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Cerium-containing MCM-41 materials as selective acylation and alkylation catalysts

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Abstract

The synthesis of Ce–MCM-41, Al–MCM-41 and Ce–Al–MCM-41-type mesoporous materials was carried out hydrothermally by refluxing the gel with magnetic stirring under atmospheric pressure for 24–36 h. The samples were characterized thoroughly in order to obtain the structural and textural properties, which reveal the presence of well-ordered M41S-type materials. The Ce–MCM-41 samples were used for catalytic acylation of alcohols, thiols, phenols and amines show good activity and selectivity including high chemoselectivity towards selective monofunctional acylation of bifunctional compounds. Quite importantly the acylation of bulky molecules such as cholesterol, ergesterol and β-sitosterol could be achieved using Ce–MCM-41 as solid catalyst. The presence of Ce along with Al in Ce–Al–MCM-41 was found to have synergistic effect as Ce–Al–MCM-41samples were more active catalysts for alkylation of naphthalene compared to either Ce–MCM-41 or Al–MCM-41 with comparable Si/Al or Si/Ce molar ratio.

Keywords: Ce containing MCM-41 materials; Alkylation; Acylation; Acidity measurements; TPD (ammonia)

1. Introduction

Zeolites have been extensively used for various acid-catalyzed reactions including alkylation and acylation reactions. However the restrictions imposed by its pore dimensions do not allow to carry out the reactions involving bulkier organic substrate, whereas the mesoporous M41S-type molecular sieves do not face such constraints. While the incorporation of various transition and non-transition metal ions in MCM-41 network is well reported [1], the incorporation of inner-transition metal ions in silica network is rather limited to few reports [2–5]. Recently, the synthesis of Ce–silicate analogue of MFI, BEA and MTW was reported [6,7]. Due to size incompatibility between lanthanides and Si^{4+} ions, causing longer ≡Si–O–Ce≡ and more strained bond angles in crystalline microporous Ce–silicates, the incorporation of Ce in zeolitic framework is rather very difficult. However, the incorporation of Ce into the amorphous silica network of ordered mesoporous materials like MCM-41 is expected to be rather easy because of the greater flexibility of the network [5]. We have recently shown that the incorporation of Ce in MCM-41 results in dual catalytic activity in acid (dehydration of cyclohexanol to cyclohexene) and redox (hydroxylation of 1-naphthaol to dihydroxy naphthalenes) catalysis [5].

Acylation of alcohols, amines, phenols and thiols is an important and frequently used organic transformation as it provides not only an efficient and inexpensive route for the protecting hydroxy, amino, phenolic and thiol groups but also produces important organic intermediates in multi-step synthetic processes which are widely used in the synthesis of fine chemicals, pharmaceuticals, perfumes, plasticizers, cosmetics, chemical auxiliaries, etc. Acylation reactions are usually carried out in the homogenous systems either in basic medium by using amine bases [8–10] or in acidic medium by using protic acids [11]. However, replacing homogeneous catalytic systems into heterogeneous ones is advantageous mainly because of easy catalyst recovery, reusability and work-up of the reaction products. Similarly,

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alkylation of naphthalene is also of importance from both industrial as well as academic point of view. Attention has been paid over the liquid-phase alkylation of naphthalene over zeolites to yield 2,6- and 2,7-diisopropylnaphthalenes [12–13]. Use of mesoporous materials has also been reported for the alkylation of naphthalene [14–16].

Here, we report chemoselective acylation of alcohols, amines and thiols in the presence of Ce–MCM-41 as a reusable solid catalyst. More importantly the acylation of large and bulkier molecules such as cholesterol, ergesterol and β-sitosterol is also carried out for the first time using any solid catalysts like mesoporous Ce–MCM-41. Further, the synergistic effect of the simultaneous incorporation of Ce and Al in MCM-41 during liquid-phase isopropylation of naphthalene is also demonstrated for the first time in this communication.

2. Experimental

2.1. Materials and synthesis

Fumed silica (Sigma, USA), 25 wt.% aqueous solution of tetramethylammonium hydroxide (TMAOH, Loba Chemie, India), sodium aluminate ($NaAlO_2$, 43.65% Al_2O_3, 39.0% Na_2O and 17.35% H_2O; Loba Chemie, India), cetyltrimethylammonium bromide (CTMABr; Loba Chemie, India) and ceric sulfate [$Ce(SO_4)_2 \cdot 4H_2O$; Loba Chemie, India] were used as raw materials to synthesize Al–MCM-41, Ce–MCM-41 and Ce–Al–MCM-41 samples. For the acylation reactions the alcohols, amines, phenols, thiols and acetic anhydride were obtained commercially and used without any further treatment or prepared by standard methods. Solvent (acetonitrile) was purified and dried by standard procedures before use. For alkylation isopropanol (S.d. Fine Chem. Ltd., India) naphthalene (S.d. Fine Chem. Ltd., India) and cyclohexane (Loba Chemie, India) were also used as purchased.

The hydrothermal syntheses of Al–MCM-41, Ce–MCM-41 and Ce–Al–MCM-41 were carried out by refluxing the magnetically stirred gel mixtures at atmospheric pressure. The detail for the synthesis of Ce–MCM-41 is described in our recent paper [5]. Al–MCM-41 was also synthesized in the same way using aqueous solution of $NaAlO_2$ instead of $Ce(SO_4)_2 \cdot 4H_2O$. Whereas the Ce–Al–MCM-41 samples were synthesized, obviously, using both aluminum and cerium sources. The molar gel compositions of the synthesis gels were $1SiO_2{:}xCeO_2{:}yAl_2O_3{:}0.30TMAOH{:}0.25CTMABr{:}125H_2O$, where $x = 0.04$ and $y = 0$ for Ce–MCM-41, $x = 0$ and $y = 0.02$ for Al–MCM-41, and $(x, y) = (0.0133, 0.02)$ and $(0.04, 0.0066)$ for two different Ce–Al–MCM-41 samples. All samples were washed thoroughly first with deionized water and then with acetone and dried at 353 K followed by calcination at 813 K for 8 h in the presence of air. The calcined samples were treated with 0.5 M ammonium acetate solution (50 ml for 1.0 g sample) twice at room temperature to obtain the NH_4-cation form and then again calcined in an air atmosphere at 773 K for 6 h to finally obtain the H-form of different MCM-41 samples.

2.2. Characterization

The details of the characterization of Ce-containing MCM-41 samples are given in our recent publication (5). The Ce–MCM-41 and Ce–Al–MCM-41 samples were characterized using powder X-ray diffraction (Rigaku Miniflex diffractometer with Cu Kα radiation (λ = 1.5406 Å) between 2θ =1.5 and 50° with a scanning rate of 1°/min). The diffuse reflectance UV–vis spectra in the 200–600 nm range were recorded with a Shimadzu UV-2101 PC spectrometer equipped with a diffuse reflectance attachment using $BaSO_4$ as a reference. The FTIR spectra were obtained in the 400–4000 cm^{-1} range on a Shimadzu FTIR-8201 PC (in Nujol on KBr disc technique). The solid-state MAS NMR spectroscopic studies were carried out on a Bruker MSL 300 NMR spectrometer where finely powdered samples were placed in 7.0 mm zirconia rotors and spun at 2.5–3.5 kHz and the chemical shift for ^{27}Al MAS NMR was determined using aqueous solution of $Al(NO_3)_3$ $[Al(H_2O)_6^{3+}]$ as the reference compound. The SEM micrographs of the calcined samples were obtained in a Leica Stereoscan 440. Transmission electron microscopy (TEM) was performed on a JEOL JEM-1200EX instrument with an acceleration voltage of 100 kV. The metal contents of the calcined samples were determined by energy-dispersive X-ray analysis with Kevex equipment attached with Jeol JSM-5200 scanning microscope. The specific surface areas of the calcined samples were determined by BET method using the adsorption of N_2 measured with Omnisorb 100 CX Colulter instrument.

2.3. General procedure for acylation and alkylation reaction

In a typical procedure, the reactant (alcohol/amine/phenol/thiol) (10 mmol) was added to acetic anhydride (11 mmol) and the mixture was refluxed under stirring in acetonitrile (5 ml) in the presence of Ce–MCM-41 catalyst (20 wt.% with respect to the substrate) for stipulated period of time for the completion of the reaction (monitored by TLC). After completion of the reaction, the catalyst was separated by centrifugation/filtration and then the filtrate was concentrated, diluted with water (15 ml) and extracted with CH_2Cl_2 (3 × 15 ml). The organic layer was separated, washed with 10% aqueous $NaHCO_3$, water, and dried over Na_2SO_4. The solvent was removed to produce crude product, which was then purified by column chromatography over silica gel (3% EtOAc in light petroleum ether) to furnish pure product. The structure was confirmed by ^1H NMR, FTIR, mass spectrometry, and also by comparison with authentic sample. The isopropylation of naphthalene was carried out in a batch reactor under autogeneous pressure by using cyclohexane as a solvent. The reaction products were analyzed using Agilent 6890 series GC system (HP chiral, 20% permethylated β-cyclodextrin, 30 m × 0.32 mm × 0.25 μm film thickness), GCIR (Perkin Elmer, GC-IR 2000) and GCMS (Shimadzu, GCMS-QP 2000A). The catalyst recovered from the reaction mixture was reactivated by calcining it at 813 K for 8 h in the presence of air and was reused again for acylation reactions.

3. Results and discussion

3.1. Characterization

The XRD profiles of Ce–MCM-41, Ce–Al–MCM-41 and Al–MCM-41 sample were comparable showing high degree of ordering. Selected samples (Ce–MCM-41 and Ce–Al–MCM-41) were also scanned for high-angle regime to find out whether any nanosized CeO_2 phase is present in Ce-containing MCM-41. Fig. 1 exhibits the XRD (powder) patterns of Ce–MCM-41 (diffractogram A), Ce–Al–MCM-41 (diffractogram B) and amorphous CeO_2–Al_2O_3–SiO_2 mixture (diffractogram C) with similar Ce and Al contents compared to that of Ce–MCM-41 and Ce–Al–MCM-41 samples. While amorphous CeO_2–Al_2O_3–SiO_2 mixture showed high-angle diffractions characteristic of ceria, no such characteristic peaks for CeO_2 were observed in Ce–MCM-41 and Ce–Al–MCM-41 samples. This clearly indicates that Ce-containing MCM-41 samples are free from CeO_2 phase. The chemical composition and BET surface area of the samples used are given in Table 1 and other characterization details are given elsewhere [5]. Fig. 2 depicts the UV spectra of the calcined Ce-containing MCM-41samples. Ce–MCM-41 and Ce–Al–MCM-41 samples, obtained by direct synthesis method, show a single symmetrical broad peak centered at ca. 300 nm, where a mixture of CeO_2 and SiO_2 show a major absorption around 400 nm along with an ill-defined absorption in lower wavelength. The position of ligand to metal charge transfer ($O^{2-} \rightarrow Ce^{4+}$) spectra depends on the ligand field symmetry

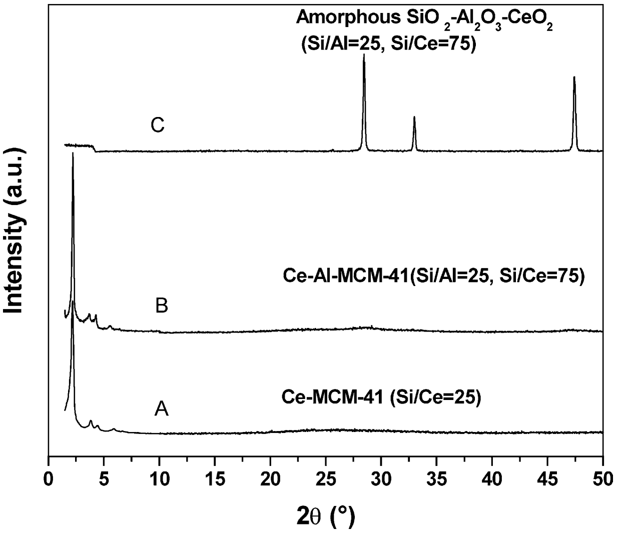


Fig. 1. XRD (powder) pattern of Ce–MCM-41 (Si/Ce = 25), Ce–Al–MCM-41 (Si/Al = 25, Si/Ce = 75) and amorphous SiO_2–Al_2O_3–CeO_2 (Si/Al = 25, Si/Ce = 75) samples.

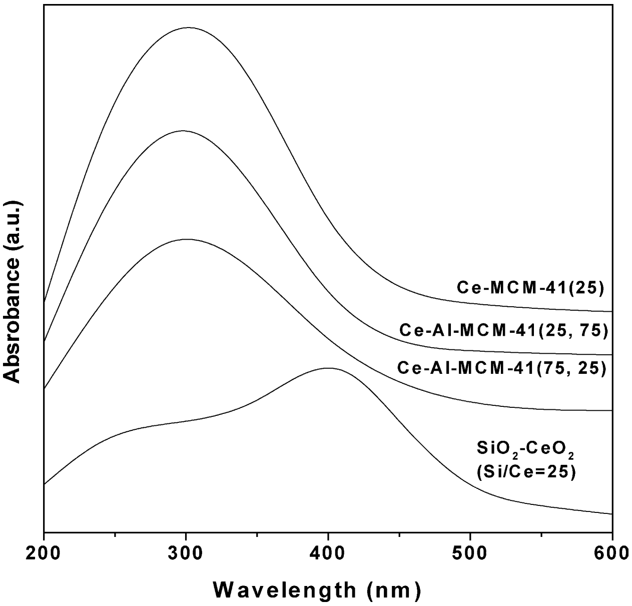


Fig. 2. Diffuse reflectance UV–vis spectra of calcined (a) Ce–MCM-41 (25), (b) Ce–Al–MCM-41 (75, 25), (c) Ce–Al–MCM-41 (25, 75) and (d) SiO_2–CeO_2 (25); the values in the parenthesis in case of samples (a) and (d) represent Si/Ce ratio whereas in samples (b) and (c) indicates Si/Ce and Si/Al ratios, respectively.

Table 1
Elemental analysis, d_{100} spacing, unit cell parameter (a_0), BET surface area and pore diameter of M-MCM-41 (M = Si, Al and/or Ce) samples

Sample	Si/Ce$_{gel}$	Si/Ce$_{solid}$	d_{100} (Å)	a_0[a] (Å)	BET surface area ($m^2 g^{-1}$)	Pore diameter (Å)
Si-MCM-41	–	–	38.2	44.1	1296	27.6
Ce–MCM-41 (25)	25	26.8	40.7	47.0	983	31.8
Ce–Al–MCM-41 (Si/Ce = 75, Si/Al = 25)	Si/Ce = 75, Si/Al = 25	Si/Ce =78, Si/Al = 26.8	40.5	46.7	980	29.5
Al–MCM-41 (25)	25	27	40.8	47.1	1169	28.2
Ce-Ex MCM-41	25	37	38.0	43.9	1088	27.1
Ce-Im MCM-41 (25)	25	25.4	38.0	43.9	1041	28.4

[a] Calculated by the equation $a_0 = 2d_{100}/\sqrt{3}$.

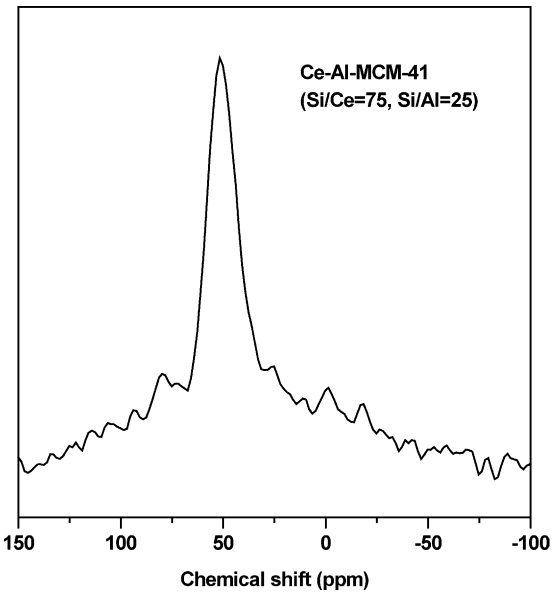


Fig. 3. ^{27}Al MAS NMR spectra of calcined (a) Ce–Al–MCM-41 (75, 25) where the values in parenthesis represents Si/Ce and Si/Al ratios, respectively.

surrounding the Ce center. The electronic transitions from oxygen to cerium require higher energy for a tetra-coordinated Ce^{4+} than for a hexa-coordinated one. Therefore, it may be inferred that the absorption band centered at 300 nm for Ce–MCM-41 samples is due to the presence of one type of well-dispersed Ce^{4+} species (presumably in tetra-coordinated environment), while amorphous SiO_2–CeO_2 sample predominantly contain hexa-coordinated Ce. To ascertain whether any Ce^{3+} phase is also present in Ce–MCM-41 and Ce–Al–MCM-41 samples, EPR measurements were carried out as Ce^{3+} is EPR active and Ce^{4+} is inactive. Cerium containing samples were found to be EPR inactive indicating the absence of Ce^{3+} in Ce-containing MCM-41 sample. This is also clear from the NMR studies where no effect of paramagnetic Ce^{3+} is seen. The ^{27}Al MAS NMR spectra of Ce–Al–MCM-41 (75–25) sample (Fig. 3) shows only single peak at 52 ppm which can be assigned to the tetrahedral coordination of the aluminum suggesting the total incorporation of aluminum in the silica network.

3.2. Acylation

The results of acylation of 1-hexanol used as probe molecule, over Ce–MCM-41, Si–MCM-41 and CeO_2 are given in Table 2. It is observed that the complete conversion of 1-hexanol with 95% yield of hexylacetate was obtained in just 3 h. However Si–MCM-41 and CeO_2 gave just 10 and 35% yield of hexylacetate, respectively, indicating the importance of the presence of isolated Ce ions in silicate network for high catalytic activity. The leaching of Ce from the MCM-41 lattice was checked. To verify the leaching of Ce as well as recyclability and reusability of Ce–MCM-41 catalyst, the used Ce–MCM-41 was recycled twice and used for the acylation of 1-hexanol. There was no significant decrease in the conversion or yield. The results of chemoselective acylation for substrates having more than one functional groups such as amino alcohols, mercaptoalcohols and diols over Ce–MCM-41 are also given in Table 2 exhibiting high chemoselective and preferred acylation of (i) NH_2 group vis-à-vis OH group, (ii) OH group vis-à-vis SH group and (iii) primary OH vis-à-vis secondary OH. These observations can be explained on the basis of higher nucleophilicity of the groups acylated preferentially. However, a mixture of mono- and di-acylated products was obtained in the ratio (82:18) in the case of 1,2-propanediol. The use of Ce–MCM-41 material was further explored to the bulkier molecules such as cholesterol, ergesterol and β-sitosterol (Table 3). Although it has been found that the reaction takes longer time in comparison with that of homogenous system [17], the replacement of homogenous system by heterogeneous one is desirable.

3.3. Alkylation

3.3.1. Effect of reaction parameters

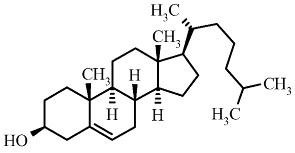
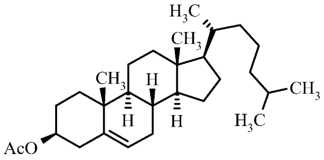
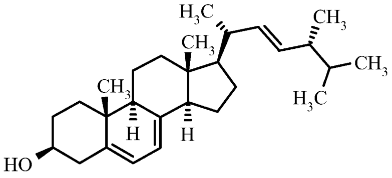
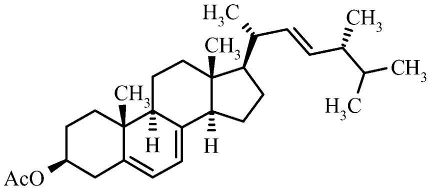
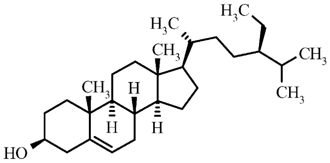
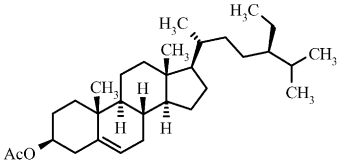
The cerium containing MCM-41 molecular sieves along with Al–MCM-41were also tested for the isopropylation of

Table 2
Chemoselective acylation of *n*-hexanol, amino alcohol, thiol and diol with acetic anhydride as acylating agent

Catalyst[a]	Substrate	RT[b] (h)	Product[c]	Yield[d] (mol%)
Ce–MCM-41	*n*-C_6H_{13}–OH	3[e]	*n*-C_6H_{13}–OAc	95
Si–MCM-41	*n*-C_6H_{13}–OH	9[e]	*n*-C_6H_{13}–OAc	10
CeO_2	*n*-C_6H_{13}–OH	9[e]	*n*-C_6H_{13}–OAc	35
Ce–MCM-41	HO–CH_2–CH_2–NH_2	4[e]	HO–CH_2–CH_2–NHAc	95
Ce–MCM-41	HS–CH_2–CH_2–OH	6[f]	HS–CH_2–CH_2–OAc	95
Ce–MCM-41	CH_3–CH(OH)–CH_2–OH	24[g]	CH_3–CH(OH)–CH_2–OAc	82
			CH_3–CH(OAc)–CH_2–OAc	18

[a] For Ce–MCM-41 Si/Ce ratio is 40.
[b] Reaction time.
[c] Products were characterized by usual spectral analyses.
[d] The isolated yield obtained after purification.
[e] Reaction was performed at 298 K.
[f] Reaction was performed at 358 K.
[g] Reaction was performed at 338 K.

Table 3
Acylation of bulkier molecules over Ce–MCM-41 (Si/Ce = 40)

Entry	Substrate	Reaction time (h)	Product[a]	Yield[b] (mol%)
1		24		76
2		24		72
3		24		72

Reaction conditions—substrate: acetic anhydride (mol/mol) = 1.0:1.1; temperature = 338 K; solvent = 5 ml acetonitrile.

[a] Products were characterized by usual spectral analyses.

[b] Isolated yield.

naphthalene and the results are summarized in Table 4. It was observed that Ce–Al–MCM-41 (75–25) having Si/Ce = 75, Si/Al = 25 is more active than the corresponding Al–MCM-41 (Si/Al = 25). Ce-impregnated Al–MCM-41 (Si/Ce = 75, Si/Al = 25) and Ce-exchanged Al–MCM-41 show much lower conversion than the parent Al–MCM-41. However, the selectivity of 1-isopropylnapththalene (1-IPN) and 2-isopropylnaphthalene (2-IPN) does not differ significantly under the same reaction conditions. Ce–MCM-41 was found to be inactive in the isopropylation of naphthalene under identical conditions. Almost 6 h were found to be sufficient for the reaction reaching to its maximum value and no further increase was observed with reaction time after 6 h.

It is therefore clear that for the isopropylation of naphthalene the presence of Al, i.e. Brönsted acidity, is required. Further, the Ce incorporation in Al–MCM-41 by exchange or impregnation method leads to decrease the activity probably due to possible blocking of the acidic Al sites and therefore reduces the overall acidity. However, Ce and Al are incorporated in Ce–Al–MCM-41 samples synthesized by in situ method leading to increased catalytic activity. Further experiments were carried out using Ce–Al–MCM-41 and Al–MCM-41.

Table 5 exhibits the effect of NP/IPA mole ratio. When naphthalene:isopropanol (NP/IPA) mole ratio was 4.0 (Table 5) no diisopropylated products were formed. As the ratio decreases from 4.0 to 0.25 through 1.0 more

Table 4
Isopropylation of naphthalene with isopropanol (IPA)[a]

Catalyst	NP Conv.[b]	$S_{\text{1-IPN}}$[c]	$S_{\text{2-IPN}}$[c]	S_{DIPN}
Ce–MCM-41 (25)[d]	0	0	0	0
Al–MCM-41 (25)[e]	32.9	28.4	71.6	0
Ce–Al–MCM-41 (75, 25)[f]	58.4	27.6	72.4	0
Ce–Al–MCM-41 (25, 75)[f]	2.5	20.1	71.9	0
Ce-Ex Al–MCM-41 (75, 25)[f]	24.5	26.7	72.3	1.0
Ce-Im Al–MCM-41 (75, 25)[f]	1.5	29.6	70.4	0

[a] Reaction conditions: catalyst = 10 wt.% of the substrate (naphthalene); $T = 423$ K; naphthalene: isopropanol (mol/mol) = 4.0; solvent = cyclohexane; cyclohexane—naphthalene (w/w) = 4.0; reaction time = 6 h.

[b] (Naphthalene conversion/theoretically possible naphthalene conversion) × 100.

[c] 1-IPN, 1-isopropylnaphthalene; 2-IPN, 2-isopropylnaphthalene.

[d] Numerical values in the parenthesis represents Si/Ce ratio.

[e] Numerical values in the parenthesis represents Si/Al ratio.

[f] Numerical values in the parenthesis represents Si/Ce and Si/Al ratio.

Table 5
Effect of naphthalene (NP) to isopropanol (IPA) molar ratios on the isopropylation of naphthalene with isopropanol[a]

Catalysts[b]	NP/IPA (mol/mol)	Naphthalene conversion (mol%)	Product distribution (mol%)		
			$S_{\text{1-IPN}}$	$S_{\text{2-IPN}}$	S_{DIPNs}
Al–MCM-41 (25)	4	32.9	28.4	71.6	–
	1	12.0	24.0	67.4	8.6
	0.25	3.9	21.2	61.6	17.2
Ce–Al–MCM-41 (75, 25)	4	58.4	27.6	72.4	–
	1	23.4	25.1	60.2	14.7
	0.25	10.0	21.5	45.2	33.3

[a] Reaction conditions: catalyst = 10 wt.% of the substrate (naphthalene); naphthalene: isopropanol (mol/mol) = 4.0; solvent = cyclohexane; cyclohexane: naphthalene (wt./wt.) = 4.0; reaction time = 6 h.

[b] Values in the parenthesis for Al–MCM-41 represents Si/Al ratio and Ce–Al–MCM-41, Si/Ce and Si/Al ratios respectively.

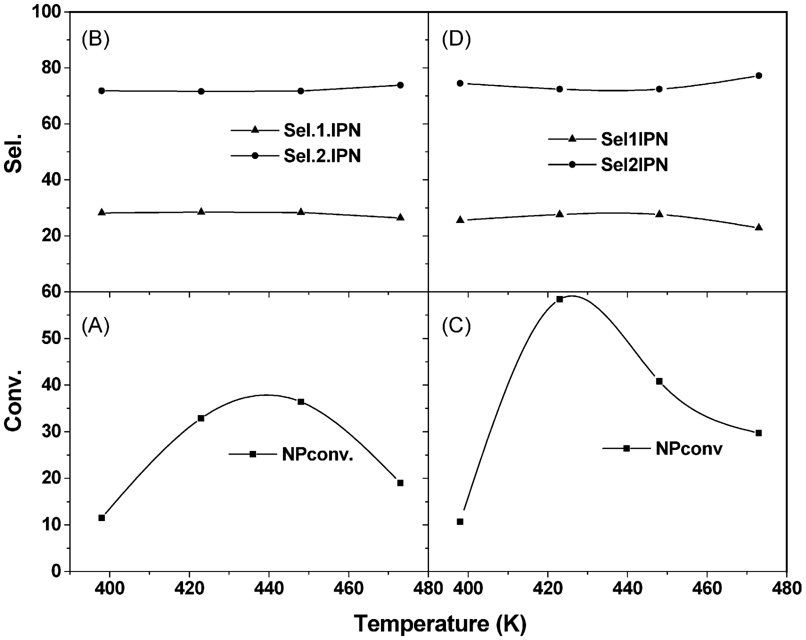


Fig. 4. Effect of temperature on the isopropylation of naphthalene using Al–MCM-41 (Si/Al = 25) and Ce–Al–MCM-41 (Si/Ce = 75, Si/Al = 25) in a pressure autoclave. Reaction conditions: naphthalene, IPA (mol/mol) = 4:1. (A) Conversion of naphthalene over Al–MCM-41 (75, 25) (■); (B) selectivity for 1-IPN (▲); selectivity for 2-IPN (●) over Al–MCM-41; (C) conversion of naphthalene over Ce–Al–MCM-41 (75, 25) (■); (D) selectivity for 1-IPN (▲); selectivity for 2-IPN (●) over Ce–Al–MCM-41 for the various temperature range from 398 to 473 K.

diisopropylnaphthalenes (DIPNs) were formed, as expected. Probably faster diffusion of 1-IPN and 2-IPN through the mesopores may also reduce the possibility of the formation of DIPNs.

The effect of reaction temperature on NP conversion obtained over Al–MCM-41 and Ce–Al–MCM-41 samples is compared in Fig. 4. As the reaction temperature increases the conversion also increases initially, as expected, and passes through maximum. It was observed that for Ce–Al–MCM-41 and Al–MCM-41 samples the optimum temperature was 423 and 448 K, respectively. Below the optimum temperature the NP conversion is low, as expected. However, a decrease in conversion with further increase in temperature beyond optimum temperature is rather intriguing. Probably at higher temperature the isopropanol may increasingly convert into propylene, which in a batch reactor may not be fully available for isopropylation reaction. Obviously, more work needs to be done to find out unambiguous explanation for this observation.

Both the Ce–Al–MCM-41 and Al–MCM-41 catalysts were tested for reusability where the used catalysts were reused two more times (Fig. 5). No significant change in either NP conversion or product selectivities was observed demonstrating that the catalysts can be reused. Interestingly, the selectivity of 1-IPN and 2-IPN remains almost constant throughout the course of reaction. It, therefore, proves that the relative concentration of 1-IPN and 2-IPN at any stage of the reaction is controlled thermodynamically and not kinetically. It may also be concluded that the formation of 1-IPN and 2-IPN are not diffusion controlled.

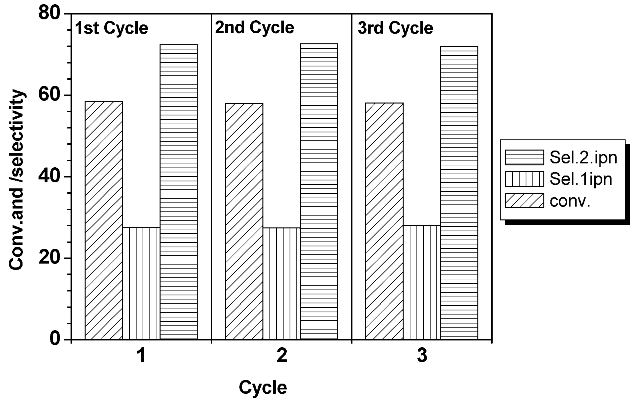


Fig. 5. Recycle studies of Ce–Al–MCM-41 (Si/Ce = 75, Si/Al = 25) upto three cycles.

3.3.2. Synergistic effect of simultaneous incorporation of Ce^{4+} and Al^{3+} in Ce–Al–MCM-41

It is clear from the above-mentioned results that Ce–Al–MCM-41 exhibits higher activity compared to Al–MCM-41 with comparable Si/Al molar ratio in both the samples. Hence, temperature-programmed desorption of ammonia (TPD-NH_3) experiments were carried out using H-form of Al–MCM-41 and Ce–Al–MCM-41 to find out the type and strength of acid sites in both the samples. Fig. 5 depicts the TPD-NH_3 spectra of Al–MCM-41 (Fig. 6A) and Ce–Al–MCM-41 (Fig. 6B). Deconvolution of broad peak clearly shows two peaks one centered at lower temperature and the other at higher temperature due to the presence of Lewis and Brönsted acid sites. However, quite interestingly, the maxima of both these peaks were at higher temperature

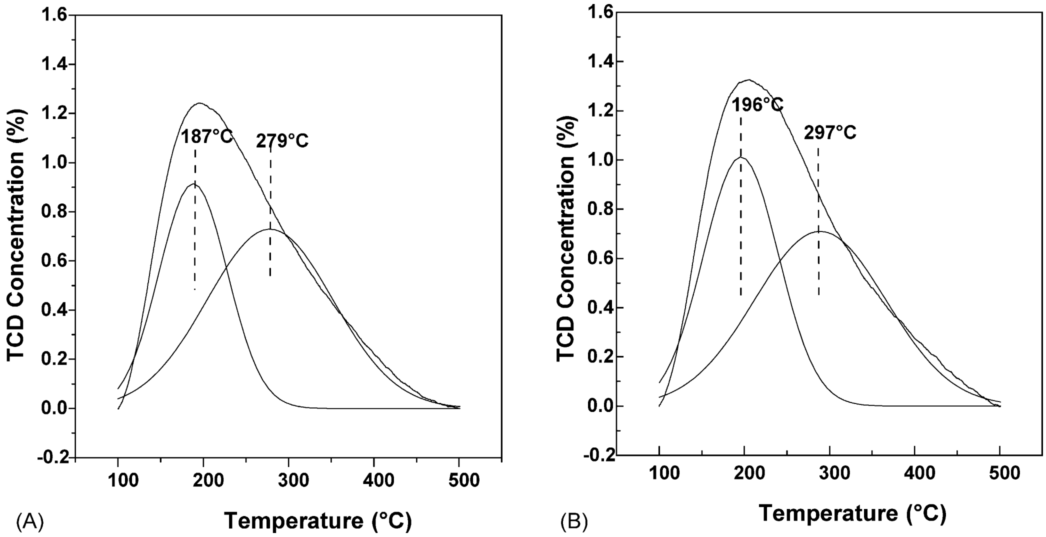


Fig. 6. Temperature-programmed desorption (TPD-NH_3) of (A) Al–MCM-41 (25) and (B) Ce–Al–MCM-41 (75, 25).

in the case of Ce–Al–MCM-41 vis-à-vis Al–MCM-41 with comparable Si/Al ratio of 25 clearly demonstrating the synergistic effect of simultaneous presence of cerium and aluminum in MCM-41 imparting higher acid strength and, therefore, higher activity to Ce–Al–MCM-41 compared to that of Al–MCM-41. Although, presently it is not clear why the simultaneous presence of both cerium and aluminum leads to increased acid strength, it is plausible that the presence of Lewis acid sites increases the strength of vicinal Brönsted acid sites. Efforts are going on to find unambiguous reason for this interesting new observation.

4. Conclusion

Ce–MCM-41 was found to be a good catalyst for the acylation of alcohols, amines and thiols in comparison with Si–MCM-41 and CeO_2. Bulkier molecules such as cholesterol, ergesterol and β-sitosterol are successfully acylated. Simultaneous incorporation of Ce and Al in MCM-41 (Ce–Al–MCM-41) leads to increased acid strength and therefore increased activity in the isopropylation of bigger molecules such as naphthalene. The reusability of the catalyst enables its use several times without substantial decrease in the activity.

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