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Dalton Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 11838

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PAPER

Chemoselective oxidation of primary alcohols catalysed by Ce(III)-complex intercalated LDH using molecular oxygen at room temperature†

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Received 17th June 2011, Accepted 19th August 2011
DOI: 10.1039/c1dt11140j

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Herein we describe the preparation of an efficient heterogeneous catalyst consisting of an anionic Ce(III)-complex immobilized Zn/Al-layered double hydroxide (LDH) and its use in the catalytic liquid phase oxidation of primary alcohols using molecular O_2 at room temperature. Various primary alcohols could be transformed to their corresponding aldehydes in good to excellent yields using the set of optimal conditions. The heterogeneous catalytic system can also be recovered and reused for several cycles without a significant loss of catalytic activity.

Introduction

Selective methods allowing for the oxidation of primary alcohols to aldehydes without over oxidation to carboxylic acids remain a challenging task from both laboratory and synthetic industrial chemistry points of view.[1] The desired carbonyl compounds serve as important and versatile intermediates for the synthesis of fine chemicals.[2] Many oxidations of these types are carried out using a stoichiometric amount of oxidising agent (*i.e.* $KMnO_4$, MnO_2, CrO_3, Br_2 *etc*) with considerable drawbacks such as high cost, by-products and serious environmental issues.[3] From the standpoint of green and sustainable chemistry, the development of catalytic systems that use molecular oxygen as the only oxidant has attracted great interest.[4] This has many remarkable advantages, including abundance, low cost, and the by-products are benign. In recent years, it has been targeted for use in various oxidation reactions because it is cheap, readily available and gives no co-product as pollutant.[5]

The creation of a well-defined, active metal site on a solid surface not only opens up an avenue to materials that boost catalytic performance but also aids an understanding of the molecular basis of heterogeneous catalysis.[6] Layered double hydroxides (LDHs) are a class of naturally occurring and synthetic materials, which can be described by the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{z+}(A^{n-})_{z/n}\cdot yH_2O$. M^{II} and M^{III} are divalent and trivalent metals respectively and A^{n-} is the anion that compensates for the positive charges of the metal hydroxide layers.[7] These hydrotalcite materials have received much attention as materials for advanced heterogeneous catalysts due to some promising avenues such as cation-exchange ability of brucite layers, the anion-exchange ability of the interlayer, its adjustable surface basicity, and adsorption capacity.[8] The immobilizations of different metal complexes within mesoporous supports have been extensively studied.[9] However studies on the intercalation of anionic transition metal complexes into LDH layers are rather limited.[10]

It has been demonstrated that LDH meets the requirement of an inorganic support for immobilizing anionic metal complexes[11] and may provide an alternative for homogeneous metal complexes. Recently main group element[12] and lanthanide[13] complexes with SALEN-type ligands were studied. Moreover, a heterogeneous catalyst in the liquid-phase offers several advantages over homogeneous ones, such as an ease of recovery and recycling, atom utility, and enhanced stability in the oxidation reactions. Noble metals, such as a styrene-divinylbenzene copolymer anchored Ru(III) complex,[14] a Pd(II) acetate–pyridine complex supported by hydrotalcite,[15] Ru hydrotalcites,[16] and a trimetallic $Ru/CeO_2/CoO(OH)$ catalyst[17] were reported to be active as heterogeneous catalysts for the oxidation of alcohols with molecular oxygen. V. R. Choudhary et.al. have reported solvent free oxidation of benzyl alcohol to benzaldehye using *tert*. butyl hydroperoxide as the oxidant using a transition metal containing LDH.[18] Kawabata *et al.* reported a nickel containing Mg–Al hydrotalcite-type anionic clay catalyst for the oxidation of alcohols with molecular oxygen, where they found a maximum of 69% conversion by using different Ni wt.%.[19] The oxidation of alcohols to aldehydes and ketones using Pd(II)-hydrotalcite in the presence of air has been reported by N. Kakiuchi *et al.*,[15] where they found a high conversion rate, but selectivity towards the aldehyde is less than 100% and the reaction was performed at 80 °C. Recently Bielawski *et al.* have reported the oxidation of alcohols to carbonyl compounds using inexpensive graphene oxide as a heterogeneous catalyst.[20] Aerobic oxidation of alcohols using metal–organic framework supported gold nanoparticles as a heterogeneous catalyst has been reported by Liu *et al.*[21]

The oxidation of alcohols using a heterogeneous catalytic system at room temperature would be more feasible from an industrial point of view. Here we describe a new protocol that offers

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1dt11140j

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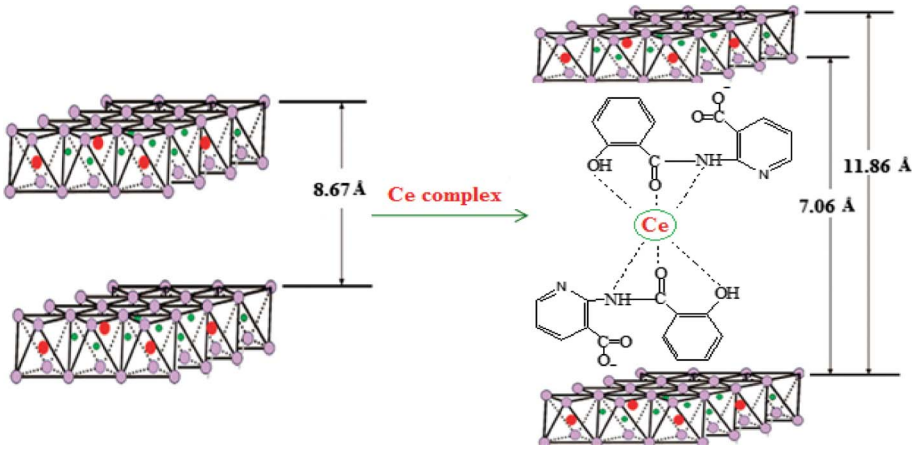

Scheme 1 The increase in gallery height due to intercalation of the Ce-complex.

a strategy for the design of a heterogeneous alcohol-oxidation catalyst *i.e.* anionic Ce(III)-complex intercalated LDH, for use in conjunction with molecular oxygen as the oxidant at room temperature.

Results and discussion

Catalyst characterization results

Fig. 1 shows the XRD patterns of (a) Zn/Al-LDH and (b) LDH/Ce-complex. The XRD pattern of Zn/Al-LDH shows sharp, symmetrical peaks at low angles corresponding to basal and higher order reflections. The basal spacing value (d_{003}) of Zn/Al–LDH is 8.67 Å, which agrees well with the literature.[22] In comparison with the Zn/Al-LDH, the (00l) reflections of LDH/Ce-complex moved to a lower 2θ angle, *i.e.*, from 10.2° to 7.8° (003) and from 20.3° to 15.4° (006). This corresponds to an increase in interlayer distance from 8.67 to 11.86 Å, which is indicative of the intercalation of the Ce-complex into the interlayer galleries of the LDH by anion exchange with NO_3^-. The gallery height was found to be 7.06 Å when the thickness of the brucite layer was subtracted (4.8 Å) from the basal spacing (Scheme 1). The (110) reflection at about 60° showed no obvious shift after intercalation, indicating that no significant change occurred in the LDH host layers.[23] In the case of the recycled catalyst (Fig. 1 (C) insert), all the peaks are retained in their respective position with respect to LDH/Ce-complex, suggesting the properties of the recycled catalyst remain unaltered.

FTIR spectroscopy is very helpful in the study of LDHs, especially those containing interlayer organic anions, as it is very sensitive to the symmetry of the organic anion and to the interactions of the anion with its environment such as hydrogen bonding and coordinate bonding. For the LDH nitrate precursor (Fig. 2(a)) the intense and broad absorption band centred at 3445 cm^{-1} corresponds to the stretching vibrations of the hydroxyl groups of both the layer hydroxide moieties and interlayer water.[24] The broadening of this band is due to hydrogen-bond formation. The band close to 1640 cm^{-1} corresponds to the deformation mode (δ H_2O) of water molecules. The band at 1384 cm^{-1} is assigned to the stretching vibration of interlayer NO_3^-. The bands around

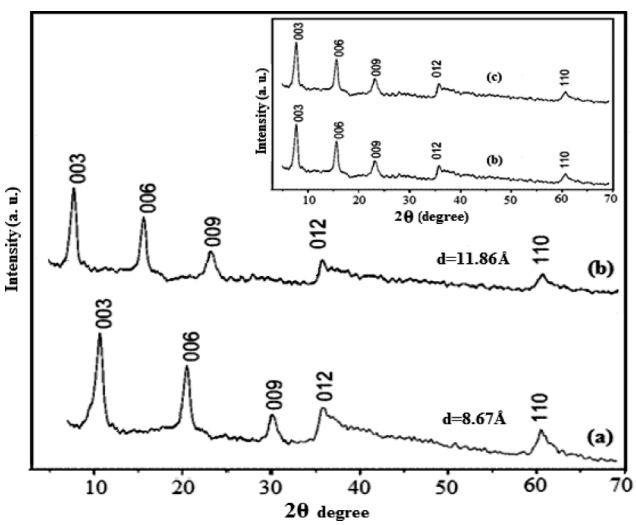

Fig. 1 XRD patterns of (a) Zn/Al-LDH (b) LDH/Ce-complex (c) recycled catalyst (insert).

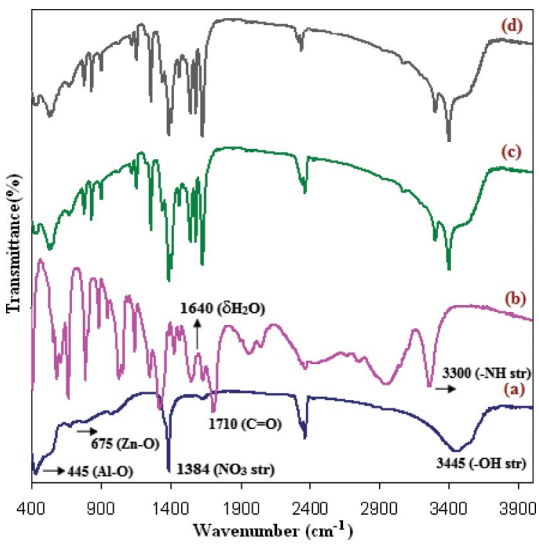

Fig. 2 FT-IR spectra of (a) Zn/Al-LDH, (b) Ce-complex, (c) LDH/Ce-complex and (d) recycled catalyst.

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445 and 675 cm^{-1} are due to Al–O and Zn–O lattice vibrations respectively. In Fig. (2(b) & (c)) the bands around 3300 cm^{-1} and 1577 cm^{-1} are due to N–H stretching and N–H bending for the secondary amide, respectively. The strongest and most characteristic absorption band for the carboxylate group is due to the antisymmetric COO^- vibration (ν_{as}) and appears in the region of 1570–1660 cm^{-1} for both the Ce-complex and LDH/Ce-complex. In case of LDH/Ce-complex, the bands are merged in the region of 3250–3450 cm^{-1}, which may be due to overlap of the N–H band of the amide and the O–H band of the brucite layer. All the above results indicate the successful intercalation of the Ce-complex in the interlayer space of LDH. All the vibrations do not change significantly in the recycled catalyst (Fig. 2(d)) compared to LDH/Ce-complex, which suggests the existence of all the properties.

The UV-vis DRS spectra of (a) LDH/Ce-complex (b) Ce-complex (c) Zn/Al-LDH are shown in Fig. 3. The spectra for the Ce-complex and complex intercalated LDH are very similar. Peaks around 250, 310 and 360 nm are due to intra-ligand transition. A broad peak around 480 nm is due to 4f–5d transition of the metal. But the peaks for the complex intercalated LDH slightly shifted to a higher wavelength compared to the metal complex. This is a direct indication for intercalation of the metal complex in between LDH layers. The heterogeneous catalyst was also well characterized by SEM, TGA and solid state NMR study (see ESI†).

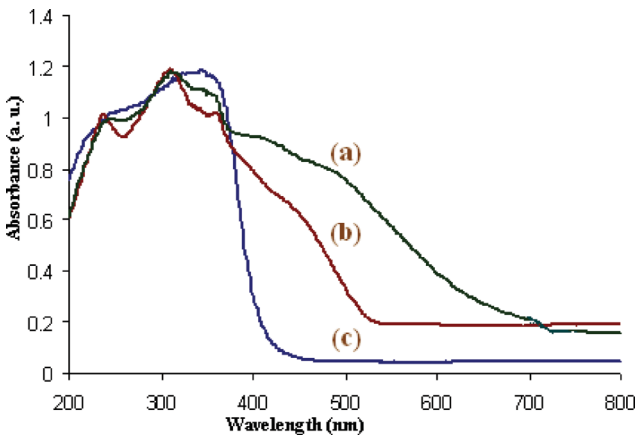

Fig. 3 UV-vis DRS spectra of (a) LDH/Ce-complex, (b) Ce-complex and (c) Zn/Al-LDH.

The oxidation of alcohols using different metal supported hydrotalcite hosts has been widely studied. M. L. Kantam *et al.* have reported a Cu–Al hydrotalcite/rac-BINOL system, where the aerobic oxidation of alcohols was performed at room temperature using K_2CO_3 as the base to promote the conversion.[25] In this present investigation, the oxidation of benzyl alcohol was examined as a standard substrate in the presence of a catalytic amount of LDH/Ce-complex, taking toluene as the solvent in the presence of molecular O_2. Generally, the possible oxidation products are benzaldehyde, benzoic acid and benzyl benzoate depending upon the reaction conditions and mechanistic pathway. It has been found in our experiment that benzaldehyde is the sole oxidation product with 100% selectivity (Table 1, entry 1). The oxidation of alcohols by activating molecular O_2 using different modified hydrotalcites (RuMnMn on hydrotalcite surface and nickel in Ni–Al hydrotalcite) have been reported by Ebitani *et al.*[26] and Choudhary *et al.*,[27] respectively, where the reactions were performed at higher temperatures. Compared to these previous studies, the most important feature in this investigation is that the reaction has been carried out at room temperature. In our present study, primary alcohols are quantitatively oxidized to aldehydes with good to excellent results, without any noticeable oxidation to carboxylic acid under optimal reaction conditions. In this context, the electronic influence of substitution on the phenyl ring has also been studied (Table 1, entries 5–7). An electron withdrawing group accelerates the reaction rate, while a donating group retards the reaction rate. Cinnamyl alcohol (Table 1, entry 8) is oxidized to give cinnamaldehyde and primary diol (Table 1, entry 9) is converted to dialdehyde. The oxidation of straight chain aliphatic alcohols (Table 1, entry 2 and 3) under standard reaction conditions took place effectively over this catalyst. The process reported here allows a convenient method for the oxidation of primary alcohols to aldehydes.

The possible mechanistic pathway for the oxidation of primary alcohols proceeds through the formation of a Ce-alcohol complex (ESI†). The subsequent step involves the reductive elimination to afford the aldehyde product.[28] Direct contact of gaseous oxygen with the catalytic active site is necessary for oxidation of alcohols, as only a trace amount of product was obtained when oxygen was not bubbled through the reaction mixture.[29] The LDH/Ce-complex catalytic system can be used for the selective oxidation of primary alcohols compared to secondary alcohols. Secondary alcohols are often oxidized faster than primary alcohols owing to the increase of electron density on the former. However, in our experiment we found primary alcohols are selectively oxidized in the presence of secondary ones (Table 2). An equimolar mixture of benzyl alcohol and 1-phenyl ethanol (Table 2, entry 1) gave a mixture of benzaldehyde and acetophenone in 96 and 37% conversion, respectively. Similarly, the competitive oxidation of 1-octanol and 4-octanol (Table 2, entry 2) showed 82 and 25% conversions. Furthermore, the process exhibits an unprecedented degree of chemoselectivity for the oxidation of primary hydroxyl groups in the presence of secondary ones. A similar type of results was observed by Kaneda *et al.*[16]

The effect of organic solvents on the oxidation was examined by choosing toluene as the model solvent, as polarity plays an important role in alcohol oxidation. Very little oxidation product was obtained with polar solvents such as acetonitrile and methanol (29 and 7% conversion, respectively). Non polar solvents such as benzene, hexane, cyclohexane and toluene lead to 76, 73, 79 and 96% conversion, respectively, in 8 h at room temperature. These results are in good agreement with those obtained by Choudhary *et al.*[27,30] It may presumably be due to the reason that polar solvents can be more strongly adsorbed than non polar solvents on the active sites of the catalyst surface and prevent the adsorption of alcohols, resulting in a net lowering in the reaction rate. To examine the effect of reaction time on the conversion percentage we have conducted the reaction up to 24 h. As expected, the conversion rate increases with time up to 8 h (Fig. 4) and maintained a steady rate up to 24 h, *i.e.* no appreciable change in conversion is observed with further increase in reaction time.

We believe that the employment of a chelating ligand has provided the major driving force behind the active metal catalyst,

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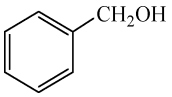
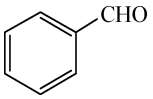
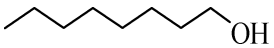
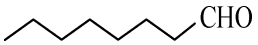
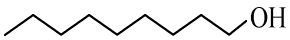
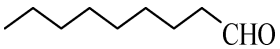
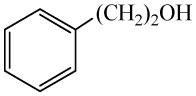
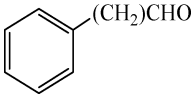
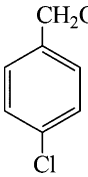
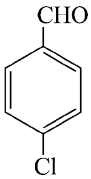
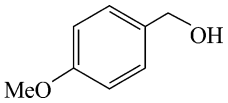
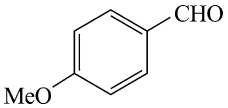
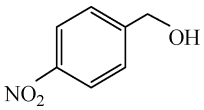
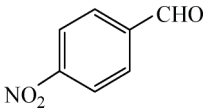
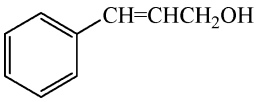
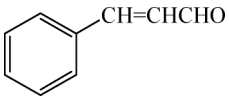
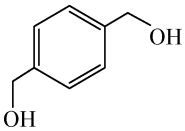
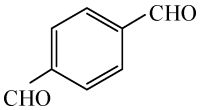
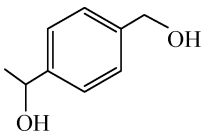
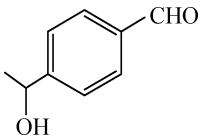
Table 1 The results of oxidations of various alcohols catalyzed by LDH/Ce-complex with molecular oxygen[a]

Entry	Substrate	Product	Time[b]/h	Conv./%	Selectivity/%	TOF[c]/h^{-1}
1			8	96	100	133
2			12	82	100	75
3			12	80	100	74
4			10	91	98	101
5			10	87	100	96
6			10	85	100	94
7			8	91	100	126
8			8	92	98	127
9			8	92	100	127
10			8	74	87	102

[a] *Reaction conditions*: alcohol (1 mmol), catalyst (50 mg, 0.09 mol% Ce), reaction performed at room temperature, molecular O_2 as oxidant, toluene as solvent (5 mL), conversion and selectivity were determined by gas chromatography. [b] Time required for maximum conversion. [c] Turnover frequency (TOF) = Turnover number (TON) per hour, TON calculated as (mol% of product)/(mol% of metal catalyst).

which in turn activates the molecular O_2 in the oxidation process. We have also tested our reaction by using the homogeneous Ce-complex, but it showed a maximum of 72% conversion for benzyl alcohol in similar reaction conditions in 12 h (Table 3). The lowering of the conversion rate in the case of the homogeneous complex compared to the heterogeneous catalyst may be attributed to the effect of immobilization. Again, this may presumably be due to the formation of a catalytic inactive μ-oxo dimer by the metal complex in the absence of the LDH support. For example, the iron(III) porphyrins and phthalocyanines under oxidising conditions form a dimer containing LFe-*O*-FeL linkages (where L is a macrocyclic ligand), and in this form they are unable to bind oxygen. But the enhanced catalytic activity could be attributed to the isolated catalytic sites in case of the complex immobilized LDH, which could prevent the formation of inactive dimers and other polymeric species.[31] Reutilization is one of the greatest advantages of a heterogeneous catalyst, which can also provide useful information about the intercalation process and catalytic

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Table 2 The selective oxidation of primary alcohols[a]

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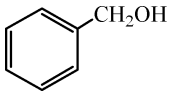
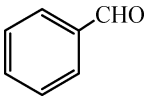
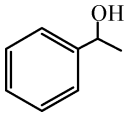
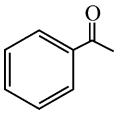
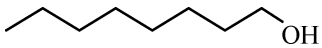
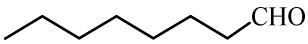
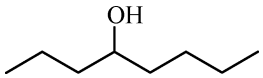
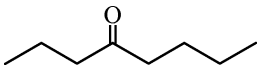
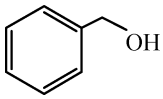
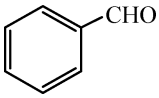
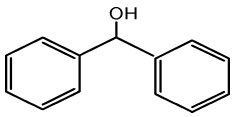
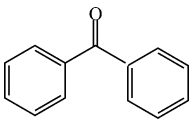
1			8	96
				37
2			12	82
				25
3			8	96
				33

[a] *Reaction conditions*: alcohol (1 mmol), catalyst (50 mg, 0.09 mol% Ce), reaction performed at room temperature, molecular O_2 as oxidant, toluene as solvent (5 mL), conversion was determined by gas chromatography. [b] Time required for maximum conversion.

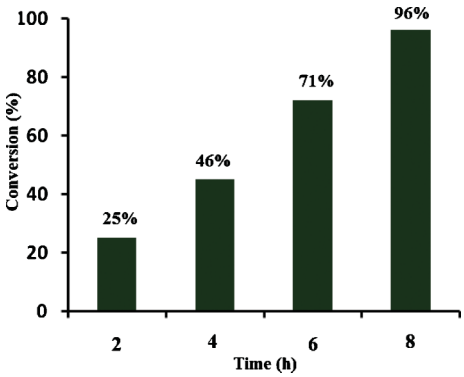


Fig. 4 The effect of time on the oxidation of benzaldehyde.

stability along the catalytic cycles. To test if metal is leached out from the solid catalyst during the reaction, the liquid phase of the reaction mixture is collected by filtration at the reaction temperature. It was confirmed by AAS technique that the Ce content of the used LDH/Ce complex catalyst was the same as that of the fresh catalyst and that no Ce was observed in the filtrate. In addition, the oxidation of alcohol (benzyl alcohol) was completely stopped by removal of the LDH/Ce complex from the reaction solution. The recovered catalyst was then subjected to XRD and FT-IR spectroscopy. Comparison of the XRD patterns and IR spectra of the LDH/Ce-complex and recovered catalyst convincingly demonstrates that the structural integrity of the complex intercalated LDH remains unaltered after the oxidation reaction. Notably, the recovered catalyst can be reused in oxidation reactions several times without appreciable loss of activity *i.e.* conversion and selectivity. (Table 4)

Table 3 The oxidation of benzyl alcohol by different catalysts[a]

Catalyst	Time[b]/h	Conv./%	Selectivity[c]/%
LDH	24	7	81
$Ce(NO_3)_3 \cdot 6H_2O$	12	41	87
Ce-amide complex	12	72	100
LDH/Ce-complex	8	96	100

[a] *Reaction conditions*: benzyl alcohol (1 mmol), catalyst (50 mg), reaction performed at room temperature, molecular O_2 as oxidant, toluene as solvent (5 mL), conversion and selectivity were determined by gas chromatography. [b] Time required to get maximum conversion. [c] Selectivity for benzaldehyde.

Table 4 Heterogeneity test up to 4 cycles[a]

Entry	Conv./%	Selectivity/%
Fresh	96	100
Cycle 1	96	100
Cycle 2	95	100
Cycle 3	94	100
Cycle 4	94	100

[a] *Reaction conditions*: benzyl alcohol (1 mmol), catalyst (50 mg), reaction performed at room temperature, molecular O_2 as oxidant, toluene as solvent (5 mL), conversion and selectivity were determined by gas chromatography.

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Conclusions

In summary, we have developed a heterogeneous catalyst by immobilizing an anionic Ce(III)-complex into the interlayer space of LDH, which provides a chemoselective oxidation of primary alcohols. The use of a heterogeneous reusable catalyst in the oxidation of alcohols at room temperature is an important protocol from an industrial point of view for large scale production, as it offers several advantages over the existed conventional method.

Experimental

Materials preparation

Preparation of LDH. Zn/Al-LDH was prepared by a co-precipitation method similar to that already reported in the literature.[32] A mixed metal nitrate solution containing mixtures of $Zn(NO_3)_2 \cdot 6H_2O$ (0.133 M) and $Al(NO_3)_3 \cdot 9H_2O$ (0.066 M) salts was prepared. The synthesis was carried out by the slow addition of 200 mL of mixed metal solution and 2 M NaOH solution simultaneously to a reaction vessel containing 50 mL of deionized water. The reaction pH was found to be 11 during the precipitation by the continuous addition of 2 M NaOH solution under magnetic stirring. A nitrogen atmosphere was maintained throughout the addition. The white precipitate obtained after 2 h was collected by filtration, washed several times with deionized water till washings were neutral and then dried at 100 °C overnight.[33] Elemental analysis showed the following composition; found/calcd (%) for $Zn_{0.68}Al_{0.32}(OH)_2(NO_3^-)_{0.32} \cdot 0.38H_2O$ (Zn,Al-LDH-NO_3): Zn 38.87/39.07, Al 7.53/7.63, N 3.86/3.93, H 2.19/2.26. IR (KBr, cm^{-1}) 3445, 1640, 1384, 675, 445.

Synthesis of the metal complex

2-aminonicotinic acid treated with Na_2CO_3 in an ethanolic medium produces the sodium salt of 2-aminonicotinic acid. Equimolar amounts of the sodium salt of 2-aminonicotinic acid (0.69 g, 5 mmol) and methyl salicylate (0.65 mL, 5 mmol) were refluxed in 20 mL of ethanolic solution to produce an amide ligand.[34] The final product was filtered, washed several times with ethanol and recrystallised from diethyl ether. The cerium complex was formed by refluxing 0.57 g (2 mmol) of ligand and 0.434 g (1 mmol) of $Ce(NO_3)_3 \cdot 6H_2O$ on a water bath at 50 °C using ethanol as the solvent for 4 h. The metal complex was isolated by filtration and washed repeatedly with ethanol to get rid of the unreacted ligand. Finally the metal complex was dried in vacuum and kept in a desiccator. Anal. found/calcd (%) for the ligand: C 55.9/56.31, H 3.21/3.24, N 10.05/10.10. For the Ce-complex: C 44.2/44.57, H 2.54/2.57, N 7.9/8. For the amide ligand: IR (KBr, cm^{-1}) 3300, 1705, 1660, 1590, 1570. For the Ce-complex: IR (KBr, cm^{-1}) 3295, 1703, 1655, 1587, 1564. For the amide ligand: ^{13}C CP MAS NMR (100.62 MHz, $CDCl_3$, δ) 115.1, 118.7, 130.4, 130.9, 132.1, 134.3, 134.7, 139.4, 142.1, 148.7, 158.4, 167.4, 169.8. For the Ce-complex: ^{13}C CP MAS NMR (100.62 MHz, $CDCl_3$, δ) 117.1, 120.2, 129.7, 131.6, 133.0, 133.7, 134.3, 137.8, 143.7, 147.9, 157.2, 165.8, 167.9.

LDH/Ce complex

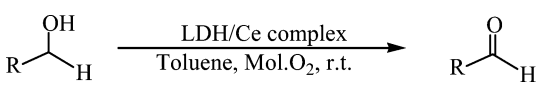
Zn/Al-LDH was dried under reduced pressure at 100 °C. To an ethanolic suspension of 1 g of dried LDH, 0.5 mmol of the metal complex was transferred and refluxed at 60 °C for 24 h with constant stirring. The final product was isolated by filtration, washed with ethanol and kept overnight in vacuum at 70 °C. Anal. found/calcd (%) for $[Zn_2Al(OH)_2(NO_3^-)_{0.01}](Ce\text{-complex})_{0.33} \cdot 0.63H_2O$ (Zn,Al-LDH/Ce complex): Zn 29.76/29.94, Al 6.01/6.18, C 23.22/23.57, N 4.18/4.24, H 2.08/2.1, Ce 10.58/10.63. IR (KBr, cm^{-1}) 3445, 3300, 3295, 1703, 1655, 1587, 1564, 1384, 675, 445.

Characterization techniques

Powder XRD measurements were performed on a Rigaku D/MAX2500 diffractometer, using Cu-Kα radiation at 40 kV, 30 mA, a scanning rate of 5° min^{-1}, and a 2θ angle ranging from 3° to 80°. The Fourier transform infrared (FTIR) spectra of the samples were recorded using a Varian 800-FTIR spectrometer. The powered samples were mixed with KBr and pressed in form of pellets for measurement of FTIR analysis in the range 4000–400 cm^{-1}. The co-ordination environments of the samples were examined by diffuse reflectance UV–vis spectroscopy. The spectra were recorded using a Varian-100 spectrophotometer in the wavelength range of 200–800 nm in $BaSO_4$ phase. Scanning electron microscopy (SEM) images were obtained using HITACHI 3400 N microscope. The samples were placed on a copper tape and then coated with a thin layer of platinum (layer thickness 3 nm) using a sputter coater. Thermogravimetric analysis (TGA) was performed under air with a Shimadzu TGA-50 system at a heating rate of 5 °C min^{-1}. The chemical composition of the products was confirmed quantitatively and qualitatively by energy dispersive X-ray (EDX) using a HITACHI 3400 N microscope. The Ce content in the catalyst and in the leaching solution was determined using atomic absorption spectroscopy (Perkin–Elmer AAS 300 with acetylene (C_2H_2) flame). The ^{13}C CP MAS NMR spectrum was recorded at 100.62 MHz using a Bruker Avance 400 MHz spectrometer.

Catalytic oxidation reaction

The oxidation of alcohols (Scheme 2) was typically carried out as follows: A suspension of LDH/Ce complex (50 mg) in toluene (5 mL) was stirred for 10 min. 1.0 mmol of alcohol was added to the reaction mixture and the suspension was purged with molecular oxygen. The concentration of the molecular oxygen (oxygen stream) in toluene is 10 mL min^{-1}. The reaction was started by bubbling O_2 gas through the reactor under vigorous stirring at room temperature for 8 h. After completion of the reaction, the catalyst was separated by filtration/centrifugation. The solid residue was washed with EtOAc to make the catalyst free from organic matter for further reuse. The product was analyzed by GC-2010 (Shimadzu) equipped with a capillary column (ZB-WAX, 30 m, 0.25 mm I.D) and flame ionization detector (FID).



Scheme 2

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Acknowledgements

The authors are extremely thankful to Prof. B. K. Mishra, Director, IMMT, Bhubaneswar 751013, Orissa, India, for his constant encouragement and permission to publish the paper. One of the authors S. Singha is obliged to CSIR for a senior research fellowship.

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