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Facile and Highly Selective Deprotection of Aryl Propionates/Acetates Using a Supported Lewis Acid Catalyst (20% $InCl_3$/MCM-41)

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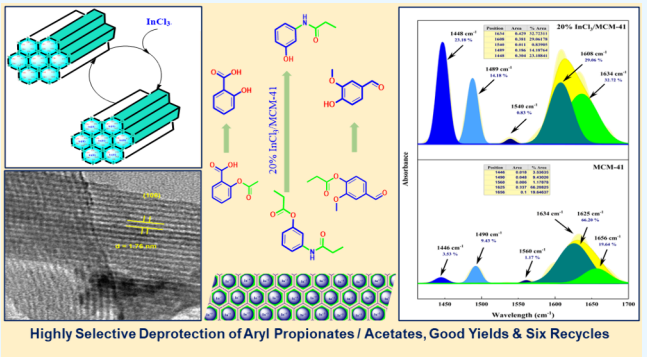
ABSTRACT: The selective deprotection of substituted aryl esters like acetates and propionates in the presence of different electron-donating and -withdrawing functional groups to the corresponding phenols in good yields was reported using the Lewis acid supported solid acid catalyst 20% $InCl_3$/MCM-41 prepared by the wet impregnation method. The textural and microscopic properties of the catalyst were studied, which revealed a high degree of dispersion of $InCl_3$ over MCM-41, promising quantification of Lewis acidity, and well-ordered honeycomb structure. The methodology was further explored for the selective deprotection of acetates and propionates in the presence of substituted amides that remain unaltered. Reusability studies revealed the robust nature of the catalyst without losing the catalytic activity for up to six recycles corroborated with hot leaching test studies monitored by ICP-AES analysis, which was further authenticated with XPS studies of the catalyst before and after the reaction.



INTRODUCTION

The protection and deprotection of different functional groups are basic important strategies in synthetic organic chemistry. In designing medicinally important large organic molecules in the presence of various functional groups (Figure 1),[1−3] the selective deprotection in the presence of targeted active functional groups is the key for the organic synthesis.[4] Phenolic group protection was achieved using different protecting groups to yield different esters such as acetates, propionates, benzoates, sulfonates, pivalate ethers, etc.[5] Among these reported methods in the literature, the protection and deprotection of hydroxyl (−OH), phenolic (−OH), and substituted amide (−NHCOR) groups by acetylation/propylation is widely used in organic synthesis.[6]

Testified methods for the deprotection of aryl acetates involve treatment with borohydride-exchanged resin,[7] Al_2O_3/μw,[8] metal complexes,[9] BBTO,[10] metalloenzymes,[11] enzymes,[12] antibodies,[13] cyclodextrin,[14] micelle-catalyzed saponification,[15] 1,1,3,3-tetramethylguanidine as a nitrogen organic base,[16] sodium perborate,[17] lipase catalysis for selective deprotection,[18,19] and use of organocatalytic protocols.[20] Similarly, Chakraborti et al. reported a mild and nonhydrolytic condition using KF/NMP,[21] diphenyl disulfide and sodium in NMP,[22] and catalytic PhSH-KF in *n*-methyl-2-pyrrolidone[23] as an efficient protocol for the cleavage of aryl esters. Deprotection of aryl benzoates is executed using acids and bases.[4] Nevertheless, these reported methods have certain limitations of using costly reagents, harsh reaction conditions, and exhibiting a limited scope for multifunctional substrates as well as for selectivity.

As studied, the use of a Lewis acid for carbon−carbon bond formation is a preeminent process in organic synthesis.[24] Fries rearrangement of substituted aryl acetates catalyzed by Lewis acids such as $AlCl_3$,[25] $FeCl_3$,[26] $ZnCl_2$,[27] and $TiCl_4$[28] or strong Brønsted acids like trifluoromethanesulfonic acid[29] and methanesulfonic acid[30] produced ortho and para substituted hydroxy phenols. Lewis acids are also extensively employed for reactions like the Diels−Alder reaction,[31] Ene reaction,[32] Friedel−Crafts reactions,[33] Mukaiyama aldol synthesis,[34] and other organic transformations.[35]

Lewis or Brønsted acids impregnated on different mesoporous supports like MCM-41, HMS, SBA-15, and MMT[36,37] have been explored for different applications in organic transformation,[38] biomass conversion,[39] and biodiesel production[40,41] and similarly for dye degradations and wastewater treatment as a remedial solution.[42]

From the above-mentioned literature survey, it was observed that very few methods were reported for the deprotection of the aryl acetates/propionates using the supported solid acid

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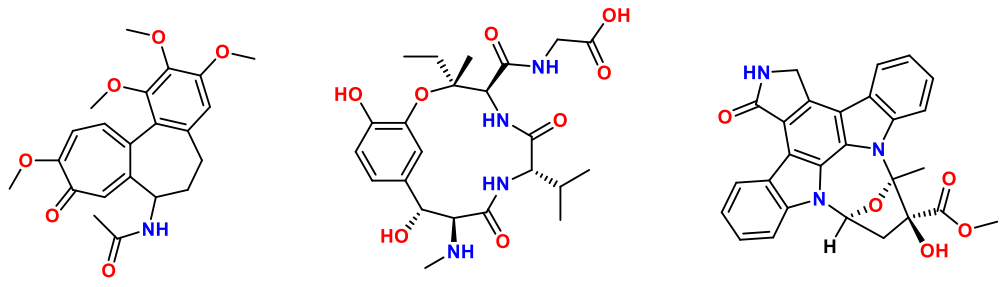

Figure 1. Medicinally important molecules synthesized using the protection and deprotection of aryl esters.

Table 1. Comparison of the Present Work with the Previously Reported Literature for the Deprotection of Aryl Acetates/Aryl Propionates

sr. no.	reagent/reaction condition	reaction time	yield	ref.
1	$NaHCO_3$/aq. MeOH 25 °C or ammonium acetate or $NaBO_3$	0.75 h	94%	4
2	activated Zn-MeOH		91%	4
3	TsOH, SiO_2, toluene, H_2O, 80 °C	6−40 h	79−100%	4
4	$NaBH_4$, $HO(CH_2)_2OH$, or $LiBH_4$, 40 °C	18 h	87%	4
5	borohydride-exchanged resin in MeOH	12 h	92%	7
6	Al_2O_3/μw-850W	0.4−50 h	85%	8
7	Bi(III)-mandelates under oxygen, 1 atm, DMSO, 95 °C	24 h	96%	9
8	*bis*(tributyltin) oxide, toluene, reflux, 110 °C	24 h	63%	10
9	1,1,3,3-tetramethylguanidine, acetonitrile, 50 °C	1 h	81−92%	16
10	sodium perborate, MeOH, 25 °C	30 min	80−94%	17
11	cyanuric chloride activated dimethyl sulfoxide,	10−12 h	87−99%	20
12	K_2CO_3 in NMP at 100 °C	3 h	62−92%	21
13	diphenyl disulfide and sodium in NMP at 90 °C	30 min	80−100%	22
14	catalytic PhSH-KF in *n*-methyl-2-pyrrolidone, 100 °C	60 min	80−90%	23
15	20% $InCl_3$/MCM-41	6−8 h	62−86%	present work

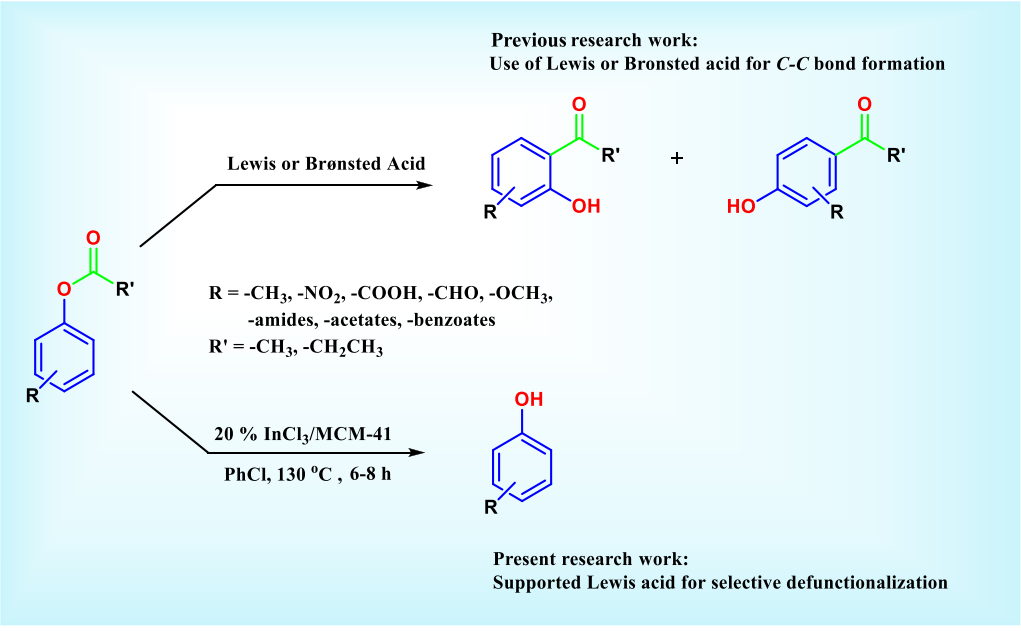

Figure 2. Previous and present research work using a Lewis acid catalyst.

catalysts (Table 1). The effectiveness of $InCl_3$ as a Lewis acid catalyst has gained much attention due to its compatibility, moderate acidity, and stability in a wide range of solvents.[43]

Indium(III) salts are often stable toward moisture and air,[44,45] allowing for reactions to be carried out under a standard atmosphere and, in some cases, water as the solvent. Indium(III) catalysts are associated with a relatively low acute toxicity[45−47] and have been shown to be recyclable.[48−51] The low oxo- and azaphilicity of In(III) lead to a high functional group tolerance of In(III)-catalyzed reactions. Compared to

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conventional Lewis acids, $InCl_3$ has some advantages including water stability, recyclability, operational simplicity, and a strong tolerance to oxygen and nitrogen containing substrates and functional groups.[52] $InCl_3$ has emerged as a useful Lewis acid catalyst in organic synthesis due to its compatibility with both organic and aqueous media.

In the present research work (Figure 2), we have established a simple, sustainable, and selective deprotection methodology for aryl propionates and acetates in the presence of substituted amides, esters, ethers, and carboxylic acid functional groups using 20% $InCl_3$/MCM-41 as a heterogeneous catalyst. The selective deprotection was achieved in about 6−8 h in good yields (62−86%). The *c*−*o* bond cleavage in esters was observed instead of *c*−*c* bond formation because of the strong Lewis acidity, which was further corroborated using the Py-FTIR studies. Activity studies reveal the high stability of 20% $InCl_3$/MCM-41 confirmed with the high degree of dispersion showing an amorphous nature in XRD studies and TEM studies.

EXPERIMENTAL SECTION

Preparation of the Mesoporous MCM-41 Support. As per the literature procedures,[36,37] 2.4 g of CTAB, 100 g of distilled water, and 6.2 mL of ethyl amine (70 wt %) were mixed together at ambient temperature. After a homogeneous mixture was formed, 10 mL of tetraethyl orthosilicate (TEOS) was added dropwise under continuous stirring. The mixture was stirred for a further 4 h and was then placed in a PTFE-lined stainless-steel autoclave that was subsequently heated to 100 °C for 48 h. The product was recovered by filtration, washed with distilled water, and air-dried. The template was removed by calcination of the as-synthesized sample at 550 °C in air for 6 h, with a heating rate of 1 °C min^{-1} from room temperature to 550 °C.

Preparation of the Catalyst. A series of $InCl_3$ (10, 15, and 20 wt %) impregnated on MCM-41 catalysts were prepared by a wet impregnation method.[36,37] In a typical procedure, the calculated quantity of $InCl_3$ was dissolved in 15 mL of methanol, which was stirred for 5 min, followed by slow addition of MCM-41 to the solution, and kept for 6 h at room temperature under stirring. Then, the solvent was evaporated on a rotary evaporator, and finally, the catalyst was calcined at 100 °C for 1 h. The prepared catalyst was characterized using different sophisticated characterization techniques and used further for reactions.

General Procedure for the Synthesis of the Aryl Esters. Aryl propionates were prepared by using ILs morpholinium bisulfate [morH][HSO_4] and [TMBSA]-[HSO_4][53,54] In a round-bottom flask, to a solution of substituted phenol (1 mmol) and propionic anhydride (1:4 mmol), a calculated amount of ionic liquid was added. The reaction mixture was kept stirring continuously for 10−15 min. The completion of the reaction was monitored by TLC, and the reaction mixture was extracted with ethyl acetate, washed two times with 10% NaOH solution to remove the unreacted substituted phenol, and further washed with ice cold water. The organic layer was treated with anhydrous sodium sulfate and evaporated under reduced pressure on a rotary evaporator, and the crude product was purified using column chromatography and characterized by using spectroscopic techniques.

General Procedure for the Selective Deprotection of Aryl Esters. To a solution of aryl esters (1 mmol) in chlorobenzene (5 mL), 20% $InCl_3$/MCM-41 (100 mg) catalyst was added, and the reaction mixture was refluxed for 6−8 h continuously at 130 °C. The completion of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was pipetted out, and the catalyst was washed many times with 2−4 mL chlorobenzene, dried, and used for the next reaction. Chlorobenzene was evaporated from the reaction mixture under reduced pressure using a rotary evaporator, and the oily product was further purified using column chromatography. The purified product was characterized using FTIR and ^1H and ^{13}C NMR spectroscopy.

RESULTS AND DISCUSSION

Catalyst Characterization. The mesoporous material MCM-41 motif has a very high surface area with a uniform hexagonal shape pore, which gives a high degree of dispersion of active species. It also has stability at elevated temperatures and nonsolubility in solvents that enable carrying out the reactions in polar and nonpolar solvents at higher temperatures.

The prepared support MCM-41 and catalyst were well characterized using various advanced analytical techniques like BET surface area, small-angle XRD, wide-angle XRD, Py-IR, XPS, HR-TEM, etc. Surface areas of MCM-41 and 20% $InCl_3$ were found to be 1073 and 686 m^2/g respectively, which were in accordance with the 20% loading of $InCl_3$ on the support MCM-41. From the BET studies, it was confirmed that the pore volume reduced from 0.6790 to 0.4234 mL/g; this clearly supports the strong adherence of $InCl_3$ to the MCM-41 pores (Figure 3).

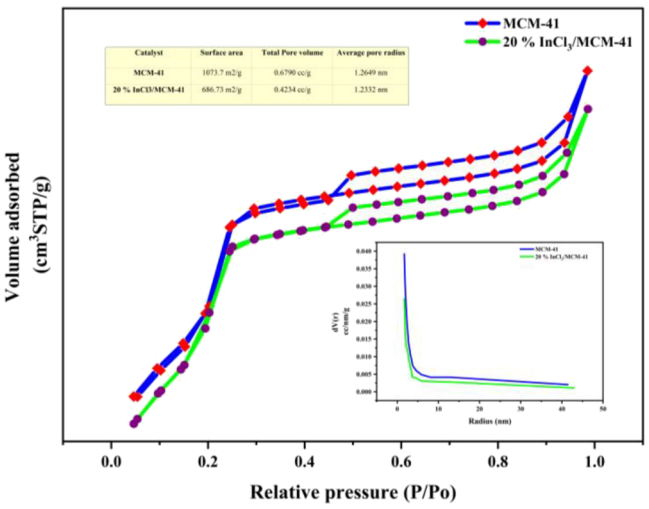

Figure 3. N_2 adsorption−desorption isotherms and pore size distribution curves.

The small-angle XRD pattern of the synthesized MCM-41 and 20% $InCl_3$/MCM-41 showed three distinctive peaks in a low angle region ($2\theta < 10°$) that can be indexed as 100, 110, and 200 for the 2θ angle 2.50, 4.34, and 5.00°, respectively, with a *d* spacing of 1.76 nm for the 200 plane, indicating the formation of an ordered hexagonal mesoporous structure.[37] The 20% $InCl_3$/MCM-41 (Figure 4b) showed an XRD pattern similar to that of MCM-41 (Figure 4a). Nevertheless, the intensity of spectra was seen to be diminished with the loading of indium(III) chloride[55] due to the impregnation of indium(III) chloride on the surface of MCM-41.

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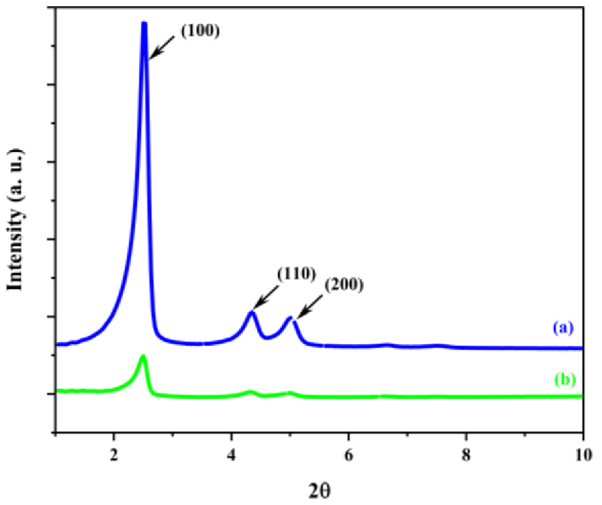

Figure 4. Small-angle XRD patterns of (a) MCM-41 and (b) 20% $InCl_3$/MCM-41.

The wide-angle XRD diffraction pattern of MCM-41and 20% $InCl_3$/MCM-41 showed a broad band in the range of 20−30°, which is a distinctive peak of the silicious mesoporous MCM-41 material.[56] The 20% $InCl_3$/MCM-41 does not show any characteristic peak corresponding to $InCl_3$, indicating very high degree of dispersion on the large surface area of MCM-41 (Figure 5).

The textural property like surface acidity of the catalyst was determined by Py-IR studies as reported by Parry.[57] Py-IR studies showed the presence of Lewis acidity with the formation of a coordinate bond between the metal ion and pyridine, whereas Brønsted acidity showed the formation of the pyridinium ion. During Py-IR analysis of MCM-41, the presence of bands at 1490 and 1634 cm^{-1} was assigned to the Lewis acidity of MCM-41 (Figure 6a). Additional bands at

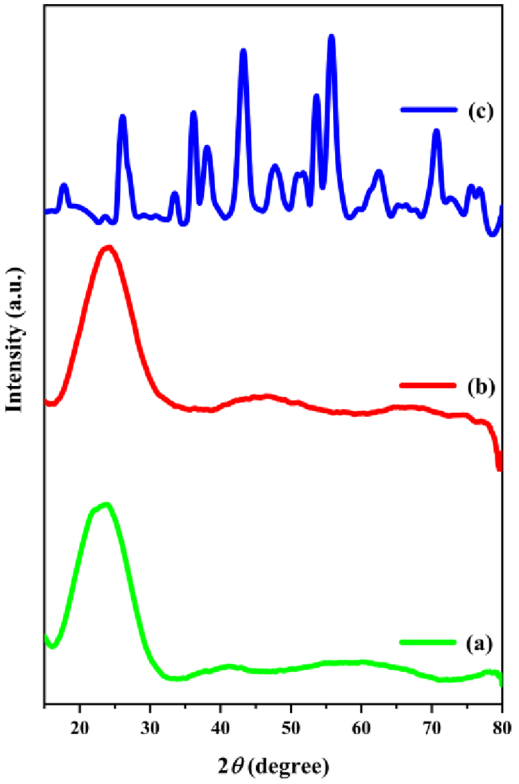

Figure 5. Wide-angle XRD of (a) MCM-41, (b) 20% $InCl_3$/MCM-41, and (c) $InCl_3$.

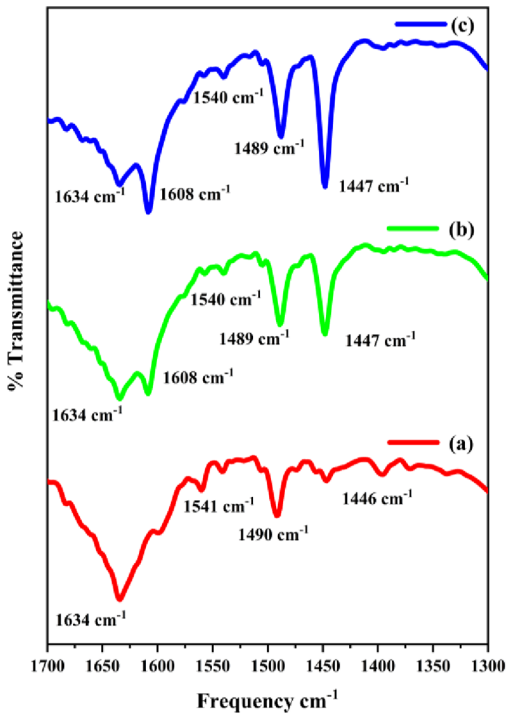

Figure 6. Py-FTIR spectra of (a) MCM-41, (b) 10% $InCl_3$/MCM-41, and (c) 20% $InCl_3$/MCM-41.

1489 and 1608 cm^{-1} were induced with the loading of 10% $InCl_3$ on MCM-41 (Figure 6b), which were assigned to the Lewis acidity of $InCl_3$. Also, a small peak at 1540 cm^{-1} developed due to the formation of pyridinium ion, which revealed the presence of Brønsted acidity in the catalyst. In 20% $InCl_3$/MCM-41 (Figure 6c), all of the peaks observed in 10% $InCl_3$/MCM-41 were found to be intensified and prominent, which clearly demonstrate that as the loading of indium(III) chloride increased, the Lewis as well as Brønsted acidity of the catalyst was also increased.

The NH_3-TPD technique is used mostly for quantitative analysis of the total acidity of a catalyst without the differentiation of the Lewis and Brønsted acidic sites.[58,59] To quantify the Lewis and Brønsted acidity of the catalyst, Venugopal et al. reported pyridine adsorbed DRIFTS.[60,61] Similarly, in the present study, the Gaussian function was used to find out the area under the Lewis and Brønsted acidic peaks in Py-FTIR of 20% $InCl_3$/MCM-41 spectra (Figure 7). The percentage of the respective acidic sites was derived by deconvoluting Py-FTIR spectra of MCM-41 and 20% $InCl_3$/MCM-41 spectra, in which the area under the peaks 1447, 1489, 1608, and 1634 cm^{-1} was found to be 99.16%, corresponding to the Lewis acidity of the catalysts. Similarly, the area under the peak 1540 cm^{-1} was found to be 0.839%, corresponding to the Brønsted acidic character of the catalyst. These values confirm that the Lewis acidic character of the 20% $InCl_3$/MCM-41 catalyst was increased by 2.58 times as compared with the MCM-41 (Table 2).

The total XPS scan of the 20% $InCl_3$/MCM-41 impregnated catalyst shows the presence of Si_{2p}, O_{1s}, Cl_{2p}, C_{1s}, and In_{3d} in

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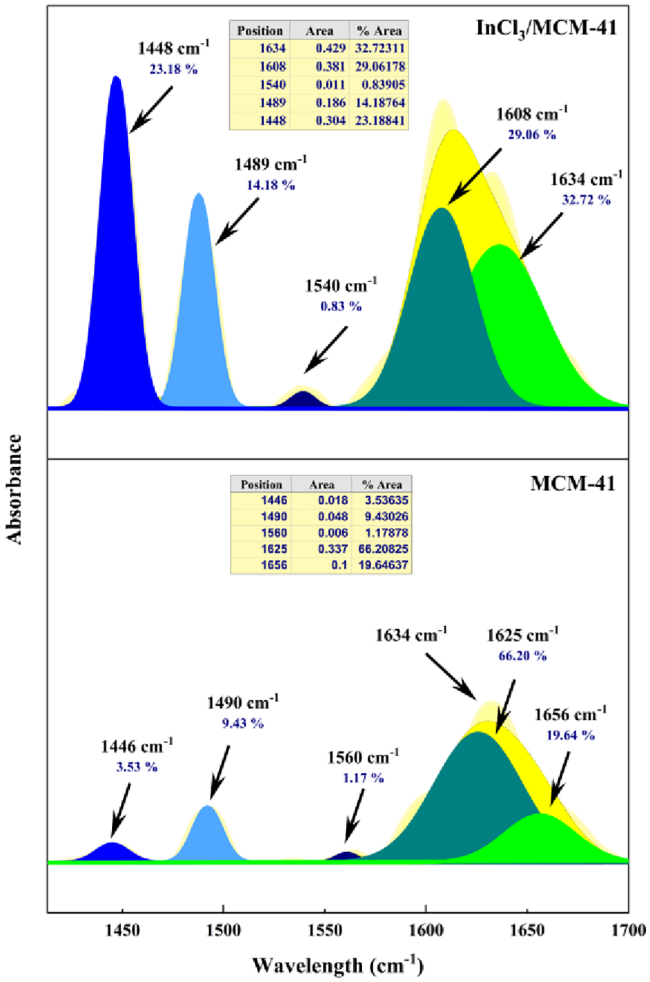

Figure 7. Deconvoluted Py-FTIR of 20% $InCl_3$/MCM-41 and MCM-41.

Table 2. Percentage Distribution of Acidities of MCM-41 and 20% $InCl_3$/MCM-41

20% $InCl_3$/MCM-41			MCM-41		
position cm^{-1}	area	% area	position cm^{-1}	area	% area
1634	0.429	32.72311	1656	0.1	19.64637
1608	0.381	29.06178	1625	0.337	66.20825
1540	0.011	0.83905	1560	0.006	1.17878
1489	0.186	14.18764	1490	0.048	9.43026
1448	0.304	23.18841	1446	0.018	3.53635

Figure 8a, and no other impurity except carbon was present in the sample. The detailed scans of In $3d_{5/2}$ and In $3d_{3/2}$ are illustrated in Figure 8b. Deconvolution of O 1s spectra resulted into single peaks with a binding energy value of 532.9 eV (Figure 8c) assigned to oxygen present in SiO_2.[62]

The 20% $InCl_3$/MCM-41 shows binding energies for In $3d_{5/2}$ and In $3d_{3/2}$ observed at 446.12 and 453.72 eV respectively with spin orbital splitting of 7.6 eV.[63,64] Whereas, In_2O_3 shows binding energies for In $3d_{5/2}$ and In $3d_{3/2}$ observed at 443.9 and 451.47 eV.[65,66] This clearly suggests that for 20% $InCl_3$/MCM-41 (impregnated) catalyst, indium was not in the form of oxide but present in the form of $InCl_3$ that was dispersed on the surface of the MCM-41 support.

The loading of indium species as indium chloride in 20% $InCl_3$/MCM-41 was carried out by using the ICP-AES analysis and EDX. The results show that the 31.15 ppm indium was present as indium chloride on the MCM-41 when freshly prepared. The expected ICP-AES (10.31 mg) results match with those of the analyzed catalyst (7.78 mg). These results are also evidenced by EDX analysis that confirms the presence of indium species as indium chloride in the 20% $InCl_3$/MCM-41 catalyst elaborated in the Supporting Information.

A more detailed structural characterization like a highly ordered distribution of indium(III) chloride species on the MCM-41 surface of prepared catalysts was explored by HR-TEM studies. Indium(III) chloride incorporated silica exhibits a highly ordered mesoporous structure with an average spacing of 1.76 nm (Figure 9a), which could be correlated with the value obtained by XRD, i.e., 1.764 nm for 2θ at 2.50° presenting at the 100 plane of MCM-41.[67] From the above observations, it can be concluded that indium(III) chloride is well incorporated in MCM-41 as a honeycomb matrix of MCM-41 (Figure 9b,c), which was in corroboration with the amorphous nature of silica in small- and wide-angle XRD.

Catalytic Activity Testing. *Optimization Studies for the Deprotection of Aryl Esters.* For the optimization study, 3,5-dimethylphenyl propionate was used as a model substrate. The activity of 10, 15, and 20% $InCl_3$/MCM-41 was tested for the deprotection of 3,5-dimethylphenyl propionate (Scheme 1). Initially, no substrate conversion was observed up to 12 h for 3,5-dimethylphenyl propionate without any catalyst and in the presence of only MCM-41 at 60, 80, and 130 °C in ethanol, acetonitrile, and chlorobenzene, respectively (Table 3 entries 1−6). In the presence of only $InCl_3$ as a homogeneous catalyst, deprotection of 3,5-dimethylphenyl propionate gives 3,5-dimethyl phenol in acetonitrile and chlorobenzene (yield 42−62%, Table 3 entries 8−9). The 10% $InCl_3$/MCM-41 and 15% $InCl_3$/MCM-41 were tested for deprotection with ethanol, acetonitrile, and chlorobenzene. In the presence of chlorobenzene at 130 °C for 6−8 h, conversions with good % yields of the deprotected product were observed (yield 36−64%, Table 3 entries 11−12 and 14−15). Encouraging results were obtained for 20% $InCl_3$/MCM-41, giving 60% deprotected product in acetonitrile solvent and the highest value of 85% deprotected product in chlorobenzene at 130 °C (Table 3 entries 17−18). No substrate conversion was observed for 3,5-dimethylphenyl propionate in the presence of ethanol solvent (Table 3 entries 7, 10, 13, and 16).

Substrate Scope for the Selective Deprotection of Aryl Esters. With the optimized reaction conditions, the broad spectrum of the substituted esters electron-rich and electron-deficient functional groups were studied to yield corresponding phenols (Table 4). Unsubstituted aryl propionate and polyaromatic naphthalen-2-yl propionate give deprotected phenol and naphthol (76 and 72%, Table 4 entries 1−2). It was observed that 1,2; 1,3; 1,4-phenylene dipropionate and 1,3,5-phenylene tripropionate require increased amounts of the catalyst (200 and 300 mg) for the deprotection to yield dihydroxy phenols and trihydroxy phenols in good yields (68−86%, Table 4 entries 3−6). Electron-donating substituents like *o*-, *m*-, and *p*-methyl-substituted propionates and disubstituted 3,5-dimethyl phenyl propionate compared to the unsubstituted aryl propionates yield corresponding phenols with higher % of yields (80−85%, Table 4 entries 7−10). The chloro substituent in *o*- and *p*-chloro and 2,6-dichlorophenol substituted aryl propionates gave the corresponding phenol

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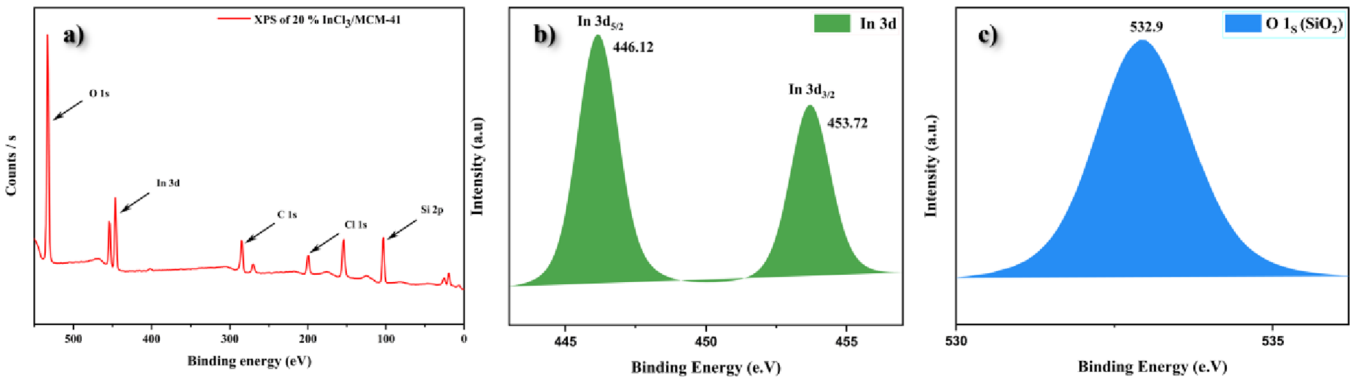


Figure 8. (a) XPS survey spectrum of 20% $InCl_3$/MCM-41, (b) XPS spectra of In 3d from 20% $InCl_3$/MCM-41, and (c) XPS of O 1s from 20% $InCl_3$/MCM-41.

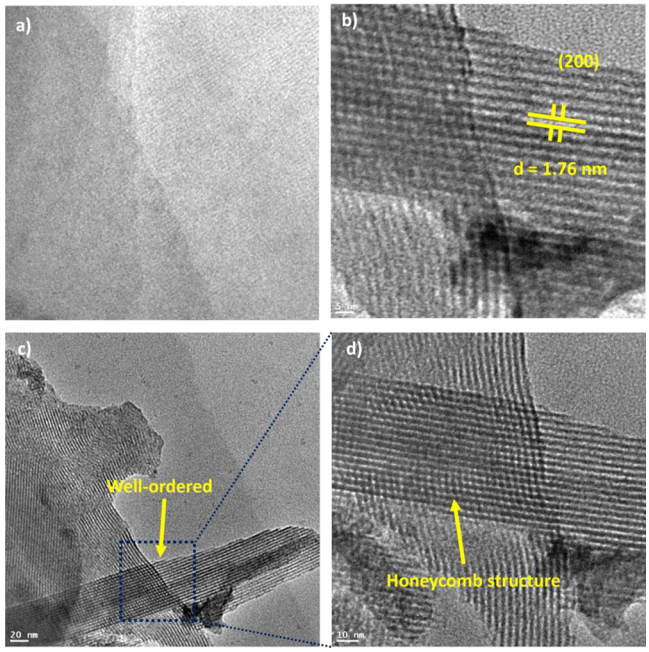
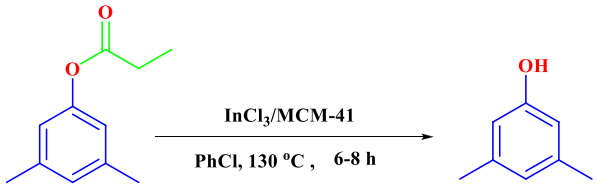


Figure 9. HR-TEM images of (a) MCM-41, (b) 20% $InCl_3$/MCM-41 showing a *d* spacing of 1.76 nm, (c) well-ordered mesoporous structure with average pore radius of 1.26−1.23 nm, and (d) honeycomb structure.

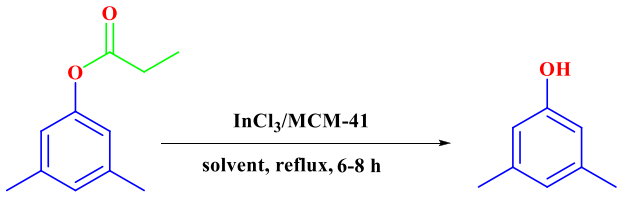
Scheme 1. Deprotection of Aryl Esters[a]



[a]Reaction conditions:3,5-dimethylphenyl propionate (0.178 g, 1 mmol), chlorobenzene (5 mL), catalyst (100 mg), temperature 130 °C, 6−8 h, isolated yield 85%.

in increased yields as compared to the simple aryl propionates (78−86%, Table 4 entries 11−13). As expected, the electron-deactivating nitro group affected the deprotection of 4-nitroaryl and 2,4,6-trinitrophenyl propionate to give 4-nitrophenol and 2,4,6-trinitrophenol with reduced yields (62−65%, Table 4 entries 14−15). Using 20% $InCl_3$/MCM-41, deprotection of the aryl esters with electron-donating

Table 3. Optimization Study of the Reaction Conditions for the Deprotection of Aryl Esters[a]



Entry	Catalyst	Solvent	Temperature °C	% Yield[b]
1		ethanol	60	
2	no catalyst	acetonitrile	80	
3		chlorobenzene	130	
4	MCM-41	ethanol	60	
5		acetonitrile	80	
6		chlorobenzene	130	
7	$InCl_3$	ethanol	60	
8		acetonitrile	80	42
9		chlorobenzene	130	62
10	10% $InCl_3$/ MCM-41	ethanol	60	
11		acetonitrile	80	36
12		chlorobenzene	130	52
13	15% $InCl_3$/ MCM-41	ethanol	60	
14		acetonitrile	80	48
15		chlorobenzene	130	64
16	20% $InCl_3$/ MCM-41	ethanol	60	
17		acetonitrile	80	60
18		chlorobenzene	130	85

[a]Reaction conditions: 3,5-dimethylphenyl propionate (0.178 g, 1 mmol), chlorobenzene (5 mL), catalyst (100 mg), and reflux 6−8 h. [b]Isolated yields.

substituents was obtained in excellent yields (79−85%). It was concluded that the substitution of an electron-donating group enhanced the deprotection of the aromatic esters to give excellent yields of phenols.

After the successful deprotection of aryl propionates in the presence of 20% $InCl_3$/MCM-41, the catalyst was studied for selective deprotection of substituted aryl propionate in the presence of different functional groups such as −NHCOR, −OR, −COR, −CHO, −COOH, and $-NO_2$ and cyclic esters like coumarin. The catalyst was further studied for the deprotection of substituted acetyl, carboxyl, and formyl propionate. First, deprotection of *N*-phenyl propionamide and *p*-CH_3, -Cl, and *m*-NO_2 phenyl propionamide was not observed even after the prolonged reaction conditions (Table

https://doi.org/10.1021/acsomega.4c06271
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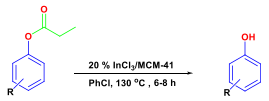
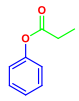
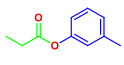
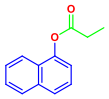
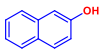
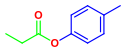
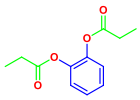
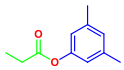
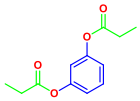
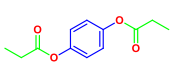
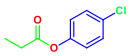
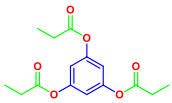
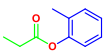
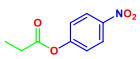
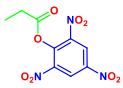
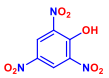
Table 4. Substrate Scope for the Deprotection of Aryl Esters[a]



Entry	Reactant	Product	Yield[b]	Entry	Reactant	Product	Yield[b]
1			76%	8			80%
2			72%	9			80%
3			86[#]%	10			85%
4			70[#]%	11			79%
5			85[#]%	12			78%
6			68[##]%	13			86%
7			82%	14			65%
				15			62%

[a]Reaction conditions: substituted aryl propionate (1 mmol), chlorobenzene (5 mL), catalyst (100 mg), [#]catalyst (200 mg), [##]catalyst (300 mg), temperature 130 °C, 6−8 h. [b]Isolated yields.

5entries 1−4). The selective deprotection study of 3-propionamidophenyl propionate and 4-propionamidophenyl propionate gave only *N*-(3-hydroxyphenyl)propionamide and *N*-(4-hydroxyphenyl)propionamide, where only the propionate group was deprotected selectively (72−76%, Table 5 entries 5−6). Further, 4-acetyl-1,3-phenylene dipropionate on deprotection yields 2,4-dihydroxy acetophenone (70%, Table 5 entry 7) with an increased amount of the catalyst. In the presence of a carboxylic acid group, the deprotection of 2-(propionyloxy)-benzoic acid and 3-formyl phenyl propionate yields 2-hydroxybenzoic acid and 3-hydroxybenzaldehyde, respectively (65−68%, Table 5 entries 8−9). Similarly, some of the medicinally important molecules like vanillin and coumarin were also studied for the selective deprotection. 4-Formyl-2-methoxyphenyl propionate and 4-methyl-2-oxo-2*H*-chromen-7-yl propionate yield vanillin and 7-hydroxy-4-methyl-2*H*-chromen-2-one, where methoxy and lactone groups were not found to be deprotected (69−72%, Table 5 entries 10−11).

In continuation with the earlier study, the deprotection of aryl benzoates was also studied to give the corresponding phenol. Deprotection of 3,5-dimethylphenyl benzoate on reaction with the 20% $InCl_3$/MCM-41 catalyst was executed in chlorobenzene at 130 °C for 12 h (Scheme 2) to give 3,5-dimethyl phenol, which was not observed even after the prolonged reaction conditions up to 24 h.

To study the deprotection of alkyl substituted benzoate, deprotection of methyl benzoate with 20% $InCl_3$/MCM-41 was executed in chlorobenzene solvent at 130 °C for 12 h (Scheme 3) to give the corresponding alcohol and carboxylic acid, which were not observed even after the prolonged reaction conditions up to 24 h.

In conclusion, with the optimized reaction studies, the present research work elaborates the deprotection of the aryl propionates/acetates in the presence of the electron-donating substituents very easily using 20% $InCl_3$/MCM-41, whereas substituted aryl propionamides did not undergo deprotection. Substituted aryl propionates were deprotected selectively in the presence of the propionamides. Medicinally important compounds were also found to be selectively deprotected in the presence of the various functional groups. In the extension, the alkyl/aryl benzoates remained protected even after the prolonged reaction times.

Plausible Mechanism. A plausible reaction pathway for the deprotection of aryl esters has been proposed in Scheme 4. Here, the oxygen site of the propionate group binding to the Lewis acid of the catalyst was the first step. The weakened *c*−*o* bond was further attacked by the Cl^- anion to form propionyl

https://doi.org/10.1021/acsomega.4c06271
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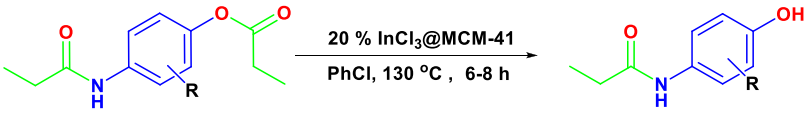
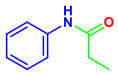
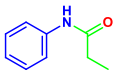
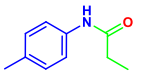
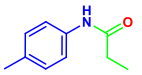
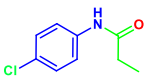
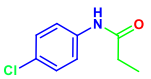
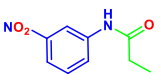
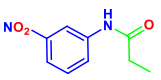
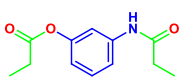
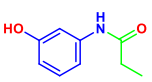
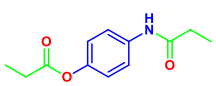
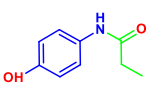
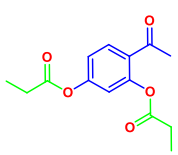
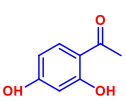
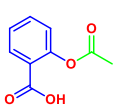
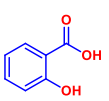
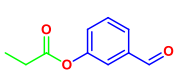
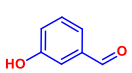
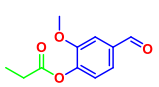
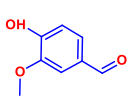
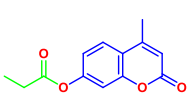
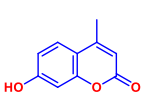
Table 5. Selectivity Study of the Catalyst[a]



Entry	Reactant	Product	Yield[b]
1			NR
2			NR
3			NR
4			NR
5			72%[#]
6			76%[#]
7			70%[#]
8			68%
9			65%
10			69%
11			72%

[a]Reaction conditions: substituted aryl propionate/aryl propionamide (1 mmol), chlorobenzene (5 mL), catalyst (100 mg), 6−8 h, temperature 130 °C, [#]catalyst (200 mg). [b]Isolated yields.

https://doi.org/10.1021/acsomega.4c06271
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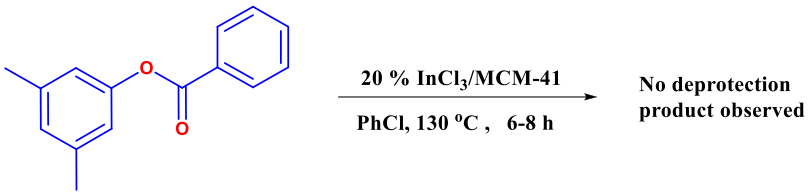
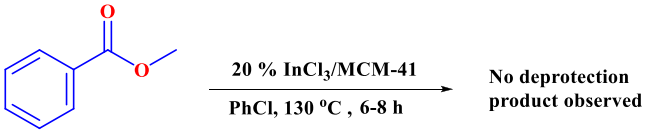
Scheme 2. Deprotection of Aryl Benzoates[a]



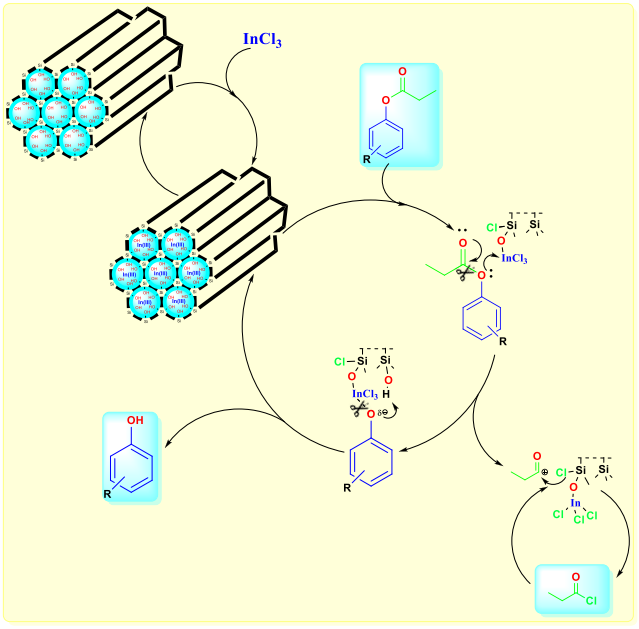
[a]Reaction conditions: 3,5-dimethylphenyl benzoate (0.226 g, 1 mmol), chlorobenzene (5 mL), catalyst (100 mg), temperature 130 °C, 24 h, no deprotection product observed.

Scheme 3. Deprotection of Alkyl Benzoates[a]



[a]Reaction conditions: methyl benzoate (0.136 g, 1 mmol), chlorobenzene (5 mL), catalyst (100 mg), temperature 130 °C, 24 h, no deprotection product observed.

Scheme 4. Plausible Pathway for the Deprotection of Aryl Esters



chloride. The phenoxide ion was further neutralized by the Brønsted acidity of the catalyst, and the catalyst was further regenerated for the further catalytic cycles.

Reusability and Stability of 20% $InCl_3$/MCM-41. The efficiency of the 20% $InCl_3$/MCM-41 catalyst was established by recycle studies (Figure 10) for deprotection of 3,5-dimethylphenyl propionate to yield 3,5-dimethylphenyl phenol. After completion of the first run, the catalyst was separated by filtration and washed two times with chlorobenzene and methanol. After careful washings, it was dried at 60 °C and used for six subsequent runs. Figure 10 shows that product formation was stable (82−70%) even after six cycles with minor loss in catalyst handling. The stability of the catalyst was further confirmed with the XPS studies. XPS analysis of the recycled catalyst shows the binding energies for In $3d_{5/2}$ and In $3d_{3/2}$ were observed at 446.12 and 453.72 eV,

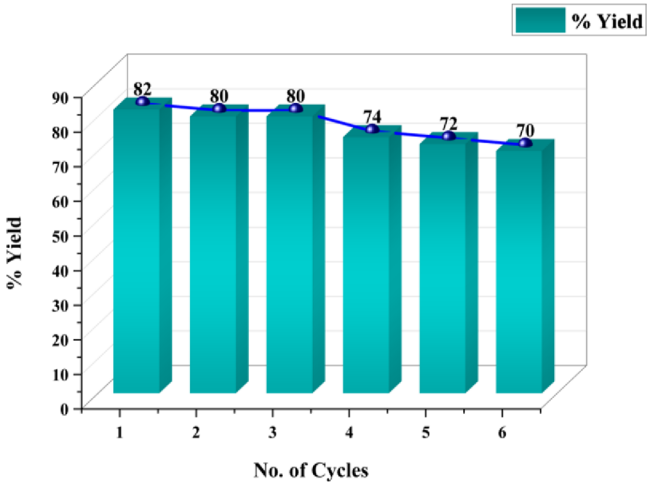


Figure 10. 3,5-Dimethylphenyl propionate (0.178 g, 1 mmol), chlorobenzene (5 mL), catalyst (100 mg), 6−8 h, and 130 °C.

respectively, which amount to the freshly prepared catalyst with spin orbital splitting of ∼7.6 eV. These results of the XPS studies reveal the high stability of the 20% $InCl_3$/MCM-41 catalyst, which is reflected in the recycle studies of the catalyst (Figure 11).

The hot filtration test for leaching of indium from 20% $InCl_3$/MCM-41 was performed. During the reaction after 3 h, the catalyst was filtered from the reaction mixture, and reaction

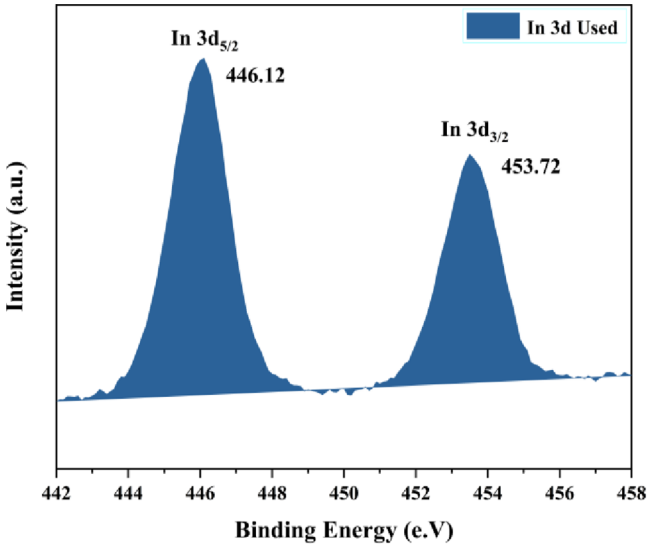


Figure 11. XPS spectra of In 3d from the used 20% $InCl_3$/MCM-41 catalyst.

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was continued for the next 4 to 5 h. It was observed that there was no increase in the isolated yield of the product even after prolonged reaction. This experiment confirms the nonleaching of indium from the 20% $InCl_3$/MCM-41 catalyst. ICP-AES studies also confirm that there were no traces of indium detected in the reaction mixture after the filtration of the catalyst.

The reason for the nonleaching of indium from the catalyst is the pore size of MCM-41, which facilitates the filling of pores with indium(III) chloride and also the physical adsorption. This was also confirmed by the amorphous nature of the XRD peaks observed in the wide-angle XRD studies because of the high degree of dispersion of active species on the high surface area MCM-41 support.

CONCLUSIONS

In the present research work, we have developed a most efficient and selective deprotection methodology for aryl esters/propionates in short times with good yields using the supported Lewis acid catalyst 20% $InCl_3$/MCM-41. The high degree of dispersion and uniform loading of indium(III) chloride over MCM-41 were demonstrated using the small- and wide-angle XRD studies. The Lewis acidity of the catalyst was confirmed with the Py-FTIR studies, which was further quantified by deconvolution of DRIFTS to establish the % of Lewis and Bronsted acidity of the catalyst quantitatively. Microscopic analysis of the optimized catalyst reveals the hexagonal well-ordered structure of the catalyst. Speciation studies of the 20% $InCl_3$/MCM-41 catalyst were performed by XPS analysis, results of which were found to be the same before and after the reaction, corroborated with the recycle studies up to six recycles exhibiting the high stability of the catalyst.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c06271.

BET surface area (Figure S1); EDX and elemental mapping (Figures S2−S4); and ^{1}H NMR (Figures S5−S47) (PDF)

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Notes

The authors declare no competing financial interest.

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