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ORIGINAL ARTICLE

New In(O^{i}Pr)$_3$-MCM-41 heterogeneous catalyst in MPV reductions of unsaturated carbonyl compounds: effect of mesoporous SBA-15 and MCM-41 as supporting surfaces on catalytic activity of In(O^{i}Pr)$_3$

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Abstract Indium tri-isopropoxide, In(O^{i}Pr)$_3$, was immobilized on mesoporous material, MCM-41, and denoted as "In(O^{i}Pr)$_3$-MCM-41". This new heterogeneous catalyst was characterized by XRD, ^{29}Si NMR-, N_2 adsorption–desorption isotherms and ICP-OES techniques. The new heterogeneous catalyst, In(O^{i}Pr)$_3$-MCM-41, was tested for the capable of catalyzed Meerwein–Ponndorf–Verley (MPV) reduction of unsaturated aldehydes and ketones with low catalyst loadings under mild conditions and showed good to excellent catalytic activities. Also, effect of supporting surfaces, both of SBA-15 and MCM-41, on catalytic activity of In(O^{i}Pr)$_3$ were examined. In(O^{i}Pr)$_3$-SBA-15 heterogeneous catalyst in comparison with the In(O^{i}Pr)$_3$-MCM-41 catalyst, display comparatively higher catalytic activity in the MPV reduction of unsaturated aldehydes and ketones. Also, similiar reaction times and selectivities for the unsaturated alcohols were obtained with the In(O^{i}Pr)$_3$-SBA-15 catalyst compared with the In(O^{i}Pr)$_3$-MCM-41 catalyst. The reason for the lower activity observed for MCM-41 sample may be due to smaller pore size of the In(O^{i}Pr)$_3$-MCM-41 catalyst as compared with In(O^{i}Pr)$_3$-SBA-15 catalyst can creat restrict site accessibility for the carbonyl compounds. Eventually, effect of supporting surfaces, SBA-15 and MCM-41, on catalytic activity of In(O^{i}Pr)$_3$ insignificant for MPV reduction of unsaturated carbonyl compounds.

Keywords Mesoporous MCM-41 · Mesoporous SBA-15 · Indium tri-isopropoxide · Unsaturated aldehydes and ketones · Chemoselectivity

Introduction

The 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 [1, 2]. The classical MPV reduction reaction is carried out in the presence of aluminum alkoxides like Al(O^{i}Pr)$_3$ and ^{i}PrOH hydride source which offers many practical advantages like the mild reaction conditions, safe and simple operations and chemo selective nature-that unsaturated aldehydes and ketones are not reduced to saturated alcohols [3]. However, the usage of stoichiometric amount of aluminum alkoxides, need for excess alcohols, low reaction rate due to the poor reactivity of traditional aluminum catalyst, as well as the formation of condensed products limits its wide applicability [4, 5]. In addition to the classical (Al(O^{i}Pr)$_3$) catalyst, catalytic applications of other isopropoxides, such as zirconium(IV) isopropoxide [6, 7], lanthanide isopropoxides [8], and indium isopropoxide [9] in the MPV reaction have been reported. The potential of boron reagents, in particular B(O^{i}Pr)$_3$, in the MPV reduction reactions is also well documented [10–13].

In recent years, MPV reduction of carbonyl compounds to the corresponding alcohols has been one of the standard procedures for the selective reduction of unsaturated

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carbonyls in laboratories and industries [14]. Extensive studies have been carried out to expand the potential of the classical MPV reduction.

Heterogenous catalysts for these reductions are superior to homogenous ones from the viewpoint of cost and are utilized for the industrial scale reduction of carbonyls in many applications [15].

Heterogeneous catalysts for the MPV reactions include Sn-, Ti-, Zr- and Al-beta-zeolites [16–19], grafted alkoxides [20, 21] and metal oxides such as magnesium oxide, zirconia, silica, alumina [22], etc. A major advantage of heterogeneously over homogeneously catalyzed MPV reactions is that the catalysts can easily be separated from the liquid reaction mixture [18, 23]. The heterogenation of the MPV catalysts also offers the advantage of reusability [24].

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 [25, 26]. Since its discovery by Mobile in 1992 [27, 28], MCM-41 and related mesoporous molecular sieves such as SBA-15 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 A° depending on the synthesis conditions, such as temperature, type and size of the templating detergent cations [29].

Among different ordered mesoporous silicas, SBA-type silicas are the most frequently studied [30–32]. SBA-15 silica (SBA = Santa Barbara amorphous) exhibits interesting textural properties, such as large specific surface areas (above 1000 m^2 g^{-1}), uniform-sized pores (in range 4–30 nm), thick framework walls, small crystallite size of primary particles and complementary textural porosity. The advantage of the use of SBA-15 material as support includes also its high surface-to-volume ratio, variable framework compositions and high thermal stability [30–34].

Modification of the MCM-41 and SBA-15 may provide an alternative strategy to obtain suitable supports to maintain high activity in the heteregeneous catalyst system for the reduction of carbonyl compounds. These materials display an open porous structure with pore sizes in the range of mesopores, which facilitates the diffusion of bulk molecules inside the material, minimizing mass transfer hindrances [35].

Several MPV reduction catalysts, such as Al-alkoxides, Zr-alkoxides, Hf and Zr alkyl complexes, as well as Boron-alkoxides have been anchored on MCM-41 or on amorphous SiO_2 in order to generate potential catalytic activity [10, 21, 23, 36–41].

Zirconium alkoxides anchored to silica surfaces, e.g. Zr-SBA-15, have been used as effective catalysts for MPV reactions of unsaturated ketones [42]. Lately, Indium tri-isopropoxide catalyst has been grafted on SBA-15 mesoporous silica, and the catalyst denoted as $In(O^{i}Pr)_3$-SBA-15 [43]. $In(O^{i}Pr)_3$-SBA-15 has been found that active catalyst in the MPV reactions of carbonyl compounds including unsaturated aldehydes and ketones with excellent conversion, selectivity and reusability [43].

In the present study, we reported a new heterogeneous catalyst $In(O^{i}Pr)_3$-MCM-41, characterized its structure, and showed the selective reduction of a variety of unsaturated aldehydes and ketones using heterogenised Indium tri-isopropoxide catalyst.

Heterogeneous MPV catalyst of similar type with different supporting surface has just previously applied to the reduction of unsaturated aldehydes and ketones using heterogenized $In(O^{i}Pr)_3$-SBA-15, and the results have been very encouraging [43]. Also, effect of supporting surfaces, SBA-15, MCM-41, on catalytic activity of $In(O^{i}Pr)_3$ was examined. Up to the present time, there has not been any literature reporting on comparison of the Indium tri-isopropoxide grafted MCM-41 and SBA-15 heterogeneous catalysts for the MVP reduction of unsaturated ketones and aldehydes to unsaturated alcohols.

Experimental

All experiments were carried out under purified dry nitrogen atmosphere by using standard Schlenk techniques. All reagents were purchased from Merck or Sigma–Aldrich and used as received.

Preparation of mesoporous support

Pure siliceous MCM-41 was synthesized following a previously reported procedure [10]. Silica MCM-41 was prepared by dissolving 19.43 g (26.4 mmol) of tetraethylammonium hydroxide (TEAOH, 20%) and 16.16 g (12.6 mmol) cetyltrimethylammonium chloride (CTMACl, 25%) in 20 mL of deionised water with stirring (1000 rpm) until a clear solution was obtained. 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 H_2O were added. The resulting mixture was vigorously stirred (1000 rpm) for another 30 min. The molar composition of the final gel mixture was as follows:

SiO_2:0.3CTMACl:0.2TEAOH:46.3H_2

The mixture was transferred into a Teflon-lined stainless-steel autoclave (BERGHOF BR-200 pressure reactor) and kept at 110 °C under static conditions for 48 h. The obtained solid material was then filtered and washed well with copious amounts of water till filtrate showed a neutral pH and was then air-dried. The surfactant inside the pores of the mesoporous material was removed by calcination at 550 °C for 6 h with a heating ramp of 1 °C/min.

Grafting of indium tri-isopropoxide ($In(O^iPr)_3$) on MCM-41 support

The grafting of indium tri-isopropoxide, $In(O^iPr)_3$, over ordered mesoporous silica support (MCM-41) was carried out by known literature reports [39, 43]. The siliceous MCM-41 supports were calcined and used immediately. Indium tri-isopropoxide grafted MCM-41 materials were prepared by stirring (750 rpm) 2.0 g of the support with a solution of (3 mL; 0.514 mmol) $In(O^iPr)_3$ (as a 5 wt% solution in iso-propanol) in 10 mL dry hexane for 4 h at room temperature. The product was filtered under N_2 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 0.214 mmol In per g final material and is denoted as $In(O^iPr)_3$-MCM-41.

In $(O^iPr)_3$-SBA-15 catalyst were prepared and characterised in Ref. [43].

Typical procedure employed for MPV reactions

The new heterogeneous $In(O^iPr)_3$-MCM-41 catalyst was tested on the MPV reduction of a series of unsaturated aldehydes and ketones. The typical procedure was used as Ref. [37, 39]. Catalytic MPV reduction reaction was carried out as follows:

The reaction mixture containing 30 mmol of the aldehyde or ketone, 200 mmol (12.02 g; 15.4 mL) isopropanol 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 thermostated 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. By this way, the formed acetone was removed by nitrogen flow. Thus the equilibrium reaction was slipped to the right hand. Aliquots were removed at different reaction times and reduction products were analysed 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 lm film thickness) (Palo Alto, CA, USA). The same procedure was used to reduce other a,b-unsaturated aldehydes and ketones in the presence of $In(O^iPr)_3$-SBA-15. To present the results we have used the conversion and selectivity values defined as Ref. [10, 39].

Characterization

Measurement of the surface area, average pore diameter and pore size distribution of MCM-41 support and the prepared heterogeneous catalyst were determined by a Micromeritics Gemini III 2375 Surface Area Analyzer, using nitrogen adsorption at −196 °C. Before measurement, the supported samples were degassed at 300 °C and 0.15 mbar 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 BJH (Barrett–Joyner–Halenda) method.

Powder X-ray diffraction (XRD) was performed to determine the bulk crystalline phases of samples. This was conducted using a X'Pert Pro MPD Diffractometer from PANalytical, with a CuKa1 radiation wavelength 0.154 nm. The spectra were scanned at a rate of 2.4°/min in the range $2\theta = 10–80^o$.

The indium content of the grafted catalyst was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The mesoporous material $In(O^{i}Pr)_3$–MCM-41 was dissolved in a mixture solution of HCl and HF. An aqueous HCl and HF solution containing indium was used as standard reference. ICP-OES was performed using Perkin Elmer Optima 4300DV.

The anchoring of indium tri-isopropoxide species on SBA-15 was followed by ^{29}Si MAS NMR spectroscopy. Solid state ^{29}Si MAS NMR spectra were recorded on a Bruker Advance 400 NMR spectrometer with a resonance frequency of 79.46 MHz for ^{29}Si using a Bruker 4 mm double resonance probe head operating at a spinning rate of 12 kHz for ^{29}Si, respectively. ^{29}Si spectra were collected with 70° rf pulses, 30 s delay and ~6000 scans.

Results and discussion

Structural as well as textural features

XRD patterns of mesoporous MCM-41 silica and indium alkoxide-grafted mesoporous MCM-41 samples are shown in Fig. 1. X-ray diffraction is one of the most important techniques for the characterization of ordered mesoporous materials. MCM-41 and $In(O^iPr)_3$-MCM-41 samples showed three (hkl) reflections of (100), (110) and (200) for

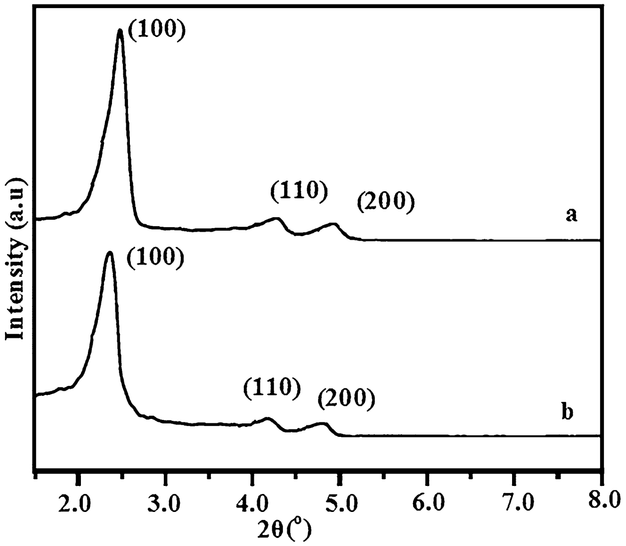


Fig. 1 Low-angle XRD patterns of *a* unmodified MCM-41, *b* In(O^i-Pr)$_3$-MCM-41

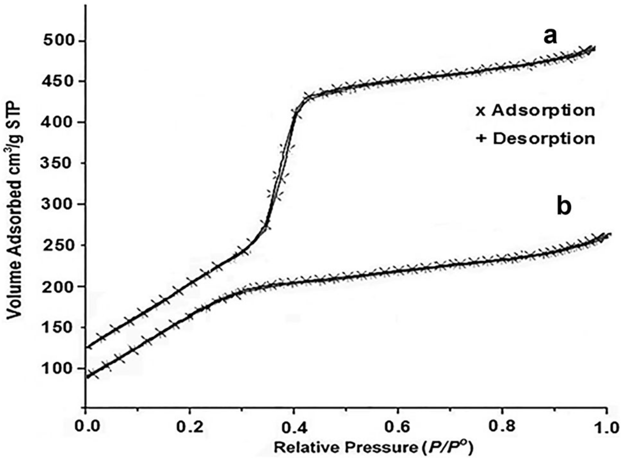


Fig. 2 N_2 adsorption/desorption isotherms of *a* MCM-41 and *b* In(O^{i}Pr)$_3$-MCM-41

a highly ordered hexagonal structure [3]. The highest peak observed for two samples (corresponding to 100 plane) indicates the order of the mesopores, as expected in MCM-41 type ordered mesoporous structure [3]. The presence of characteristic reflections even after grafting of In(O^{i}Pr)$_3$ complexes suggest that the mesoporous materials are ordered with uniform pore arrangements and the grafting process had not damaged the pore structure of the mesoporous materials [3]. After grafting indium tri-isopropoxide, the intensity of the (100) peak decreases which may relate to incorporation of indium isopropoxide complexes in the channel of MCM-41 support. This result indicates that the 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 [44]. In addition, a slight decrease in the peak intensity shows the reduction in the pore size with the grafting of indium tri-isopropoxide [43].

Figure 2 shows the nitrogen adsorption and desorption isotherms at 77 K which provides the indications of the presence of the pore size and structure. The nitrogen adsorption–desorption isotherm of MCM-41 sample exhibits type IV sorption isotherm according to IUPAC classification, which indicates the existence of mesopores in the corresponding material. The N_2 uptake in the range of 0.2–0.4 *P/P*0 indicates capillary condensation in the mesoporous of MCM-41 sample. The sharpness of this step reflects the uniform pore size [45]. Compared to the untreated MCM-41 sample, the sharp capillary condensation step in the case of incorporated MCM-41 samples shifts toward lower *P/P0* region. This suggests that the introduction of In(O^{i}Pr)$_3$ into the channel causes changes in the pore structure of the support during the incorporation process.

The observed changes of the specific surface area and pore volume as well as pore size are shown in Table 1. The BET surface area and pore volume of MCM-41 were 1079 and 0.45 cm^3/g, respectively. These two values for In(O^i-Pr)$_3$-MCM-41 dropped to 846 and 0.19 cm^3/g, due to the introduction of In(O^{i}Pr)$_3$.

ICP-OES analysis showed 2.46 wt% of indium content in the catalyst. To determine indium content, In(O^{i}Pr)$_3$-MCM-41 was dissolved in a mixture solution of HCl and HF. An aqueous HCl and HF solution containing indium was used as standard reference. 0.214 mmol In was found per g of In(O^{i}Pr)$_3$-MCM-41.

^{29}Si MAS NMR spectra of mesoporous MCM-41 and In(O^{i}Pr)$_3$-MCM-41 samples were shown in Fig. 3. ^{29}Si MAS NMR of MCM-41 shows signals with chemical shifts at −93, −100 and −110 ppm resulting from Q^2, Q^3 and Q^4 silicon nuclei, respectively, The 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. Compared to MCM-41, the ^{29}Si NMR spectrum of In(O^{i}Pr)$_3$-MCM-41 shows a marked decrease in the intensity of the Q^3 and Q^2 signals, due to the transformation of Si–OH groups into Si–OC during the incorporation process. The presence of resonance originating from Q^3 Si(OSi)$_3$(OH) and Q^4 Si(OSi)$_4$ in the catalyst indicates that MCM-41 also retains its structure.

Activity of heterogenized In(O^{i}Pr)$_3$-MCM-41 catalyst

To evaluate the catalytic performance of In(O^{i}Pr)$_3$-MCM-41 catalyst, its activity for the MPV reduction of unsaturated aldehydes and ketones was investigated. Unmodified

Table 1 Surface properties of MCM-41 and In(O^{i}Pr)$_3$-MCM-4

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
MCM-41	1079	0.45	2.5
In(O^{i}Pr)$_3$-MCM-41	846	0.19	2.1

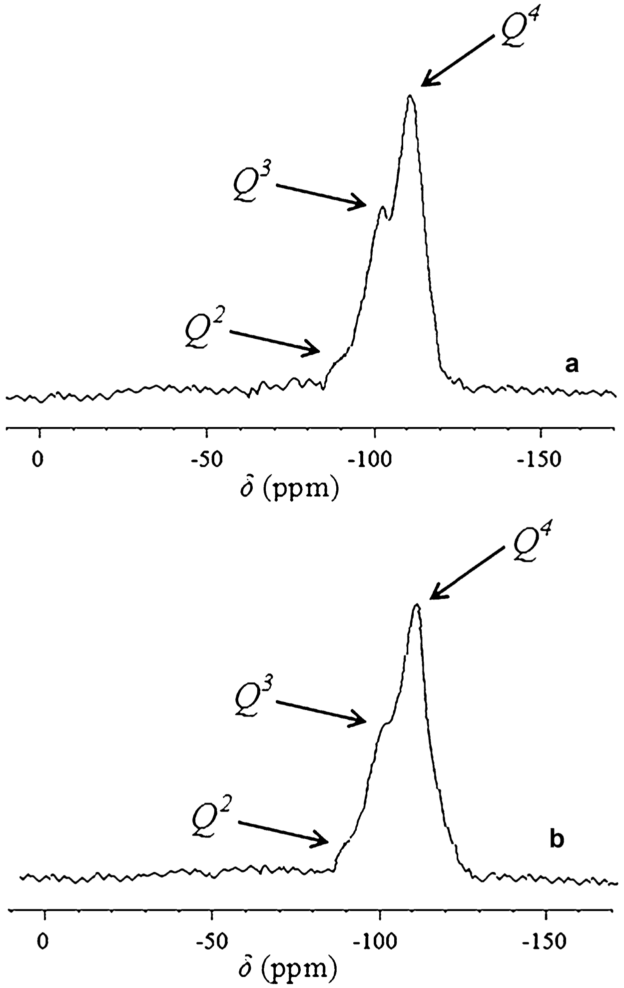


Fig. 3 ^{29}Si solid-state MAS NMR spectra of (*a*) pure MCM-41 and In(O^{i}Pr)$_3$-MCM-41

MCM-41 was not active in the MPV reduction of carbonyl compounds [39]. However, once indium tri-isopropoxide was grafted onto MCM-41, the heterogenised material showed good activity (Table 2).

In Table 2 are summarized the results of the catalytic MPV reduction of several unsaturated carbonyls in the presence of heterogeneous In(O^{i}Pr)$_3$-MCM-41 catalyst. Good catalytic activity and selectivity to the reduced unsaturated alcohols, citronellol, cinnamalcohol, α-ionol, 3-methyl-2-butanol, geraniol, nerol were observed over indium tri-isopropoxide supported on silica. Herein we wish to report that the MVP reaction can be effectively catalysed by In(O^{i}Pr)$_3$-MCM-41 catalyst to very good yields using unsaturated aldehydes and ketones and isopropanol as the solvent and the reducing agent (Table 2).

As can be seen in Table 2, unsaturated aldehydes and ketones were reduced to the corresponding *unsaturated alcohols.* No other reduction products were detected, showing the high selectivity of the reaction.

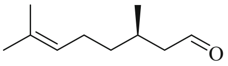
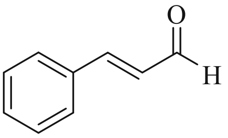
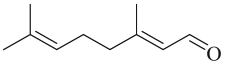
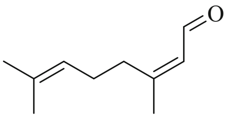
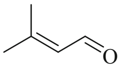
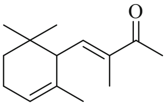
The reaction mechanism for the homogeneous MPV reaction involves a cyclic six membered transition state [12, 46]. Recent studies by Creyghton et al. [18] proposed that, over heterogeneous catalysts like zeolite beta, the MPV mechanism also involves a six-membered transition state where both the alcohol and the ketone coordinate to the same Lewis acid site. Also, in our previous studies, we proposed that, over grafted alkoxides on SBA-15 and MCM-41, the MPV reduction mechanism of unsaturated carbonyls involves a cyclic six membered transition state [39, 43] In this regard, the reaction mechanism for MPV reduction of unstaurated aldehydes and ketones with In(O^{i}Pr)$_3$-MCM-41 catalyst can be presumed to be similar to the classical MPV reduction of carbonyls reported for aluminium isopropoxide [46]. Scheme 1 shows the proposed mechanism for the MPV reduction of carbonyl compounds in the presence of In(O^{i}Pr)$_3$-MCM-41. First, the carbonyl compound is coordinated to the indium of the indium alkoxide. The reaction proceeds by hydride-transfer to the carbonyl compound from the alcohol, which is bound to the indium centre as an alkoxide. Since the reduction is reversible, the acetone was removed from the medium by a slow stream of nitrogen. The removal of the acetone from the reaction solution leads to the progress of the reaction to the right hand side (see Scheme 1).

Comparison of heterogenized In(O^{i}Pr)$_3$-MCM-41 and In(O^{i}Pr)$_3$-SBA-15 catalysts: effect of mesoporous support surface

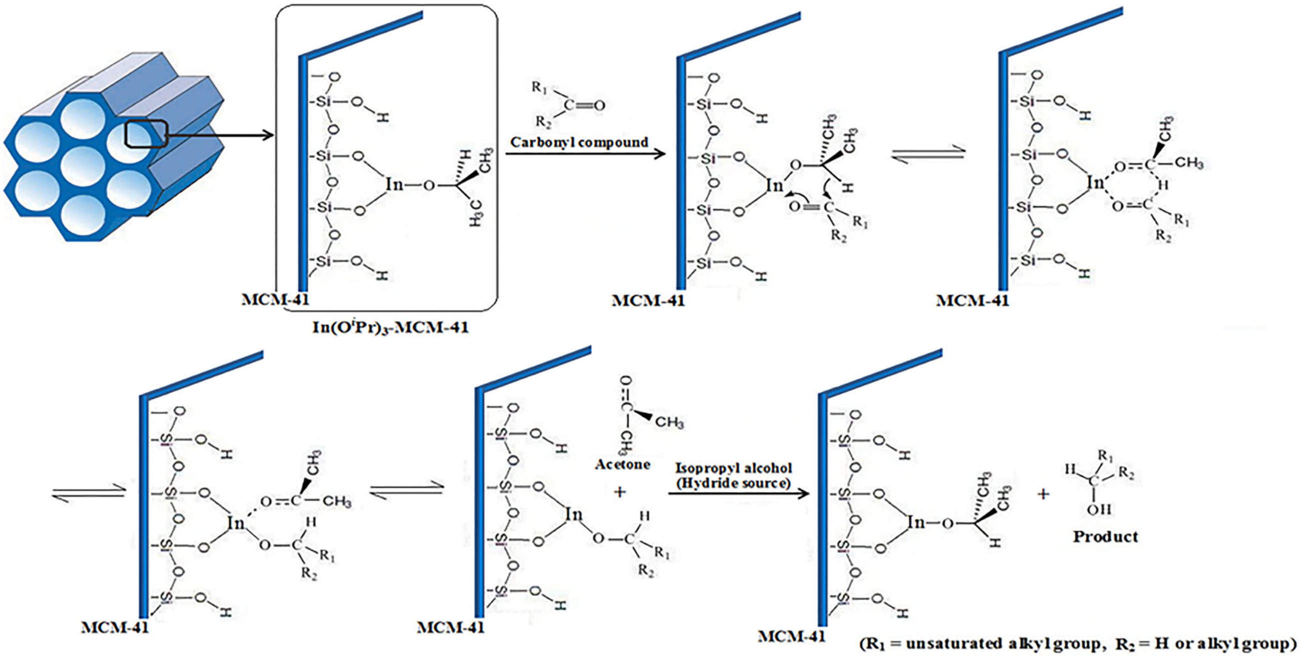
The surface properties and catalytic activity differences of indium-containing mesoporous catalysts prepared by grafting method were compared in the MPV reduction of carbonyl compounds. In(O^{i}Pr)$_3$-SBA-15 heterogeneous catalyst was previously reported by us [43] while the preparation and characterisation of In(O^{i}Pr)$_3$-MCM-41 is described in this work. We have previously reported that In(O^{i}Pr)$_3$-SBA-15 showed excellent catalytic activity and chemoselectivity for MPV reduction [43].

In(O^{i}Pr)$_3$-MCM-41 heterogeneous catalyst was tested in the MPV reduction of the same unsaturated aldehydes and

Table 2 MPV reduction of various unsaturated aldehydes and ketones in the presence of heterogenized In(O^{i}Pr)$_3$-MCM-41 and In(O^{i}Pr)$_3$-SBA-15 catalysts: selected substrats, reduction times, product alcohol yields and selectivity

Substrate	In(O^{i}Pr)$_3$-MCM-41			In(O^{i}Pr)$_3$-SBA-15 [42]		
	t (h)	Yield (%)	Chemo selectivity	t (h)	Yield (%)	Chemo selectivity
 Citronellal	8	76.4	100	8	80.2	100
 Cinnamaldehyde	9	81.5	100	9	83.9	100
 Citral A (geranial)	7	87.2	98[a]	7	89.4	98[a]
 Citral B (neral)	7	85.4	98[a]	7	87.6	98[a]
 3-methyl-crotonaldehyde	7	88.7	99[a]	7	89.6	98[a]
 α–ionone	8	83.4	98[a]	8	85.8	97[a]

[a] Chemoselectivity to allylic. *Alcohol reaction conditions* 30 mmol of substrate, 200 mmol 2-propanol, 500 mg catalyst, under reflux and stirring at 80 °C



Scheme 1 In(O^{i}Pr)$_3$-MCM-41 catalysed MPV reduction of carbonyl compounds

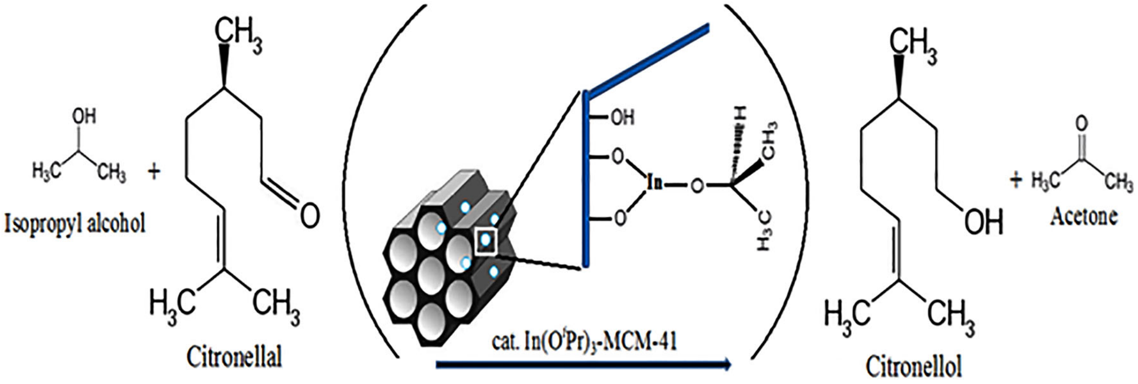
ketones. For comparison, In(O^{i}Pr)$_3$-MCM-41 was prepared using same amount of indium tri-isopropoxide as used in In(O^{i}Pr)$_3$-SBA-15. The amount of indium-grafted over different support samples was determined by the ICP-OES analysis. The percentage loading of indium was found to be almost similar over two periodic mesoporous silica materials, SBA-15 and MCM-41. ICP-OES analysis showed 2.46 wt% of indium content in the In(O^{i}Pr)$_3$-MCM-41 catalyst. Between them, In(O^{i}Pr)$_3$-SBA-15 shows the highest amount of indium grafting revealing a greater percentage of silanol groups for the stabilization of indium species. 2.72 wt% of indium content was found in the In(O^{i}Pr)$_3$–SBA-15 catalyst [43]. This result shows that the number of silanol groups available for grafting is different for the silicas thus the unstabilized indium species in silica samples get washed out during the filtration steps. Thus the low percentage of indium observed for the In(O^{i}Pr)$_3$-MCM-41 sample relate to the limited accessibility of the surface hydroxyl groups for the In(O^{i}Pr)$_3$ species or due to the different surface properties between the two classes of mesoporous solid materials.

The studied carbonyl compounds, the yields of the reduction product, selectivity and reaction times in the presence of heterogeneous catalysts are summarized in Table 2. Here, in the presence of In(O^{i}Pr)$_3$-MCM-41 catalyst, the yield of citronellol was 76.4% after 8 h. The yield of citronellol over the supported In(O^{i}Pr)$_3$-SBA-15 catalyst was slightly higher: the yield reached 80.2% in the same time [43]. In the conversions of citronellal, the isolated double bond was left intact and citronellol was obtained (Scheme 2). 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 [3]. Selective hydrogenation of unsaturated aldehydes and ketones to their corresponding unsaturated alcohols is highly desirable due to the corresponding unsaturated alcohols being useful as intermediates, pharmaceuticals, and as flavor chemicals [3]. In this instance, the selective MPV reduction of the C=O bond using MPV catalysts will be a promising process for produce unsaturated alcohols.

The reduction product, citronellol, is an acyclic monoterpenoid and an alcohol. Citronellol is used in perfumes and as insect repellents [47]. Citronellol is a good mosquito repellent at short distances, but protection greatly lessens when the subject is slightly further from the source [48]. When complexed with β-cyclodextrin, it has on average a 1.5 h protection duration against mosquitoes [49]. Citronellol is used as a raw material for the production of rose oxide. Citronellol also has been suggested to help cure cancer. Song et al. [50] demonstrated in his study "Citronellol terpenoid inhibits cancer cell proliferation and induces apoptosis in Non-Small Cell Lung Carcinoma".

As can be seen from Table 2, two heterogeneous catalyst selectively reduces the carbonyl functions without affecting the olefinic bonds. Conversion yield of unsaturated aldehydes and ketones to corresponding unsaturated alcohols range from 76.4 to 88.7% within 7–9 h of reaction time with In(O^{i}Pr)$_3$-MCM-41. Also, conversion yield of same unsaturated carbonyls to corresponding unsaturated alcohols range from 80.2 to 89.6% within 7–9 h of reaction time with In(O^{i}Pr)$_3$-SBA-15 [43]. In comparison with the In(O^{i}Pr)$_3$-MCM-41 catalyst, the In(O^{i}Pr)$_3$-SBA-15 heterogeneous catalyst shows slightly higher unsaturated alcohol yield after the same time. The reason for the lower activity observed for MCM-41 sample may be due to the presence of smaller pore volume and pore diameter than SBA-15 sample (Table 3). The indium isopropoxide-grafted may block these pores and had limited access for the substrate molecules for the formation of transition state species.

As shown in Table 2, two heterogeneous catalysts exhibited excellent chemoselectivity towards unsaturated alcohols. It was found that, for MPV reduction of unsaturated aldehydes and ketones, In(O^{i}Pr)$_3$-MCM-41 has a similiar activity with In(O^{i}Pr)$_3$-SBA-15 catalyst. These results show that the structural features of the support materials, SBA-15, MCM-41, slightly affect the catalytic



Scheme 2 MPV reduction of citronellal to citronellol using In(O^{i}Pr)$_3$-MCM-41 catalyst

Table 3 Comparison of surface properties of MCM-41, In(O^{i}Pr)$_3$-MCM-41, SBA-15 and In(O^{i}Pr)$_3$-SBA-15 [43]

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
MCM-41	1079	0.45	2.5
SBA-15	879	1.24	7.8 [43]
In(O^{i}Pr)$_3$-MCM-41	846	0.19	2.1
In(O^{i}Pr)$_3$-SBA-15	548	0.68	6.6 [43]

activity of the indium catalyst that the In(O^{i}Pr)$_3$-SBA-15 shows slightly higher activity than In(O^{i}Pr)$_3$-MCM-41. High surface area mesoporous materials like MCM-41, SBA-15 provide a useful support for the heterogenisation of indium tri-isopropoxide. These support materials, MCM-41 and SBA-15, with the hexagonal pore structure, probably favor easy access of the reactants to the In centers, and thus facilitate the MPV reduction reaction.

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 Bronsted acidity, generated after the calcination process [48, 51]. However, the absence of undesired side products even after 9 h, for the indium alkoxide-grafted mesoporous materials suggest that polarisation of carbonyl groups gets enhanced over the Lewis acid sites or Lewis acid sites be the active catalytic sites. Following this, it appears that the activity and selectivity of MPV catalysts can be improved by introducing the adequate Lewis acid sites in the mesoporous surface that can produce the right polarization of the carbonyl group [52]. Moreover, as pointed out by Anwander et al., the surface confinements effects in mesoporous hosts may prevents the indium alkoxide groups from self-association [21].

Conclusion

The new prepared In(O^{i}Pr)$_3$-MCM-41 catalyst was found as an efficient catalyst for the MPV reductions of carbonyl groups. The structure as well as pore dimensions added to its particular Lewis acid properties allows excellent conversion and selectivity to the corresponding alcohol product. Since the pores in MCM-type materials allow access of even large molecules, complex substrates such as the citronellal, cinnamaldehyde, geranial, neral, 3-methyl-crotonaldehyde and α-ionone could be reduced with good yields. In most cases, there were no side products other than the desired alcohol. The slightly higher activity (yield), similiar reduction time and selectivity is shown by In(O^{i}Pr)$_3$-SBA-15 catalyst compared with the In(O^{i}Pr)$_3$-MCM-41. The reason for the lower activity observed for MCM-41 sample may be due to smaller pore size of the supported In(O^{i}Pr)$_3$-MCM-41 catalyst as compared with In(O^{i}Pr)$_3$-SBA-15 catalyst can creat restrict site accessibility for the carbonyl compounds. Both of the heterogeneous indium alkoxide catalysts facilitate the chemoselective reduction of a variety of unsaturated ketones and aldehydes to unsaturated alcohols. Hence, In(O^{i}Pr)$_3$-MCM-41 and In(O^{i}Pr)$_3$-SBA-15 have great potential for applying in the MPV reduction of different unsaturated aldehydes and ketones.

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References

1. Minambres, J.F., Aramendia, M.A., Marinas, A., Marinas, J.M., Urbano, F.J.: Liquid and gas-phase Meerwein–Ponndorf–Verley reduction of crotonaldehyde on ZrO_2 catalysts modified with Al_2O_3, Ga_2O_3 and In_2O_3. J. Mol. Catal. A **338**, 121–129 (2011)
2. Urbano, F.J., Aramendía, M.A., Marinas, A., Marinas, J.M.: An insight into the Meerwein–Ponndorf–Verley reduction of alpha, beta-unsaturated carbonyl compounds: tuning the acid-base properties of modified zirconia catalysts. J. Catal. **268**, 79–88 (2009)
3. Shylesha, S., Mahendra, P.K., Lekh, R.J., Prinson, P.S., Srilakshmic, Ch., Singha, A.P.: Catalytic Meerwein–Ponndorf–Verley reductions over mesoporous silica supports: rational design of hydrophobic mesoporous silica for enhanced stability of aluminum doped mesoporous catalysts. J. Mol. Catal. A **301**, 118–126 (2009)
4. Ooi, T., Miura, T., Itagaki, Y., Ichikawa, H., Maruoka, K.: Catalytic Meerwein–Ponndorf–Verley (MPV) and Oppenauer (OPP) reactions: remarkable acceleration of the hydride transfer by powerful bidentate aluminum alkoxides. Synthesis **18**, 279–291 (2002)
5. Akamanchi, K.G., Varalakshmy, N.R.: Aluminium isopropoxide—TFA, a modified catalyst for highly accelerated meerwein–ponndorf–verley (MPV) reduction. Tetrahedron Lett. **36**, 3571–3572 (1995)
6. Ishii, Y., Nakano, T., Inada, A., Kishigami, Y., Sakurai, K., Ogawa, M.: Meerwein–Ponndorf–Verley type reduction of ketones and Oppenauer type oxidation of alcohols under the influence of bis(cyclopentadienyl)zirconium dihydride. J. Org. Chem. **51**, 240–242 (1986)
7. Knauer, B., Krohn, K.: A reinvestigation of the Meerwein–Ponndorf–Verley reduction a highly efficient variation using zirconium catalysts. Liebigs Ann. **4**, 677–683 (1995)
8. Namy, J.L., Souppe, J., Collin, J., Kagan, H.B.: New preparations of lanthanide alkoxides and their catalytical activity in Meerwein–Ponndorf–Verley–Oppenauer reactions. J. Org. Chem. **49**, 2045–2049 (1984)
9. Lee, J., Ryu, T., Park, S., Lee, P.H.: Indium Tri(isopropoxide)-catalyzed selective Meerwein–Ponndorf–Verley reduction of

aliphatic and aromatic aldehydes. J. Org. Chem. **77**, 4821–4825 (2012)

10. Uysal, B., Oksal, B.S.: Comparison of heterogeneous $B(O^iPr)_3$-MCM-41 and homogeneous $B(O^iPr)_3$, $B(OEt)_3$ catalysts for chemoselective MPV reductions of unsaturated aldehydes and ketones. Appl. Catal. A **435–436**, 204–216 (2012)
11. Uysal, B., Oksal, B.S.: A new method for the chemoselective reduction of aldehydes and ketones using boron tri-isopropoxide, $B(O^iPr)_3$: Comparison with boron tri-ethoxide, $B(OEt)_3$. J. Chem. Sci. **123**, 681–685 (2011)
12. Uysal, B., Buyuktas, B.S.: Kinetics of catalytic Meerwein–Ponndorf–Verley reduction of aldehydes and ketones using boron triethoxide. Chem Pap. **64**, 123–126 (2010)
13. Uysal, B., Buyuktas, B.S.: Chemoselective reduction of aldehydes and ketones to alcohols using boron tri-isopropoxide, B(O-i-Pr)$_3$ and boron tri-secondary butoxide, B(O-s-Bu)$_3$ as catalysts. Arkıvoc **14**, 134–140 (2007)
14. Mojtahedi, M.M., Akbarzadeh, E., Sharifi, R., Abaee, M.S.: Lithium bromide as a flexible, mild, and recyclable reagent for solvent-free cannizzaro, tishchenko, and meerwein–ponndorf–verley reactions. Org. Lett. **9**, 2791–2793 (2007)
15. Nishimura, S.: Handbook of heterogeneous catalytic hydrogenation for organic synthesis. Wiley, New York (2001)
16. Corma, A., Domine, M.E., Valencia, S.: Water-resistant solid Lewis acid catalysts: Meerwein–Ponndorf–Verley and oppenauer reactions catalyzed by tin-beta zeolite. J. Catal. **215**, 294–304 (2003)
17. Boronat, M., Corma, A., Renz, M.: Mechanism of the Meerwein–Ponndorf–Verley–Oppenauer (MPVO) redox equilibrium on Sn^- and Zr^- beta zeolite catalysts. J. Phys. Chem. B **110**, 21168–21174 (2006)
18. Creyghton, E.J., Ganeshie, S.D., Downing, R.S., Van Bekkum, H.: Stereoselective Meerwein–Ponndorf–Verley and Oppenauer reactions catalysed by zeolite BEA. J. Mol. Catalysis A **115**, 457–472 (1997)
19. Kunkeler, P.J., Zuurdeeg, B.J., van der Waal, J.C., van Bokhoven, J.A., Koningsberger, D.C., Van Bekkum, H.: Zeolite beta: the relationship between calcination procedure, aluminum configuration, and Lewis acidity. J. Catl **180**, 234–244 (1998)
20. Anwander, R., Palm, C.: Meerwein–Ponndorf–Verley reductions mediated by lanthanide-alkoxide-functionalized mesoporous silicates. Stud. Surf. Sci. Catal. **117**, 413–420 (1999)
21. Anwander, R., Palm, C., Gerstberger, G., Groeger, O., Engelhardt, G.: Enhanced catalytic activity of MCM-41-grafted aluminium isopropoxide in MPV reductions. Chem. Commun. **17**, 1811–1812 (1998)
22. Ivanov, V.A., Bachelier, J., Audry, F., Lavalley, J.C.: Study of the Meerwein—Pondorff—Verley reaction between ethanol and acetone on various metal oxides. J. Mol. Catal. **91**, 45–59 (1994)
23. Leyrit, P., Mc Gill, C., Quignard, F., Choplin, A.: A novel heterogeneous molecular catalyst for the Meerwein–Ponndorf–Verley and Oppenauer reactions. J. Mol. Catal. A **112**, 395–400 (1996)
24. Van der Waal, J.C., Creyghton, E.J., Kunkeler, P.J., Tan, K., Van Bekkum, H.: Beta–type zeolites as selective and regenerable catalysts in the Meerwein–Ponndorf–Verley reduction of carbonyl compounds. Top. Catal. **4**, 261–268 (1998)
25. Anwander, R., Runte, O., Eppinger, J., Gerstberger, G., Herdtweck, E., Spiegler, M.: Synthesis and structural characterisation of rare-earth bis(dimethylsilyl)amides and their surface organometallic chemistry on mesoporous MCM-41. J. Chem. Soc. pp. 847–858 (1998)
26. O'Brien, S., Tudor, J., Barlow, S., Drewitt, M.J., Heyes, S.J., O'Hare, D.: Modification of MCM41 via ring opening of a strained [1] ferrocenophane. Chem. Commun. **6**, 641–642 (1997)
27. Kresege, C.T., Leonowicz, M.E., Roth, W.J., Vartadi, J.C., Beck, J.S.: Ordered mesoporous molecular sieves sythesized by a liquid-crystal template mechanism. Nature **359**, 710–712 (1992)
28. Beck, J.S., Vartuli, J.C., Roth, W.J., Leonowicz, M.E., Kresege, C.T., Schmitt, K.D., Chu, C.T., Olson, D.H., Sheppard, E.W., Mccullen, S.B., Higgius, J.B., Schlenker, J.L.: A new family of mesoporous molecular sieves prepared with liquid crystal templates. J. Am. Chem. Soc. **114**, 10834–10843 (1992)
29. Oberhagemann, U., Jeschke, M., Papp, H.: Synthesis of highly ordered boron-containing B-MCM-41 and pure silica MCM-41. Microporous Mesoporous Mater. **33**, 165–172 (1999)
30. Stevens, W.J.J., Lebeau, K., Mertens, M., van Tendeloo, G., Cool, P., Vansant, E.F.: Investigation of the morphology of the mesoporous SBA-16 and SBA-15 materials. J. Phys. Chem. B **110**, 9183–9187 (2006)
31. Taguchi, A., Schuth, F.: Ordered mesoporous materials in catalysis. Microporous Mesoporous Mater. **77**, 1–45 (2005)
32. Corma, A.: From microporous to mesoporous molecular sieve materials and their use in catalysis. Chem. Rev. **97**, 2373–2419 (1997)
33. Zhang, F., Yan, Y., Yang, H., Meng, Y., Yu, C., Tu, B., Zhao, D.: Understanding effect of wall structure on the hydrothermal stability of mesostructured silica SBA-15. J. Phys. Chem. B **109**, 8723–8732 (2005)
34. Rahmat, N., Zuhairi, A.A., Rahman Mohamed, A.: A review: mesoporous santa barbara amorphous-15, types, synthesis and its applications towards biorefinery production. Am. J. Appl. Sci. **7**, 1579–1586 (2010)
35. Iglesias, J., Melero, J.A., Morales, G., Moreno, J., Segura, Y., Paniagua, M., Cambra, A., Hernández, B.: Zr-SBA-15 lewis acid catalyst: activity in Meerwein–Ponndorf–Verley reduction. Catalysts **5**, 1911–1927 (2015)
36. Bruyn, M.D., De Vos, D.E., Jacobs, P.A.: Chemoselective hydrogen transfer reduction of unsaturated ketones to allylic alcohols with Solid Zr and Hf catalysts. Adv. Synth. Catal. **344**, 1120–1125 (2002)
37. Uysal, B., Aksu, Y., Oksal, B.S.: Chemoselective reduction of α, β-unsaturated aldehydes and ketones over mesoporous $B(O^iPr)3$–MCM-41 catalyst via MPV reduction process: preparation, characterization and catalytic application. J. Porous Mater. **20**, 115–127 (2013)
38. Uysal, B.: Activity of $B(OEt)_3$-MCM-41 catalyst in the MPV reduction of crotonaldehyde. J. Chem. Sci. **125**, 1385–1393 (2013)
39. Uysal, B., Oksal, B.S.: New heterogeneous $B(OEt)_3$-MCM-41 catalyst for preparation of α, β-unsaturated alcohols. Res. Chem. Intermed. **41**, 3893–3911 (2015)
40. Quignard, F., Graziani, O., Choplin, A.: Group 4 alkyl complexes as precursors of silica anchored molecular catalysts for the reduction of ketones by hydrogen transfer. Appl. Catal. A **182**, 29–40 (1999)
41. Inada, K., Shibagaki, M., Nakanishi, Y., Matsushita, H.: The catalytic reduction of aldehydes and ketones with 2-propanol oversilica-supported zirconium catalyst. Chem. Lett. **22**, 1795–1798 (1993)
42. Zhu, Y., Jaenicke, S., Chuah, G.K.: Supported zirconium propoxide—a versatile heterogeneous catalyst for the Meerwein–Ponndorf–Verley reduction. J. Catal. **218**, 396–404 (2003)
43. Uysal, B., Oksal, B.S.: Catalytic activity of SBA-15-grafted indium tri-isopropoxide in chemoselective MPV reductions. J. Porous Mater. **22**, 1053–1064 (2015)
44. Kinski, I., Gies, H., Marlow, F.: Ordered and disordered pNA molecules in mesoporous MCM-41. Zeolite **19**, 375–381 (1997)
45. Xu, J., Luan, Z., He, H., Zhou, W., Kevan, L.: A reliable synthesis of cubic mesoporous MCM-48 molecular sieve. Chem. Mater. **10**, 3690–3698 (1998)

46. De Graauw, C.F., Peters, J.A., van Bekkum, H., Huskens, J.: Meerwein–Ponndorf–Verley reductions and oppenauer oxidations: an integrated approach. Synthesis **10**, 1007–1017 (1994)
47. Taylor, W.G., Schreck, C.E.: Chiral-phase capillary gas chromatography and mosquito repellent activity of some oxazolidine derivatives of (+)− and (−)−citronellol. J. Pharm. Sci. **74**, 534–539 (1985)
48. Revay, E.E., Kline, D.L., Xue, R.D., Qualls, W.A., Bernier, U.R., Kravchenko, V.D., Ghattas, N., Pstygo, I., Müller, G.C.: Reduction of mosquito biting-pressure: Spatial repellents or mosquito traps? A field comparison of seven commercially available products in Israel. Acta Trop. **127**, 63–68 (2013)
49. Songkro, S., Hayook, N., Jaisawang, J., Maneenuan, D., Chuchome, T., Kaewnopparat, N.: Investigation of inclusion complexes of citronella oil, citronellal and citronellol with [beta]-cyclodextrin for mosquito repellent. J. Incl. Phenom. Macrocycl. Chem. **72**, 339–355 (2011)
50. Song, W., Liu, X.H., Shi, Y.: Citronellol terpenoid inhibits cancer cell proliferation and induces apoptosis in non-small cell lung carcinoma. Lat. Am. J. Pharm. **34**, 1652–1657 (2015)
51. Lopez, J., Valente, J.S., Clacens, J.M., Figueras, F.: Hydrogen transfer reduction of 4-tert-butylcyclohexanone and aldol condensation of benzaldehyde with acetophenone on basic solids. J. Catal. **208**, 30–37 (2002)
52. Samuel, P.P., Shylesh, S., Singh, A.P.: Catalytic properties of tin-containing mesoporous molecular sieves in the selective reduction of carbonyl compounds (Meerwein–Ponndorf–Verley (MPV) reaction). J. Mol. Catal. A **266**, 11–20 (2007)