance frequency of 100.6, 79.46, and 128.3 MHz for ¹³C, ²⁹Si, and ¹¹B using a Bruker 4 mm double-resonance probe head operating at a spinning rate of 10 kHz for ¹³C and 12 kHz for ²⁹Si and ¹¹B, respectively. ¹³C spectra were collected with 70° rf pulses, 5 s delay, while ²⁹Si spectra were collected with 70° rf pulses, 30 s delay, and in both cases with ~6,000 scans. ¹¹B MAS NMR spectra were accumulated for 1,024–4,096 scans with $\pi/4$ pulse width of 1.1 μs and 2 s recycle delay.

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

The $\text{B}(\text{OEt})_3$ -MCM-41 catalyst was tested on the MPV reduction of a series of α,β -unsaturated aldehydes and ketones.

The reaction mixture, containing 30 mmol of the aldehyde or ketone, 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 °C. During the reduction reaction time, a slow stream of dry nitrogen was passed just over the surface of reaction mixture. In this way, the formed acetaldehyde was removed by nitrogen flow. Thus, the equilibrium reaction was slipped to the right hand side. Aliquots were removed at different reaction times and analyzed by 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 μm film thickness) (Palo Alto, CA, USA).

The same procedure was used to reduce other α,β -unsaturated aldehydes and ketones in the presence of $\text{B}(\text{OEt})_3$ -MCM-41. The selectivity towards the α,β -unsaturated alcohol (S_{UOL}) at variable conversion levels was calculated from the following expression [16]:

$$S_{\text{UOL}} = (\text{mmol unsaturated alcohol/mmole } \alpha,\beta\text{-unsaturated carbonyl compound converted}) \times 100.$$

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 cinnamaldehyde. The reuse of catalyst was also tested for the MPV reduction of cinnamaldehyde. The yield was practically unaffected up to five cycles. The filtrate and quenched solutions of the catalyst did not show any catalytic activity. This confirms that the activity observed is due only to the solid catalyst and not partly due to the leached active species. Characterization of reused catalyst was determined by XRD.

Results and discussion

Characterization of materials

The as-obtained heterogeneous catalyst systems were investigated with various analytical methods including N_2 adsorption/desorption measurements BET, ^{13}C MAS NMR and ^{29}Si MAS NMR-spectroscopies, and XRD and TEM techniques.

The N_2 adsorption–desorption isotherms and the corresponding BJH pore size distributions based on the desorption branch for the MCM-41 and $\text{B}(\text{OEt})_3$ -MCM-41 samples are shown in Fig. 1a, b, respectively. The N_2 isotherm for the MCM-41 sample is shown in Fig. 1a. 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 [40–42]. 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 [43]. 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 $\text{B}(\text{OEt})_3$ into the channel causes changes in the pore structure of the support during the incorporation process. Also, $\text{B}(\text{OEt})_3$ -MCM-41 still displays a type IV adsorption isotherm according to the IUPAC without any hysteresis between the adsorption and the desorption curves (Fig. 1a). This is an indication for uniform pore sizes arranged in networks.

As we can see from Table 1, before functionalization with $\text{B}(\text{OEt})_3$, the calcined MCM-41 has a surface area of 1,100 m^2/g , with an average pore diameter of 25.1 \AA (Fig. 1b) as deduced using the BJH method. The specific surface decreases to

762 m²/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)₃-MCM-41 are shown in Fig. 2a, b, respectively. X-ray diffractograms of the MCM-41 and B(OEt)₃-MCM-41 materials were characterized by three distinct Bragg reflexes at low angles indexed to (1 0 0), (1 1 0), and (2 0 0), representative of ordered materials with hexagonal arrangement of mesopores (Fig. 2a, 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 [44]. After the incorporation of the 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 [45]. Furthermore, the 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).

The reused catalyst was also characterized by XRD measurement. The low-angle XRD pattern of reused B(OEt)₃-MCM-41 catalyst is shown in Fig. 2c. After using the catalyst for five cycles, the XRD pattern of the reused B(OEt)₃-MCM-41 catalyst still exhibits a high intensity, (100), and two low intensity reflections, (110) and (200), which are characteristic of the hexagonal mesoporous MCM-41 material [46]. In comparison with the XRD pattern of the unused B(OEt)₃-MCM-41 catalyst, the intensity of the reflections of the catalyst reused for five cycles was almost the same.

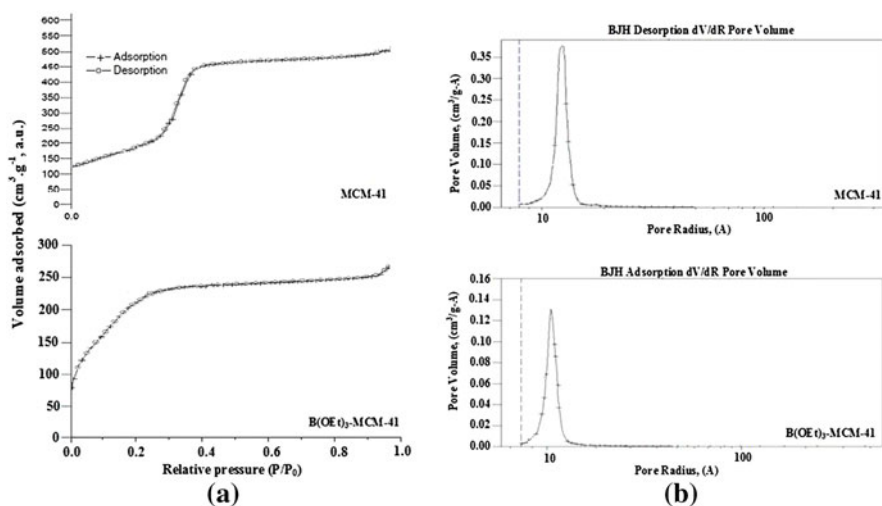


Fig. 1 a N₂ adsorption/desorption isotherms and b BJH pore size distribution curves for MCM-41 and B(OEt)₃-MCM-41

Table 1 Surface properties of MCM-41 and B(OEt)₃-MCM-41

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (Å)
MCM-41	1,100	0.38	25.1
B(OEt) ₃ -MCM-41	762	0.12	20.8

ICP-OES analysis showed 2.81 wt% of boron content in the catalyst. To determine boron content, B(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, and 2.6 mmol B was found per g of B(OEt)₃-MCM-41.

Figure 3 shows the representative TEM images of MCM-41 and B(OEt)₃-MCM-41. The highly ordered hexagonal arrays of mesoporous channels confirm the existence of a hexagonal mesostructure for B(OEt)₃-MCM-41. These images reveal that the hexagonally ordered mesostructure of the MCM-41 host material was unaffected by grafting of boron tri-ethoxide.

The grafting of the B(OEt)₃ on the calcined MCM-41 material was followed with ²⁹Si solid state NMR. ²⁹Si MAS NMR spectra of calcined mesoporous MCM-41 and B(OEt)₃-MCM-41 samples are shown in Fig. 4. The presence of broad resonance peaks from -90 to -110 ppm is indicative for a range of Si-O-Si bond angles and the formation of more tetrahedral silicon environments. The ²⁹Si MAS NMR spectrum of the calcined MCM-41 shows signals of Q⁴ species (Si(4OSi)) at -110 ppm, Q³ species (Si(3OSi,1OH)) at -100 ppm, and Q² species (Si(2O-Si,2OH)) at -92 ppm. Compared to MCM-41, the spectrum of B(OEt)₃-MCM-41 shows a marked decrease in the intensity of the Q³ and Q² signals, hence due to the substitution of the hydroxyl groups belonging to Q² or Q³ with the boron-alkoxide complex during the incorporation process. In addition, the ¹¹B NMR of the B(OEt)₃-MCM-41 reveals the presence of threefold coordinated boron with a very characteristic peak around 21 ppm as shown in Fig. 5, indicating the successful modification of MCM-41 with the boron ethoxide.

Solid state ¹³C NMR spectra of MCM-41 and B(OEt)₃-MCM-41 are shown in Fig. 6. The spectrum of unmodified MCM-41 exhibits no carbonaceous compound as impurities on the unmodified MCM-41. The signals at 18.8 and 60.2 ppm in the solid state ¹³C NMR spectrum of B(OEt)₃-MCM-41 are characteristic for the ethoxy group: ¹³C NMR (300 MHz, CDCl₃, 25 °C): δ = 18.8 (CH₃), 60.2 (-CH₂CH₃). ¹³C NMR of B(OEt)₃-MCM-41 shows the successful modification of MCM-41 material with the desired molecule.

Activity of heterogenized B(OEt)₃-MCM-41 catalyst

The MPV reaction have been catalyzed by various metal alkoxides, such as aluminum 2-propoxide, zirconium 1-propoxide, etc. [47]. Also, different boron alkoxides, such as boron 2-propoxide, boron tri-ethoxide, etc., have been used in the MPV reductions [48, 49]. In this study, we aimed to show the applicability of the new material as a heterogenous catalyst in the MPV reduction and to study the possible advantages with respect to the unsupported analogues. For this purpose,

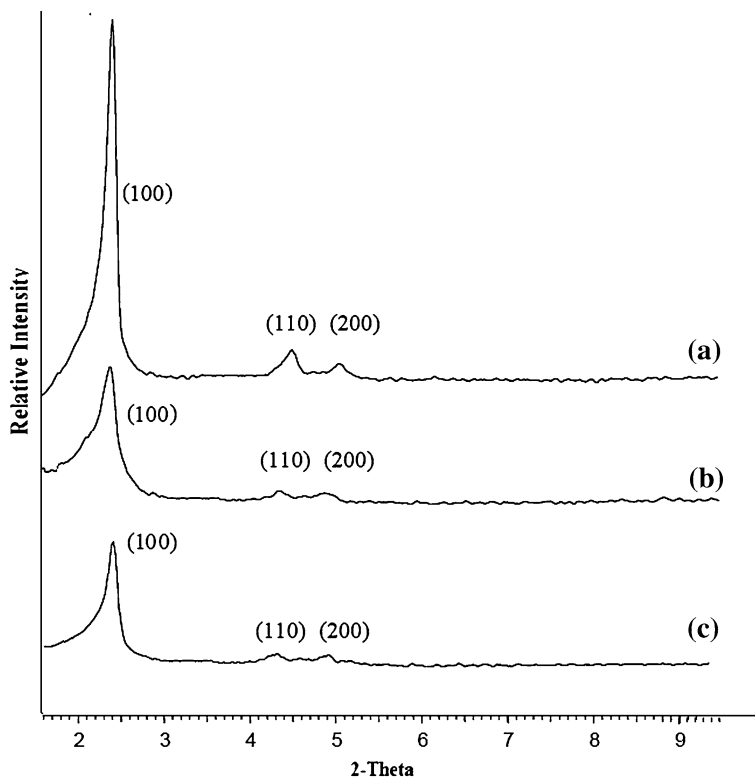


Fig. 2 Low-angle XRD patterns of *a* unmodified MCM-41, *b* $\text{B}(\text{OEt})_3$ -MCM-41, and *c* reused $\text{B}(\text{OEt})_3$ -MCM-41 catalyst

$\text{B}(\text{OEt})_3$ -MCM-41 was tested for the reduction of α,β -unsaturated aldehydes and ketones. Also, this new catalyst was compared with homogeneous $\text{B}(\text{O}^i\text{Pr})_3$ and $\text{B}(\text{OEt})_3$ analogues.

It was found that, for the heterogeneously catalyzed MPV reduction of unsaturated aldehydes and ketones, $\text{B}(\text{OEt})_3$ -MCM-41 has a similar activity with homogeneous boron alkoxide catalysts. The studied carbonyl compounds, the yields of the reduction product, reaction times, and corresponding yields in the presence of heterogeneous catalyst are summarized in Table 2, where it can be seen that heterogenization of the boron tri-ethoxide leads to a decrease in the reaction time and an increase in the reaction yield when compared with the homogeneous catalysts. Also, in the presence of $\text{B}(\text{OEt})_3$ -MCM-41, the desired allylic alcohols were obtained with high selectivity at high aldehyde and ketone conversion (Table 2).

High surface area mesoporous materials like MCM-41 provide a useful support for the heterogenisation of boron alkoxides [37, 38]. Surface hydroxyl groups are involved in the grafting reaction, probably allowing the boron tri-ethoxide to build up to a monolayer. Therefore, MCM-41 with the hexagonal pore structure favors easy access of the reactants to the B centers, and thus increases the reaction rate

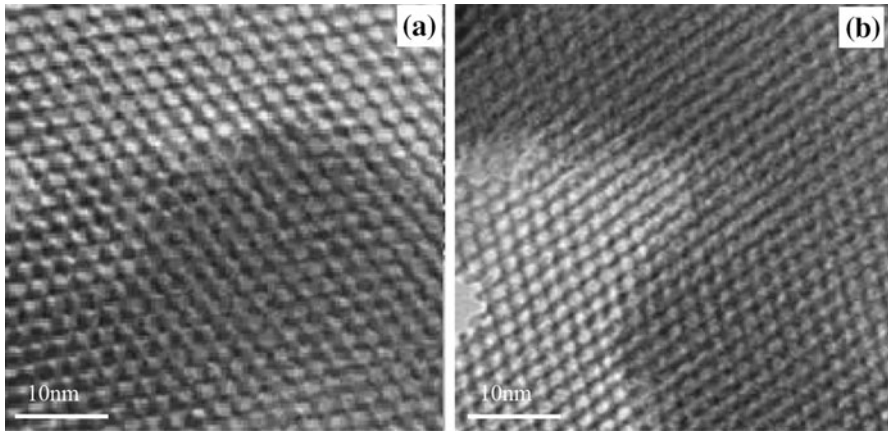


Fig. 3 TEM of **a** MCM-41 and **b** B(OEt)₃-MCM-41

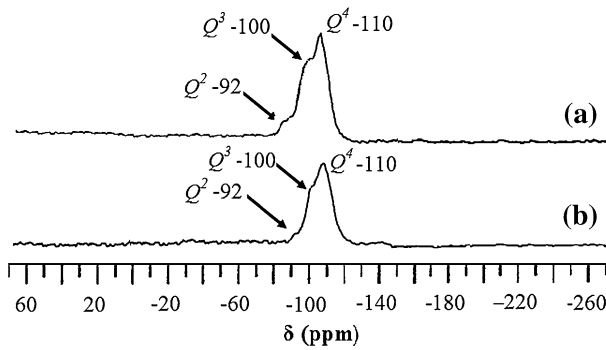


Fig. 4 ²⁹Si solid-state MAS NMR spectra of **a** pure MCM-41 and **b** B(OEt)₃-MCM-41

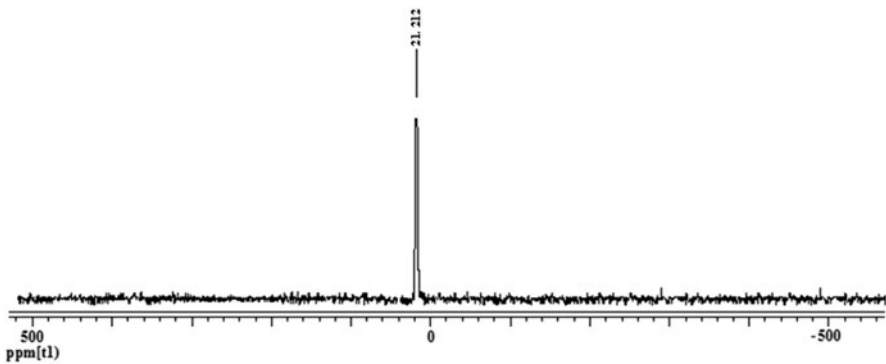


Fig. 5 ¹¹B NMR spectra of B(OEt)₃-MCM-41

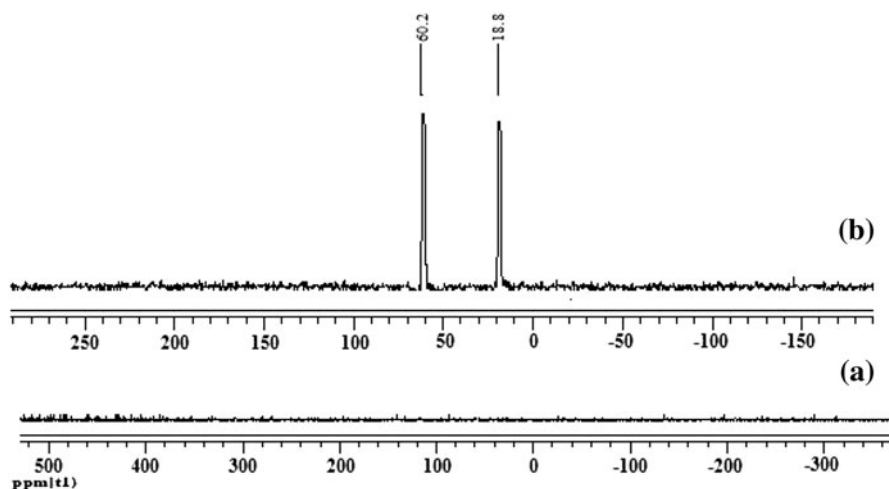


Fig. 6 ^{13}C MAS NMR spectra of **a** MCM-41 and **b** $\text{B}(\text{OEt})_3\text{-MCM-41}$

[38]. This is consistent with the tendency of B-alkoxides to form aggregates in a 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 centers for MPV reaction [50].

As can be seen in Table 2, some differences were observed in reduction yields and reduction times for the selected unsaturated aldehydes and ketones. These differences were similar for heterogeneous and homogeneous catalysts. Within the group of cyclohexenones, it is clear that an increasing number of alkyl substituents leads to a decrease in reactivity, partially due to electronic effects. In comparison with 2-cyclohexen-1-one and 3-methyl-2-cyclohexen-1-one, the smallest yield for 3,5-dimethyl-2-cyclohexen-1-one can be attributed to its steric hindrance due to the presence of two methyl groups.

Reuse of grafted catalysts

Unmodified MCM-41 was not active in the MPV reduction of α,β -unsaturated aldehydes and ketones. However, once boron tri-ethoxide was grafted onto MCM-41, the heterogenized material showed good activity and selectivity to the corresponding alcohols. To test the reused catalyst, after each round of MPV reaction, it was washed with ethanol and tested in another MPV reaction of cinnamaldehyde. Table 3 shows that, in the MPV reduction of cinnamaldehyde, the activity of the catalyst, $\text{B}(\text{OEt})_3\text{-MCM-41}$, remained high even after six rounds of reaction. The selectivity to the corresponding alcohol was 100 % in each round. The catalyst recuperating from a first run considerably conserves its activity until the sixth cycle (Table 3). The filtrate obtained after refluxing the grafted catalyst in ethanol was

Table 2 MPV reduction of various unsaturated aldehydes and ketones in the presence of heterogenized $B(OEt)_3$ -MCM-41 and homogeneous $B(O^iPr)_3$, $B(OEt)_3$ catalysts: selected substrates, reduction times, and product alcohol yields (selectivity): comparison with various MPV catalysts

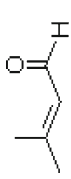
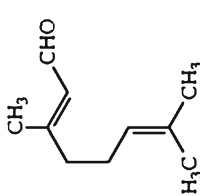
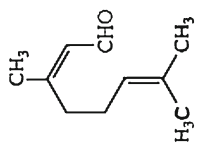
Entry	Substrat	t (h)	Yield (%), (selectivity (%))			Yield (%), (selectivity (%)) various MPV catalysts
			$B(OEt)_3$ -MCM-41 ^a	$B(O^iPr)_3$	$B(OEt)_3$	
1.	 3-methyl-2-butenal	6	86.8 (100)	87.9 (98)	88.3 (98)	95.2 (100) Zr-zeolite beta [36]
2.	 Geranial ^b	10	83.8 (98)	84.3 (93)	86.6 (94)	53.0 (>90) 11Zr-SBA-15 [57]
3.	 Neral ^c	10	82.8 (98)	83.1 (93)	85.2(94)	53.0 (>90) 11Zr-SBA-15 [57]

Table 2 continued

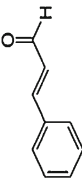
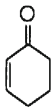
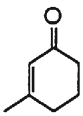
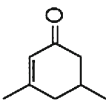
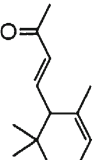
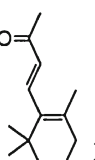
Entry	Substrat	t (h)	Yield (%), (selectivity (%))			Yield (%), (selectivity (%)) various MPV catalysts		
			B(OEt) ₃ -MCM-41 ^a	B(O i Pr) ₃	B(OEt) ₃			
4.	 Cinnamaldehyde	7	13	13	84.53 (100)	86.8 (98)	87.9 (98)	55.6 (100) (11Zr-SBA-15) [57]
5.	 2-cyclohexen-1-one	5	9	9	87.03 (100)	88.7(99)	89.5 (99)	89 (94) (Zr(O- <i>n</i> -Pr) ₂ -MCM-41) [39]
6.	 3-methyl-2-cyclohexen-1-one	6	10	10	72.30 (100)	73.6 (98)	74.8 (99)	68 (95) (Zr(O- <i>n</i> -Pr) ₂ -MCM-41) [39]
7.	 3,5-dimethyl-2-cyclohexen-1-one	6	10	10	59.2 (99)	62.6 (96)	64.8 (97)	52 (95) (Zr(O- <i>n</i> -Pr) ₂ -MCM-41) [30]

Table 2 continued

Entry	Substrat	t (h)	Yield (%), (selectivity (%))			Yield (%), (selectivity (%)) various MPV catalysts		
			B(OEt) ₃ -MCM-41 ^a	B(O ^{<i>i</i>} Pr) ₃	B(OEt) ₃		B(OEt) ₃ -MCM-41 ^a	B(O ^{<i>i</i>} Pr) ₃
8.	 α -ionone	8	13	13	81.4 (99)	83.5 (96)	86.5 (97)	89 (93) (Zr(O- <i>n</i> -Pr) ₂ -MCM-41) [39]
9.	 β -ionone	8	13	13	77.1 (99)	80.2 (97)	83.4 (97)	80 (94) (Zr(O- <i>n</i> -Pr) ₂ -MCM-41) [39]

Reaction conditions: 30 mmol of substrate, 200 mmol Ethanol, 500 mg catalyst, under reflux and stirring at 80 °C

^a Chemoselectivity to unsaturated alcohol

^b *trans*-citral

^c *cis*-citral

inactive for the MPV reduction of unsaturated aldehydes and ketones, showing the absence of leaching into the reaction medium.

In comparison with the CoHMA catalyst, the $B(OEt)_3$ -MCM-41 heterogeneous catalyst shows higher cinnamyl alcohol yield after the sixth run. As shown in Table 3, cinnamyl alcohol yield was 73 % for CoHMA and 80.2 % for the $B(OEt)_3$ -MCM-41 catalyst after the sixth run. Therefore, $B(OEt)_3$ -MCM-41 catalyst is as good as the CoHMA catalyst with respect to reusability for the reduction of cinnamaldehyde [51].

Chemoselectivity of heterogenized $B(OEt)_3$ -MCM-41 catalyst

In Table 2 are summarized the results of the catalytic MPV reduction of several unsaturated carbonyls in the presence of homogeneous $B(O^iPr)_3$, $B(OEt)_3$ and heterogeneous $B(OEt)_3$ -MCM-41 catalysts. As can be seen, the catalysts exhibited excellent chemoselectivity towards α,β -unsaturated alcohols.

Catalysis in the perfumery industry is one of the new research fields using hydrogenation catalysts. There are numerous hydrogenation processes both in gas and liquid phases, but most of them are not selective to target unsaturated alcohols. Selective hydrogenation of unsaturated aldehydes and ketones such as cinnamaldehyde, 2-cyclohexen-1-one, β -ionone, α -ionone, and benzalacetone to their corresponding unsaturated alcohols is highly desirable due to the corresponding unsaturated alcohols being useful as intermediates, pharmaceuticals, and as flavor chemicals [52]. The bond energy of C=C bond is smaller (615 kcal/mol) than that of the C=O bond (715 kcal/mol), which makes the hydrogenation of C=O bond difficult [52]. In this instance, the selective MPV reduction of the C=O bond using MPV catalysts will be a promising process for perfumery industry.

3-Methyl-2-butenal, citral, 2-cyclohexene-1-one, 3-methyl-2-cyclohexen-1-one, 3,5-dimethyl-2-cyclohexen-1-one, α -ionone, β -ionone, and cinnamaldehyde are important α,β -unsaturated aldehydes and ketones. These important carbonyl compounds possess conjugated C=C and C=O bonds. The C=C bonds are more readily hydrogenated than the C=O bonds in most usual techniques [53]. Although reduction of the C=O bonds without affecting the C=C bonds is very difficult, the C=O bonds of these compounds were reduced using homogeneous $B(O^iPr)_3$, $B(OEt)_3$ catalysts. Notably, not only the C=C double bond in the enone group of α -ionone and β -ionone but also the endocyclic C=C bond are left totally intact. Same catalytic activity was observed with the $B(OEt)_3$ -MCM-41 catalyst. The catalyst selectively reduces the carbonyl functions without affecting the olefinic bonds. Conversion yield of unsaturated aldehydes and ketones to corresponding unsaturated alcohols range from 59.2 to 87.03 % within 5–10 h of reaction time with $B(OEt)_3$ -MCM-41.

Citral occurs as *cis*- and *trans*-isomers, known as neral and geranial, respectively. Scheme 1 outlines the reduction of citral to the corresponding alcohols using ethanol as reductant. In the conversions of citral, the isolated double bond was left intact, and a mixture of the allylic alcohols geraniol and nerol was obtained. The preferential formation of geraniol as compared to nerol can be explained by steric

Table 3 Reduction of cinnamaldehyde to cinnamyl alcohol under different reaction conditions: comparison with CoHMA catalyst

Entry	System	Yield (%)	System [51]	Yield (%)
1	B(OEt) ₃ -MCM-41	86.8 ^a	CoHMA	81 ^a
2	B(OEt) ₃ -MCM-41	80.2 ^b		73 ^b
3	No catalyst	c		c
4	Filtrate	c		c
5	Quenched solution	c		c
6	B(OEt) ₃ free MCM-41	c		c

Reaction condition: Cinnamaldehyde (30 mmol), catalyst (500 mg) in ethanol (200 mmol, 15, 4 mL) refluxed at 353 K for 6 h

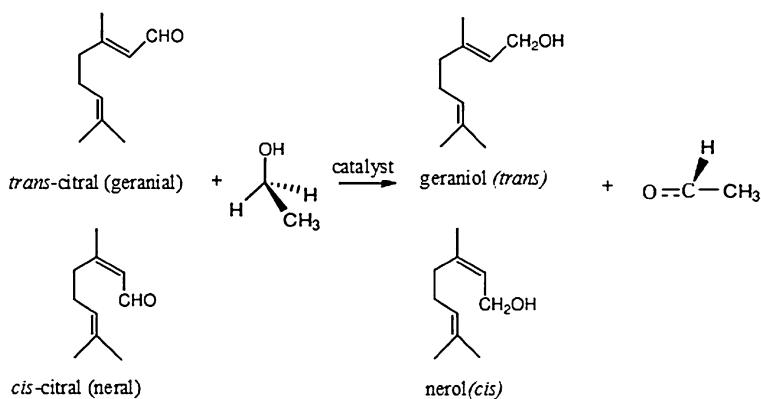
^a Yield on single experiment

^b Yield after sixth run

^c No reaction

hindrance of the bulky chain [54]. The carbonyl group of the geranial is *trans* to the bulky chain of the molecule, minimizing any steric hindrance for the binding of C=O to the boron center. Hence, the rate of reaction for geranial is faster than for neral.

The reduction product, geraniol, is a monoterpenoid and an alcohol. It is the primary part of rose oil, palmarosa oil, and citronella oil. It appears as a clear to pale-yellow oil that is insoluble in water, but soluble in most common organic solvents. It has a rose-like odor and is commonly used in perfumes. Geraniol has also been suggested to help prevent cancer. Carnesecchi et al. [55] demonstrated in his study “Geraniol inhibits growth and polyamine biosynthesis in human colon cancer cells”, that geraniol causes a 50 % decrease of ornithine decarboxylase activity, a key enzyme of polyamine biosynthesis, which is enhanced in cancer growth.

**Scheme 1** MPV reduction of citral to geraniol and nerol

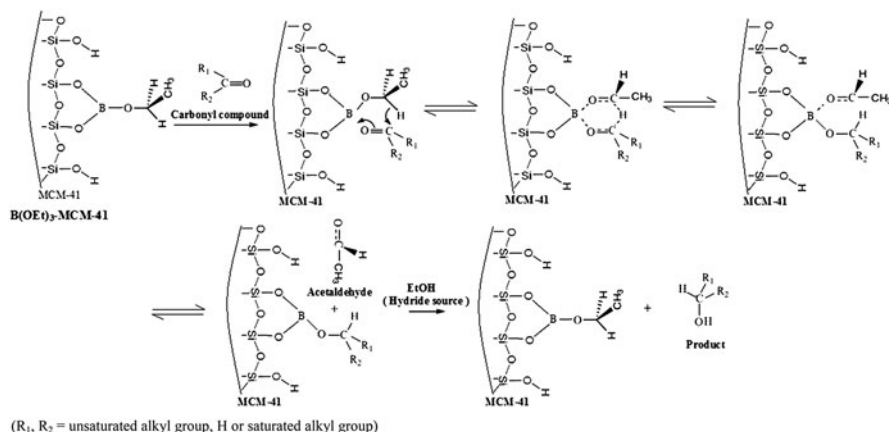
MPV reaction mechanism

The reaction mechanism for the homogeneous MPV reaction involves a cyclic six-membered transition state [56, 57]. Recent studies by Creyghton et al. [19] proposed that, over heterogeneous catalysts like 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. In this regard, the reaction mechanism for the reactions under study can be presumed to be similar to the classical MPV reduction of carbonyls reported for aluminium isopropoxide [56]. Scheme 2 shows the proposed mechanism for the MPV reduction of carbonyl compounds in the presence of $B(OEt)_3$ -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 from the alcohol, which is bound to the boron center as an alkoxide. Since the reduction is reversible, the acetaldehyde was removed from the medium by a slow stream of nitrogen. The removal of the acetaldehyde from the reaction solution leads to the progress of the reaction to the right hand side (see Scheme 2).

Catalytic MPV reduction reactions: comparison of homogeneous and heterogeneous catalysts

The heterogeneous solid supported catalyst offers further advantages like the easy catalysis and product recovery as well as a possible reuse of the catalyst systems. Hence, a mesoporous material, MCM-41, was selected for the grafting of boron alkoxides due to its potential for incorporating higher amounts of heteroatoms in the frame wall positions, as well as due to the presence of higher amounts of silanol groups, for the stabilization of boron tri-ethoxide.

The synthesized boron tri-ethoxide-containing $B(OEt)_3$ -MCM-41 was first applied as catalyst for the MPV reduction reaction of unsaturated aldehydes and



Scheme 2 Proposed mechanism of MPV reduction over $B(OEt)_3$ -MCM-41

ketones. The results showed that the catalyst showed good conversion and indicated that the Lewis acidity is strong enough, and the amount of framework boron is big enough, to proceed the reaction effectively. Hence, B(OEt)₃-grafted mesoporous MCM-41 have potential for application in the MPV reduction of different α,β -unsaturated aldehydes and ketones.

The MPV reduction times for α,β -unsaturated aldehydes and ketones were found to be higher with homogeneous catalysts than heterogeneous. An interesting result was that the selectivity towards the reduced product was $\geq 98\%$ in the presence of the heterogeneous catalyst, showing that the supported boron alkoxide catalyst is highly selective. The resulting improved conversion for the B(OEt)₃-MCM-41 catalyst shows that B(OEt)₃ is grafted as a monolayer over the support surface and the higher concentration of boron helps to increase the number of Lewis acid sites for the conversion of unsaturated aldehydes and ketones [52].

Comparing these results with the Al-beta, Zr-beta, and Sn-beta zeolites, it was inferred that the zeolite catalysts enhance undesired side reactions due to the presence of Lewis and Brønsted acidity, generated after the calcination process [54, 58]. However, the absence of undesired side products, even after 10 h, for the boron alkoxide-grafted mesoporous materials suggests that polarization of carbonyl groups gets enhanced over the Lewis acid sites or Lewis acid sites be the active catalytic sites. Moreover, as pointed out by Anwander et al. [23] the surface confinement effects in mesoporous hosts may prevent the boron alkoxide groups from self-association.

In comparison with homogeneous boron alkoxide catalysts, the structure as well as the pore dimensions added to its particular Lewis acid properties: B(OEt)₃-MCM-41 shows a higher activity and better selectivity. Also, the catalyst can be recycled several times and can be used without important loss in its activities, this being of clear interest for a potential industrial application of the catalyst.

To show catalytic efficiency of boron tri-ethoxide catalysts according to different MPV catalysts, boron tri-ethoxide catalysts was also compared with various MPV catalysts (Table 2). In comparison with the heterogeneous 11Zr-SBA-15 catalyst, for cinnamaldehyde and citral (geranial and neral), heterogeneous and homogeneous boron tri-ethoxide catalysts show higher activity (yield) and similar selectivity [59]. Also, comparing boron tri-ethoxide catalysts with the Zr(O-*n*-Pr)*n*-MCM-41 catalyst, it was found that, in the presence of B(OEt)₃-MCM-41 and homogeneous boron tri-ethoxide catalysts, 2-cyclohexen-1-one, 3-methyl-2-cyclohexen-1-one, 3,5-dimethyl-2-cyclohexen-1-one, α -ionone, and β -ionone were reduced with better chemoselectivity and similar catalytic activity [39]. Furthermore, in the presence of boron tri-ethoxide catalysts, 3-methyl-2-butenal was reduced with similar selectivity and catalytic activity compared with Zr-zeolite beta (Table 2) [36].

Conclusion

In conclusion, we have devised an essentially new boron alkoxide-based heterogeneous B(OEt)₃-MCM-41 catalyst that exerts high catalytic activity with EtOH as a hydride donor in the MPV reduction of various α,β -unsaturated carbonyls, having

importance for fine chemicals and drugs. This is the most reactive boron-based catalyst reported so far, and it has remarkable potential for practical use. Also, the yield and reaction time are highly encouraging. The catalyst is recyclable up to six cycles without any significant loss in catalytic activity.

In comparison with different heterogeneous catalysts, the advantages of ease of separation and reusability added to its particular catalytic activity and selectivity properties, we can say that $B(OEt)_3$ -MCM-41 will be of interest in potential industrial applications using similar types of catalysts.

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