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Magnetically recoverable lanthanum hydroxide as an efficient catalyst for Aerobic Oxidative Conversions of primary alcohols to the nitriles

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Herein we report a novel magnetically recoverable lanthanum hydroxide nanoparticles for oxidative synthesis of nitriles directly from corresponding alcohols with ammonia as nitrogen source. The procedure for the preparation and characterization of $La(OH)_3/Fe_3O_4$ magnetic nanoparticles were investigated and the scope and generality of the method was explored for a series of structurally diverse primary alcohols with electron-donating and electron-withdrawing groups. The best result was observed when 5 mol% of La with respect to the benzyl alcohol was used at reflux condition under O_2 atmosphere. The $La(OH)_3/Fe_3O_4$ magnetic nanoparticles could be easily isolated from the reaction mixture with an external magnet and reused at least 5 times without significant loss in activity.

KEYWORDS
direct oxidative nitrile synthesis, Lanthanum hydroxide, magnetic catalyst, primary alcohols

1 | INTRODUCTION

Nitriles are an important molecular scaffold for the synthesis of various organic moieties like esters, acids, amines, amides, and ketones which are important synthetic precursors of natural products,[1] pharmaceuticals,[2] agricultural chemicals and dyes.[3] Historically, the Sandmeyer reaction,[4] Rosenmund–von Braun reaction,[5] and gas-phase oxidation were used for the laboratorial and industrial synthesis of aryl nitriles, respectively. The nucleophilic substitution of alkyl halides with toxic inorganic cyanide salts in stoichiometric amount were also reported for the synthesis of alkyl nitriles. For the synthesis of unsaturated nitriles, aldehydes and cyano alkylphosphates were reacted via Wittig reaction.[6] A less toxic cyanation reagent $(K_3[Fe(CN)_6])$,[7] and non-metallic cyanation sources[8] have been reported previously. These methods traditionally suffered from the use of toxic reagents, production of large amounts of organic waste and inorganic salts,

low yields and difficulty of product purification, which are in contradiction with the green chemistry standpoint. Therefore, the development of new synthetic pathways under mild conditions for the synthesis of nitriles is of significant interest.

In the last years, new procedures using different catalysts and compounds have been reported. Transition metal-catalyzed dehydration of aryl oximes or amides is one of these green approaches for the synthesis of nitriles.[9] Also, different studies have been reported for oxidative dehydrogenation of benzyl alcohols,[10] azides[11] and methyl arenes.[12] The oxidative synthesis of nitriles directly from alcohols or aldehydes with ammonia as a nitrogen source instead of inorganic cyanides was investigated as an eco-friendly and green method using inexpensive and available substrates and nitrogen source with only water as byproduct which lead to the high atom efficiency. Also, a few approaches have been reported for the synthesis of nitriles directly from alcohols which in the most of them the stoichiometric amount of oxidants

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and reagents were needed.[13,14] In this regard, different reagents such as I_2, I_2/DIH, I_2/TBHP, $NiSO_4$/$K_2S_2O_8$/NaOH, MnO_2/$MgSO_4$, and $(Bu_4N)_2S_2O_8$/Cu-$(HCO_2)_2$/Ni$(HCO_2)_2$/KOH were reported.[10] Abundance of inexpensive molecular O_2 has made it an excellent oxidant with benign byproducts (usually only H_2O). Tao,[15] Huang,[16] Muldoon,[17] and Stahl[18] reports showed that Cu/TEMPO (TEMPO=2, 2, 6, 6-tetramethylpiperidine- N-oxyl) system efficiently catalyzes the aerobic oxidative transformation of alcohols or aldehydes to the corresponding nitriles in aqueous ammonia as nitrogen source under mild reaction conditions. The formation of nitriles from aldehydes has been promoted with Ag nanoparticles and $K_4Fe(CN)_6$.[19] Also, O-(4-CF_3-benzoyl)-hydroxylamine as organic acid catalyst was reported for this transformation.[20] These methods offer great improvements but purification and separation problem of these systems still needs to be improved. Recently, the Mizuno group reported that heterogeneous Ru$(OH)_x$/Al_2O_3 system acts as an efficient catalyst for aerobic oxidative transformation of alcohols into nitriles by using ammonia in THF.[21] Ishida group subsequently disclosed a method using MnO_2 under pressured oxygen and NH_3 gas.[22] These efficient systems suffer from high reaction temperature which needs to an autoclave in many cases. The metal hydroxides have both Lewis acid and Brønsted base properties. This acidic and basic properties derive from the same metal and the most of organic transformations likely be promoted by the 'concerted activation' of the Lewis acid and Brønsted base sites.[23–25] Based on literatures, the nitrile hydration with monomeric Co[III]–OH complexes occurs via coordination of nitriles to the Co[III] Lewis acid centers and intramolecular nucleophilic attack of the hydroxide species as Brønsted base on the proximal activated nitrile carbon.[26] Synthesis of nitriles from alcohols with ammonia and O_2 are likely promoted by the concerted activation of the Lewis acid and Brønsted base sites in three steps: 1) the sequential oxidation reactions of the alcohol,[27] 2) Dehydrative condensation of the formed aldehyde with ammonia, and 3) Oxidation of imine.[28] Nevertheless, the intricacy of catalysts recovery and workup procedures are the major drawback of these catalytic reactions. Recently, we have developed efficient magnetic heterogeneous catalyst for organic functional group transformation.[29] Investigation of the supported magnetic nanoparticles with easy separation ability from the reaction mixture has become an important choice. Their insolubility and magnetic nature make it possible to realize various reactions and reduce the capital and operational costs.[30]

In this project we design a novel magnetically recoverable lanthanum hydroxide nanoparticles for oxidative synthesis of nitriles directly from corresponding alcohols and ammonia as nitrogen source. To the best of our knowledge, employing Fe_3O_4/La$(OH)_3$MNPs as a catalyst in aerobic oxidative synthesis of nitriles has not been disclosed. This method is a highly desirable method due to the easy separation and recovery of catalyst, mild reaction conditions, and high yields of products.
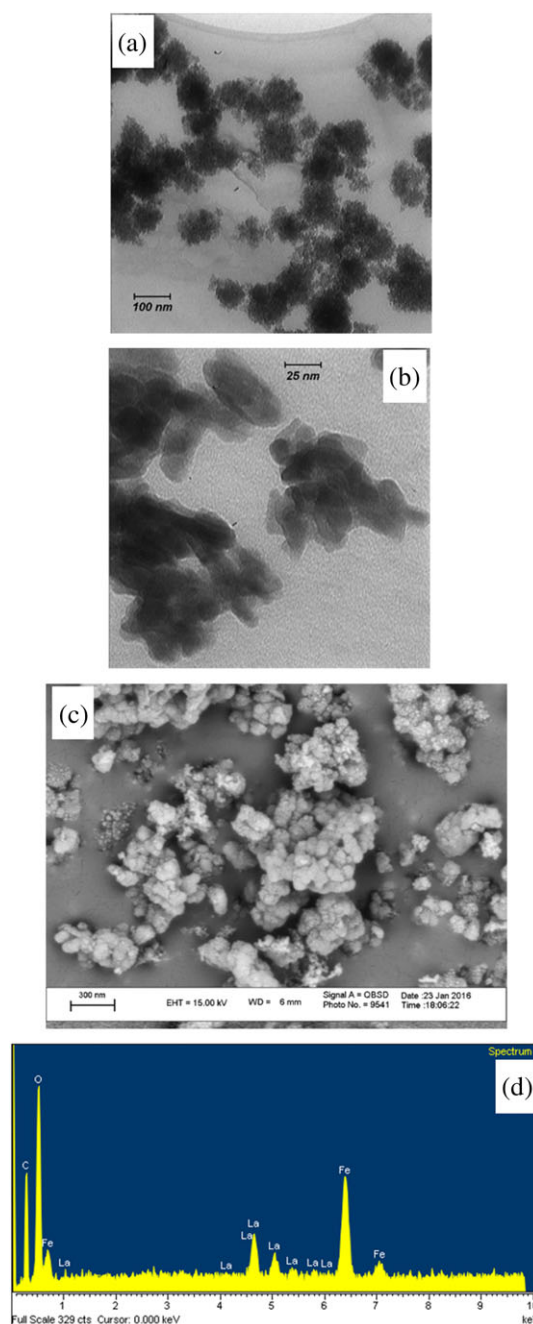

FIGURE 1 TEM images of (a) Fe_3O_4 MNPs, (b) La$(OH)_3$/Fe_3O_4, (c) SEM image of La$(OH)_3$/Fe_3O_4, (d) EDS analyzes of La$(OH)_3$/Fe_3O_4

2 | EXPERIMENTAL

2.1 | Synthesis of Fe_3O_4 magnetic nanoparticles

Fe_3O_4 Magnetic nanoparticles were prepared via a previously reported hydrothermal method.[31] $FeCl_3.6H_2O$ (0.8 g), sodium acetate (2 g,) and (0.75 g) trisodium citrate were dissolved in ethylene glycol (35 ml) under vigorous stirring for 30 min. The resulting solution was transferred into a Teflon-lined stainless-steel autoclave with 50 ml of capacity and heated to 200 °C for 16 h. The obtained black Fe_3O_4 MNPs were collected with a magnet and washed several times with water and ethanol and dried at 80 °C.

2.2 | Synthesis of $La(OH)_3/Fe_3O_4$ magnetic nanoparticles

The $La(OH)_3/Fe_3O_4$ MNPs were synthesized by a facile sol–gel method. Typically, 0.15 g Fe_3O_4 was added to the three-neck round bottom flask followed by addition of 35 ml ethanol/water solution (1:1) containing 0.5 g $LaCl_3.7H_2O$. The mixture was sonicated for 30 min, and then 15 ml 0.5 M ethanol solution of NaOH was added and stirred for 30 min. The reaction was maintained at 80 °C for 12 h. The black precipitate was collected by an external magnet and then dried at 80 °C for 6 h.

2.3 | Direct oxidative synthesis of nitriles from primary alcohols

1 mmol of primary alcohol, 5 mol% of $La(OH)_3/Fe_3O_4$, 2 ml of 1,4-Dioxane, and NH_3 (equiv. NH_3/alcohol= 2.2) were refluxed under O_2 balloon. The reaction process was monitored by thin layer chromatography (TLC). After the completion of the reaction, the catalyst was separated by an external magnet, washed with ethanol, aqueous solution of NaOH and water. The catalyst was then dried at 80 °C in oven. The products were isolated by a silica gel column chromatography and final nitriles were confirmed by Mass spectra, ^1H and ^{13}C NMR spectra (see supporting information).

3 | RESULTS AND DISCUSSION

For morphology study of $La(OH)_3/Fe_3O_4$ TEM and SEM analyzes were used. As shown in Figure **1a** the Fe_3O_4 nanoparticles are in spherical shape with average diameters of about 20 nm. TEM image of $La(OH)_3/Fe_3O_4$ are almost rod shaped lanthanum hydroxides which attached with spherical magnetic nanoparticles with average diameters of about 50 nm (Figure 1b). Figure 1c show the SEM image of $La(OH)_3/Fe_3O_4$ nanocatalyst with an aggregated spherical morphology, probably due to the magnetic nature of catalyst. The content of La in the sample was 21.55% based on inductively coupled plasma/optical electron microscopy (ICP-OES). The EDS result (Figure 1d) showed that the elemental composition of the nanocatalyst are Fe, O, and La which agrees well with the XRD analysis (Figure 2).

As shown in Figure 2, XRD analysis was used for the crystalline structure study of Fe_3O_4 and $La(OH)_3/Fe_3O_4$. Six diffraction peaks at 2θ = 30.31, 35.64, 43.31, 53.86, 57.24, 62.83 attributed to the spherical phase planes of the Fe_3O_4 crystal [34] according to the JCPDS card no. 19-0629 (Figure 2a). As shown in Figure 2b, the characteristic peaks of Fe_3O_4 becomes weak in $La(OH)_3/Fe_3O_4$ due to the heavy atom effect of La. Also, new peaks indexed according to the JCPDS card No. 36-1481 were appeared which attributed to the hexagonal $La(OH)_3$ crystalline structure.[32]

The magnetic nature of $La(OH)_3/Fe_3O_4$ was shown in Figure 3. The $La(OH)_3/Fe_3O_4$ exhibit a ferromagnetic behavior at the room temperature. The magnetic saturation value (Ms) of the $La(OH)_3/Fe_3O_4$ is 62 emu/g. These
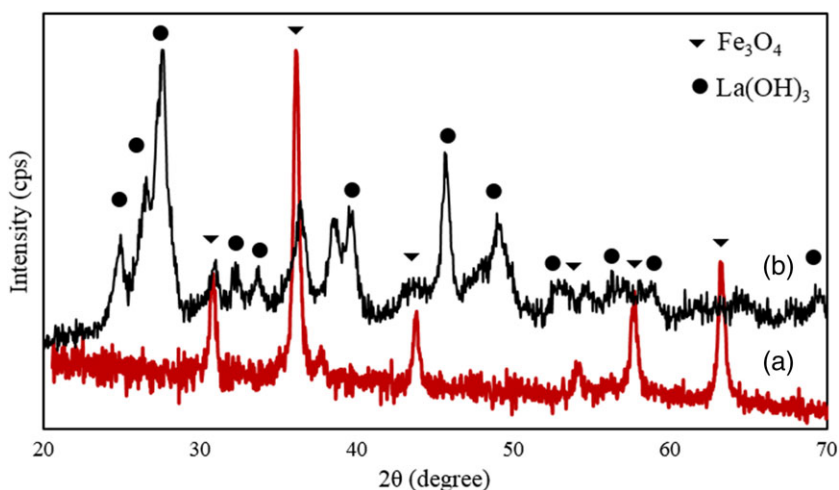
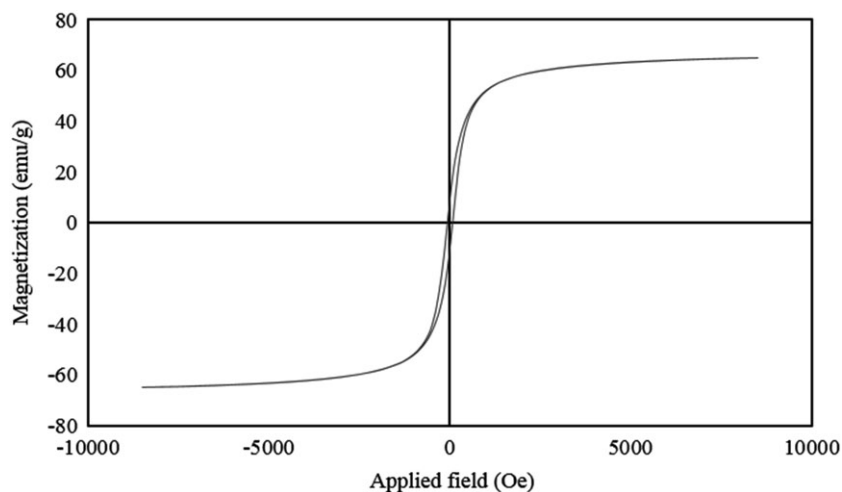**FIGURE 2** XRD patterns of (a) Fe_3O_4 and (b) $La(OH)_3/Fe_3O_4$

FIGURE 3 Magnetization hysteresis loops of La(OH)$_3$/Fe$_3$O$_4$ nanocatalyst

results demonstrate that the La(OH)$_3$/Fe$_3$O$_4$ particles possess magnetic properties.

The catalytic activity of prepared La(OH)$_3$/Fe$_3$O$_4$ evaluated in aerobic oxidative conversion of benzyl alcohol to benzonitrile as a model reaction in ammonia as a nitrogen source under an oxygen balloon. For investigation of reaction condition different parameters were studied after 1.5 h of beginning of the model reaction (Table 1). At first,

the catalyst amount was studied in the model reaction. The best result was observed when 5 mol% of La with respect to the benzyl alcohol was used at reflux condition (Table 1, entries 1-3). Dimethyl sulfoxide (DMSO), 1,4-Dioxane, and toluene were examined as reaction solvents which shows a good performance and final benzonitrile was produced in 70, 75, and 75 % of yields, respectively (Table 1, entries 2, 4, and 5). In case of toluene the

TABLE 1 Optimization of reaction conditions[a]

Entry	Cat. (mol %)	Solvent	T (°C)	1a:NH$_3$ (equiv.)	Yield 1b (%)
1	La(OH)$_3$/Fe$_3$O$_4$ (10)	DMSO	reflux	1:1	71
2	La(OH)$_3$/Fe$_3$O$_4$ (5)	DMSO	reflux	1:1	70
3	La(OH)$_3$/Fe$_3$O$_4$ (2)	DMSO	reflux	1:1	20
4	La(OH)$_3$/Fe$_3$O$_4$ (2)	1,4-Dioxane	reflux	1:1	75
5	La(OH)$_3$/Fe$_3$O$_4$ (2)	Toluene	reflux	1:1	75
6	La(OH)$_3$/Fe$_3$O$_4$ (2)	EtOH	reflux	1:1	10
7	La(OH)$_3$/Fe$_3$O$_4$ (2)	MeOH	reflux	1:1	8
8	La(OH)$_3$/Fe$_3$O$_4$ (2)	H$_2$O	reflux	1:1	10
9	La(OH)$_3$/Fe$_3$O$_4$ (2)	1,4-Dioxane	80	1:1	65
10	La(OH)$_3$/Fe$_3$O$_4$ (2)	1,4-Dioxane	50	1:1	30
11	La(OH)$_3$/Fe$_3$O$_4$ (2)	1,4-Dioxane	rt.	1:1	–
12	La(OH)$_3$/Fe$_3$O$_4$ (2)	1,4-Dioxane	reflux	1:1.2	77
13	La(OH)$_3$/Fe$_3$O$_4$ (2)	1,4-Dioxane	reflux	1:1.7	79
14	La(OH)$_3$/Fe$_3$O$_4$ (2)	1,4-Dioxane	reflux	1:2.2	87
15[c]	Fe$_3$O$_4$	1,4-Dioxane	reflux	1:2.2	–
16[c]	LaCl$_3$	1,4-Dioxane	reflux	1:2.2	–
17	–	1,4-Dioxane	reflux	1:2.2	–

[a]Reaction condition: **1a** (1 mmol), catalyst (La: 5 mol% with respect to **1a**), NH$_3$ (2.2 mmol), and solvent (2.0 mL) under an O$_2$ balloon at reflux for 1.5 h. [b] isolated yield. [c] 0.15 mg of catalyst.

TABLE 2 Scope of the La(OH)$_3$/Fe$_3$O$_4$ catalyzed direct conversion of benzyl alcohols to nitriles[a]

Reaction scheme: benzyl alcohol + OH + NH$_3$ (aq) → La(OH)$_3$/Fe$_3$O$_4$ 5 mol% / 1,4-Dioxane (2 ml) / reflux → benzonitrile CN

Entry	Substrate	Time (h)	Product	Yield (%)
1	benzyl alcohol (OH)	2	benzonitrile (CN)	95
2	Br-substituted benzyl alcohol (OH)	2	Br-substituted (CN)	94
3	Cl-substituted benzyl alcohol (OH)	2	Cl-substituted (CN)	93
4	O$_2$N-substituted benzyl alcohol (OH)	2.5	O$_2$N-substituted (CN)	90
5	HO-substituted benzyl alcohol (OH)	2.5	HO-substituted (CN)	91
6	EtO-substituted benzyl alcohol (OH)	1.5	EtO-substituted (CN)	96
7	CH$_3$-substituted benzyl alcohol (OH)	2	CH$_3$-substituted (CN)	94
8	(Me)$_2$N-substituted benzyl alcohol (OH)	2.5	(Me)$_2$N-substituted (CN)	95
9	MeO, OMe-substituted benzyl alcohol (OH)	2	MeO, OMe-substituted (CN)	90
10	OMe, OMe-substituted benzyl alcohol (OH)	3	OMe, OMe-substituted (CN)	88
11	MeO, MeO, OMe-substituted benzyl alcohol (OH)	2	MeO, MeO, OMe-substituted (CN)	93
12	pyridyl methanol (OH)	3	pyridyl (CN)	89
13	thienyl methanol (OH)	3	thienyl (CN)	91
14	pentanol (OH)	24	–	0
15	isobutanol (OH)	24	–	0

[a]Reaction conditions: benzyl alcohol (1 mmol), aqueous NH$_3$ (2.2 equiv.), La(OH)$_3$/Fe$_3$O$_4$ (5 mol%), 1.4-Dioxane (2 ml) under O$_2$ balloon at reflux.

reaction proceed in extended time, probably due to the low solubility of ammonia in toluene. Also, ethanol, methanol and water were examined as protic solvents but very low yield of benzonitrile was observed which can be attributed to strong coordination ability of protic solvents to the lanthanum active sites of catalyst (Table 1, entries 6-8). Based on these results 1,4-Dioxane was selected as a reaction solvent. As the reaction temperature decrease from 80 °C to room temperature the product yield was dropped (entries 9-11). Also, when

equivalent of ammonia was increased the higher yield of benzonitrile was achieved in shorter time (entries 12-14). Results revealed that in the absence of any catalyst the reaction does not proceed. The same results were achieved when Fe_3O_4 and $LaCl_3$ was used as reaction catalyst (Table 1, entries 15-17).

The above results showed the high efficiency of $La(OH)_3/Fe_3O_4/NH_3/O_2$ system in the conversion of benzyl alcohols to aryl nitriles. Based on the optimized conditions, the scope and generality of the process was explored for a series of structurally diverse primary alcohols as summarized in Table 2. Benzyl alcohols with electron-donating and electron-withdrawing groups could convert into the corresponding substituted benzonitriles with excellent yields (90–96%, Table 2, entries 1-8). The position of substituents on benzyl alcohol did not much affect the reaction. The reaction conversions of multi substituted benzyl alcohols (Table 2, entries 9-11) and hetero-aromatic alcohols (Table 2, entries 12 and 13) were also good. However, aliphatic primary alcohols could not be converted to the desired products in this catalytic system (Table 2, entries 14 and 15).

The heterogeneity of the catalyst was also studied. The transformation of benzyl alcohol to benzonitrile was proceed under the optimized reaction condition and after 1 h the $La(OH)_3/Fe_3O_4$ was removed from the reaction mixture by an external magnet. After removal of the catalyst the filtrate was analyzed with ICP-OES analysis that no lanthanum was detected. This study revealed that no lanthanum species was leached into the reaction solution and showed the heterogeneity of the catalyst.[33]

Recovery and reusability of $La(OH)_3/Fe_3O_4$ was studied in the model reaction. After completion of the reaction $La(OH)_3/Fe_3O_4$ was separated from the reaction mixture by an external magnet, washed with ethanol, aqueous solution of NaOH, and water and then dried at 80 °C for 2 h. The catalyst was used at least in 5 successful runs without significant decrease in activity (Figure 4a). Reaction conditions: benzyl alcohol (1 mmol), aqueous NH_3 (2.2 equiv.), $La(OH)_3/Fe_3O_4$ (5 mol%), 1.4-Dioxane (2 mL) under O_2 balloon at reflux. Based on ICP-OES results the La content of $La(OH)_3/Fe_3O_4$ after 5 recycles was 19.47% which shows about 2% of La leaching after 5 recycle. For the morphology study of recycled catalyst TEM image of $La(OH)_3/Fe_3O_4$ after 5 recycle was taken which in comparison with TEM of catalyst before any catalytic use (Figure 1b) no morphology changes were found. Based on this observation we can conclude that the morphology of catalyst remains unchanged after 5 recycle (Figure 4b). The yield dropping of oxidation product after 5 recycle can be attributed to the leaching of La moieties.
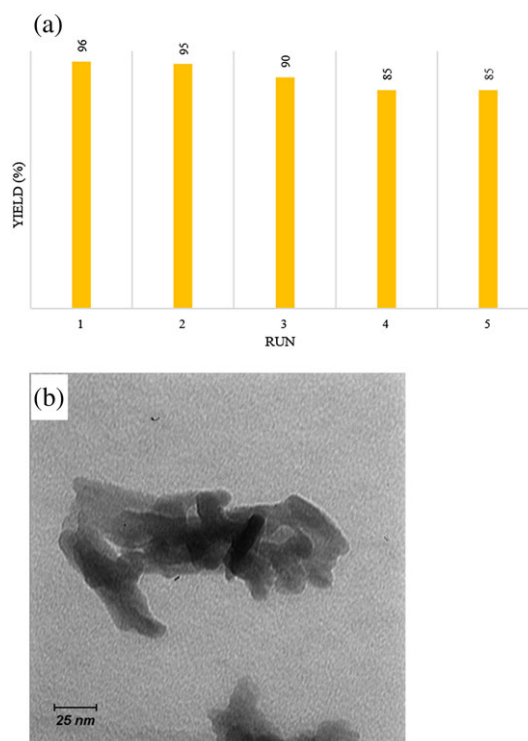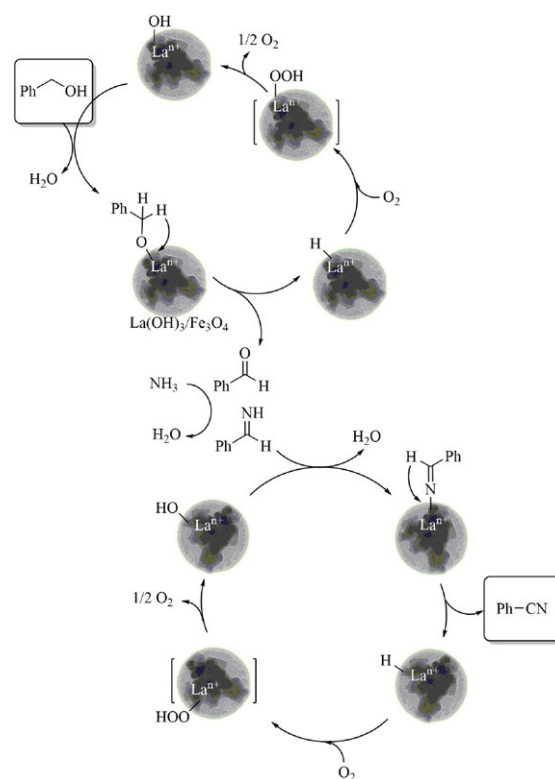

FIGURE 4 (a) Recycling test for $La(OH)_3/Fe_3O_4$ catalyzed oxidative synthesis of benzonitrile, (b) TEM image of recycled catalyst

SCHEME 1 A possible mechanism of $La(OH)_3/Fe_3O_4$ catalyzed synthesis of nitriles from alcohols

The model reaction process which was monitored by TLC showed that in the early stages of the reaction benzaldehyde was formed which followed by the formation of benzonitrile. These results are similar to the previously proposed mechanism for this reaction.[49] Thus, the La(OH)$_3$/Fe$_3$O$_4$-catalyzed transformation of benzyl alcohols to the corresponding benzonitriles possibly proceeds through three sequential reactions: 1) The aerobic oxidative dehydrogenation of alcohols to aldehydes,[51] 2) Dehydrative condensation of the aldehydes and ammonia into imines and 3) The aerobic oxidative dehydrogenation of the imines to produce the corresponding nitriles.[52] A possible mechanism of the reaction summarized in Scheme 1.

4 | CONCLUSION

A novel magnetically recoverable lanthanum hydroxide nanoparticles were synthesized for the oxidative synthesis of nitriles directly from corresponding alcohols with ammonia as nitrogen source. The scope and generality of the process was explored for a series of structurally diverse primary alcohols with electron-donating and electron-withdrawing groups with 5 mol% of La with respect to the benzyl alcohol at reflux condition under O$_2$. This catalyst can be easily separated and recovered with an external magnet from the reaction mixture for further use which act as an efficient heterogeneous catalyst for the aerobic oxidative synthesis of nitriles directly from alcohols without producing the over-oxidation products-benzoic acids. This catalyst provides a green method for nitrile synthesis, which avoids the use of the conventional inorganic cyanides. Also, the catalyst was recovered and reused at least for 5 successful runs without significant decrease in catalytic activity.

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SUPPORTING INFORMATION

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