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NANO-SIZED $La_{0.5}Ca_{0.5}CoO_3$-MEDIATED REDUCTION BY $NaBH_4$ OF ARYL NITRILES TO BIS-(BENZYL) AMINES

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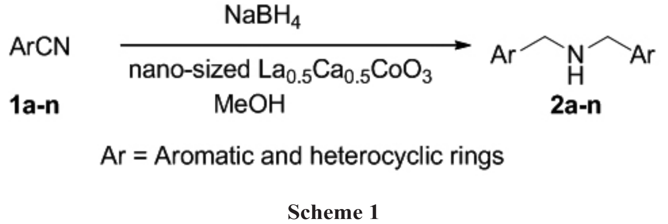
ABSTRACT

Nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite, which was produced via the sol-gel method, was an efficient heterogeneous catalyst in combination with $NaBH_4$ for the rapid chemoselective reduction of aryl nitriles to bis-(benzyl)amines at 40 ºC in good to excellent yields. The physico-chemical properties of the catalyst were characterized by means of differential thermal analysis (DTA), thermogravimetric analysis (TGA), X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and particle size distributions images. The results show that nanoparticles have regular shapes with well-defined crystal faces with an average size of 30 nm.

Keywords: perovskite, nanocatalyst, sec-amines, reduction.

INTRODUCTION

The prevalence and extensive use of amines as starting materials for plastics, agrochemicals, and dyes in industry make them one of the most important functional groups in organic chemistry.[1-2] Due to their interesting physiological activities, secondary amines are extremely important pharmacophores in numerous biologically active compounds.[3] Among many procedures developed to synthesize amines, the reduction of nitriles is an attractive method because of the commercial availability of nitriles and high atom efficiency of these reductions.[4-7] The most important approaches are use of strong hydride donors such as metal hydrides and catalytic hydrogenation.[8-9] Although great advances have been made in the reduction of nitriles, however, these methods always suffer from lack of chemoselectivity and need complicated procedures to obtain the target compounds.[10-11] Therefore, the development of novel and mild methods to reduce nitriles chemoselectively into their corresponding symmetrical secondary amines remains an attractive endeavor. On the other hand, sodium borohydride (SBH) in combination with various metal salts and oxides, such as nickel, cobalt and aluminum have been reported to use for reducing nitriles.[12-16] It is a mild, inexpensive, high stability and invaluable reagent for applications in a wide range of reduction processes.[17] The reducing behavior of sodium borohydride undergoes a drastic change with addition of transition metals.[17-18] Moreover, perovskite type mixed metal oxides possess unique physical and chemical properties.[19] They have had many possible applications like in electrical devices,[20] in ferromagnetic materials,[21] in membranes for gas separation,[22] in sensors,[23] as catalysts[24-25] and as promising adsorbents.[26-27] Perovskites also effectively catalyse organic reactions at very low catalyst loadings.[28-30] Furthermore, these catalysts are readily removed by filtration and lead to extremely low leaching into solution which provides them as good alternative to the other heterogeneous catalysts. An important feature of perovskites is their ability to reversibly adsorb and desorb hydrogen into the crystal lattice by continuous and spontaneous changes in transition metal oxidation state, without changing the overall bulk crystal structure.[31] In continuation of our interest in developing organic transformations using simple reagents, catalysts and reaction media[32-34] herein, we report the direct chemoselective reduction of nitriles to symmetrical secondary amines by $NaBH_4$ in the presence of catalytic amount of nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite. (Scheme 1)



Scheme 1

RESULTS AND DISCUSSION

Thermal characterization

The DTA curve of nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite has been shown in **Fig. 1**. The DTA curve has the exothermic peak at 155 °C which is related to the decomposition of the citrate into calcium oxide. The second exothermic peak at 250 ˚C is attributed to the decomposition of the cobalt citrate into cobalt oxide.[35-36] The third exothermic peak at 380 °C is corresponds to the formation of lanthanum oxide.[37-38] No obvious change is observed above 380 °C.

Fig 1 DTA curve of the nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite precursors obtained by the metal nitrate polymerized complex.

Fig. 2 shows the TGA curve of the thermal decomposition process of nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite obtained at room temperature to 1000 ˚C in the heating rate of 10 ˚C/min. The total weight loss of the xerogel is approximately 77% and the decomposition process can be divided into two distinct steps. The first weight loss occurs during the heating step from 100 to 260 ˚C (47.5%) which is due to the dehydration and decomposition of nitrates. In this area, TGA curve shows two exothermic peaks at 155 and 250 ˚C. A weight loss of about 30% is observed from 340 ˚C to around 640 ˚C which is related to the oxidizing combustion of the organic compounds such as citric acid (forming carbonate and oxide with cation). The TGA curve also reveals a strong exothermic peak at 380 ˚C which is likely due to the oxidation or combustion of the chelate complex which has been occurred along with forming the metal oxides. No obvious change was observed above 650 ˚C. Therefore, it is plausible to conclude that the optimum calcination temperature is about 700 ˚C.

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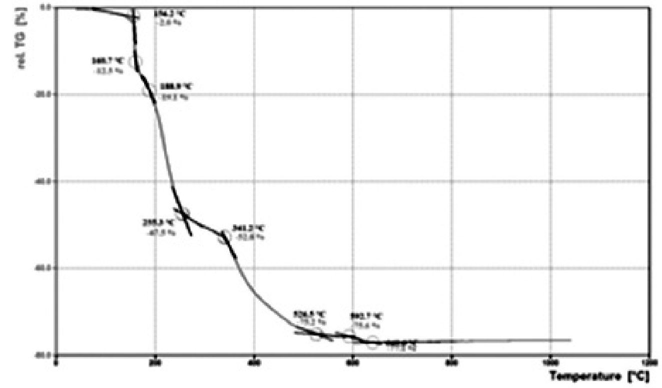

Fig 2 TGA curve of the nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite carried out at room temperature to 1000 °C in air.

X-ray diffraction studies

Fig. 3 shows the X-ray diffraction pattern of nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite when the gel was calcinated at 700 ˚C for 10 h. The diffractograms reveal that the crystalline perovskite structure is the main phase for the synthesized powders.

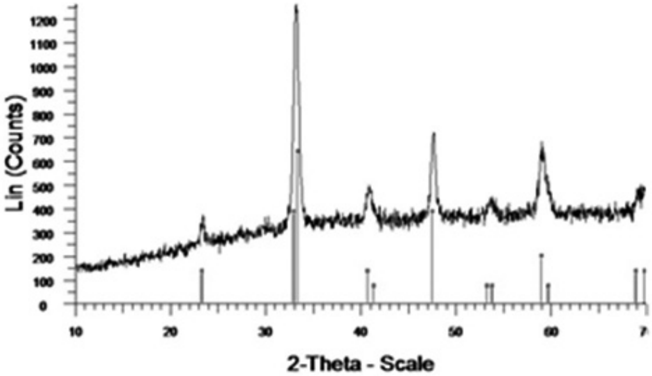

Fig 3 The XRD pattern of nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite calcinated at 700 ˚C**.**

As it has been shown in **Fig. 3**, the presence of (0 1 2), (1 1 0), (2 0 2), (0 2 4), (1 1 6), (2 1 4) and (2 2 0) crystal planes of metallic hexagonal-rhombohedral structure for nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite (JCPDS-36-1390) can be identified. No additional peak is observed in XRD pattern of the catalyst which reveals the high purity of the prepared perovskite nanoparticles. The crystallite sizes are calculated using XRD peak broadening of the (110) peak using Scherer's formula:

$$D_{hkl} = \frac{0.9\lambda}{\beta_{hkl}\cos\theta_{hkl}} \qquad \text{(Scherer's formula)}$$

where D_{hkl} (nm) is the particle size perpendicular to the normal line of (hkl) plane, β_{hkl} is the full width at half maximum, θ_{hkl} (Rad) is the Bragg angle of (hkl) peak and λ (nm) is the wavelength of X-ray. The calculated particles size of $La_{0.5}Ca_{0.5}CoO_3$ perovskite nanoparticles calcinated at 700 ˚C is about 30 nm.

Powder morphology

The size of nanoparticles is evaluated and confirmed by TEM. **Fig. 4** shows representative TEM image of $La_{0.5}Ca_{0.5}CoO_3$ perovskite nanoparticles. The image of the sample which is calcinated at 700 ˚C confirms the particle size of about 30 nm. These values are in agreement with the results achieved from XRD measurements. As the TEM image shows, the morphology of nanoparticles is homogeneous.[39]

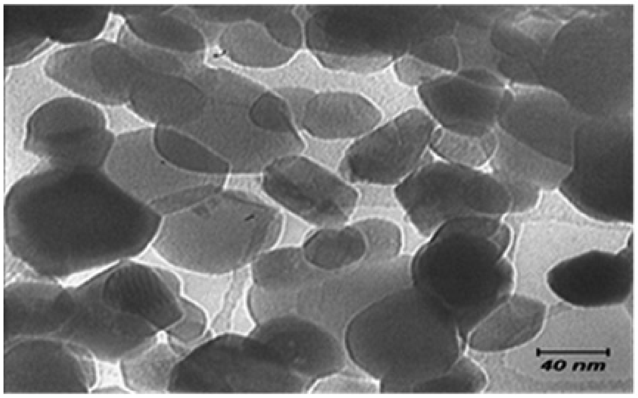

Fig 4 TEM image of $La_{0.5}Ca_{0.5}CoO_3$ perovskite nanoparticles**.**

The nanoparticle size affects many properties of nanomaterials, and is a major indicator of quality and performance. **Fig. 5** shows the nano-$La_{0.5}Ca_{0.5}CoO_3$ perovskite particle size distribution; this was determined from the TEM image, based on more than 100 particles.

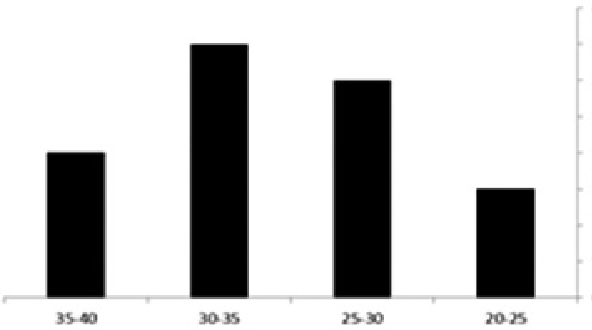

Fig. 5 Particle size distribution for calcinated nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite catalyst.

The morphology of the $La_{0.5}Ca_{0.5}CoO_3$ perovskite nanoparticles has been displayed in **Fig. 6**. It shows the micrograph of the sample synthesized by the sol–gel modified Pechini method and calcinates at 700 ˚C. Based on the SEM image, porosity of the surface is evident and it seems that the nanoparticles have grown with uniform size. The size of pores varied from 25 to 80 nm. It is better to be mentioned that catalytic pores of large geometric dimensions are more suitable for application in the adsorption process in liquid phase due to the simplicity in solid–liquid separation and thus with much improved versatility for catalytic reactions. The surface looks nearly fully covered with the particles grown on it. Furthermore, it can also be seen from the SEM image that in addition to the larger particles, the surface contains also rather smaller particles. However, appearance of bigger particles on the surface looks to be dominant. The aggregation of the smaller particles (in the nm range) may result in bigger $La_{0.5}Ca_{0.5}CoO_3$ perovskite nanoparticles on the surface.

The EDX analysis was performed for further confirmation of the obtained product composition. **Fig. 7** shows EDX spectrum which indicates the existence of La, Ca, Co and O elements in this nanopowder.

Catalytic application of $La_{0.5}Ca_{0.5}CoO_3$ perovskite nanoparticles in reduction of nitriles to secondary amines using $NaBH_4$

Initially, 4-chlorobenzonitrile as a model was investigated in a reductive hydrogenation reaction using SBH catalyzed by nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite in MeOH and the results were summarized in Table 1.

The reduction of 4-chlorobenzonitrile with $NaBH_4$ using $La_{0.5}Ca_{0.5}CoO_3$ perovskite nanoparticles as catalyst was screened in several solvents and the results showed MeOH was the best solvent in terms of activity among the other hydroxylic ones. In EtOH, the amine was also obtained in 65% conversion, but this reaction required 180 min to complete (entry 2).

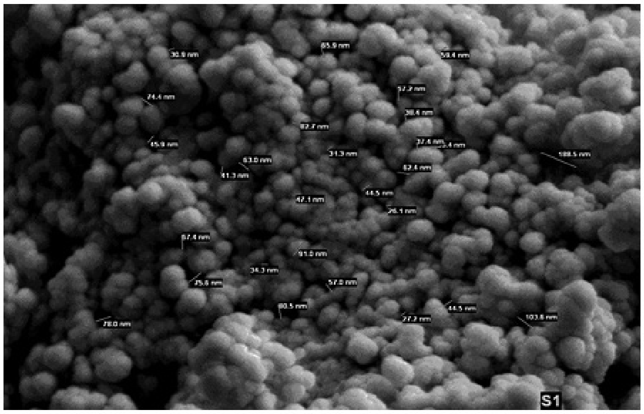

Fig. 6 The SEM image of $La_{0.5}Ca_{0.5}CoO_3$ perovskite nanoparticles.

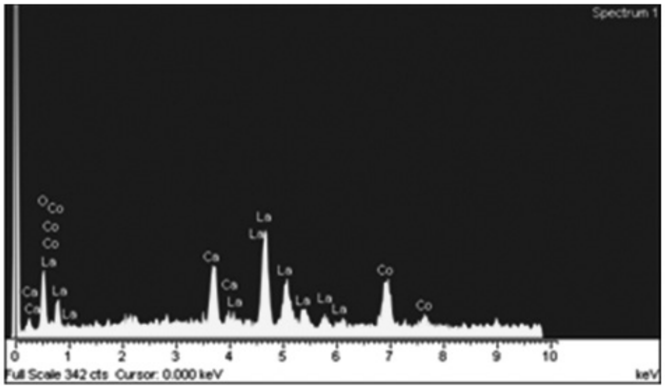

Fig. 7 The EDX analysis results of the $La_{0.5}Ca_{0.5}CoO_3$ perovskite nanoparticles.

Table 1 also lists the results of reductive reagent optimization experiments. To increase the yield of secondary amine and at the same time to restrain the formation of primary amine, various amounts of $NaBH_4$ was used. We tried various ratio of $NaBH_4$ and the results showed that the minimum amount of substrate/$NaBH_4$ ratio which can be used to result no obvious decrease of the yield of bis(4-chlorobenzyl)amine as a secondary amine was 1:2. (entries 7-10)

The catalytic role of the nano-sized $La_{0.5}Ca_{0.5}CoO_3$ was clarified by performing the model reaction in the absence of the nanocatalyst (entry 6). No reaction was observed even after 12 h and only a trace of secondary amine was obtained. Consequently, the model reaction was performed in different molar ratios of the catalyst in the presence of reductive reagent in order to obtain the optimum reaction conditions. The amount of the nano catalyst (0.1-0.001 mol ratio) in the reduction of 4-chlorobenzonitrile was also efficient; allowing the complete conversion of 4-chlorobenzonitrile into the corresponding *sec*-amine, but 0.001 mol ratio was selected as the optimum amount of nano catalyst (entry 11-14).

Temperature variations also affected the yields. (entries 15-17) When the reaction was carried out at 40 ºC, the yield is higher than the reaction held at 60 ºC, but slightly longer reaction time was needed. So the best choice of molar ratio of substrate /$NaBH_4$ /$La_{0.5}Ca_{0.5}CoO_3$ perovskite nanoparticles selected for the reduction of nitriles to secondary amines was 1: 2: 0.001 at 40 ºC.

To explore the scope and substrate limitations of the reaction, the applicability of this method for the synthesis of a wide variety of diverse secondary amines has been demonstrated in Table 2. The reactions were carried out by mixing the various substituted nitriles with $NaBH_4$ in methanol under normal atmosphere at 40 ºC, until TLC showed complete disappearance of the mentioned nitrile and appearance of the corresponding secondary amine. Generally, excellent preparation of secondary amines with different aryl groups were obtained under the optimized reaction conditions, including those bearing electron-withdrawing or electron-donating groups and the corresponding products were obtained in relatively short reaction times with excellent yields in all cases.

Table 1. Effect of variation of solvent, temperature and duration of reaction and $NaBH_4$/catalyst-loading on the yield of bis(4-chlorobenzyl)amine (**2c**; R = 4-Cl-C_6H_4) formed by the reduction of 4-chlorobenzonitrile (**1c**; R = 4-Cl-C_6H_4) by $NaBH_4$ in the presence of nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite (Scheme 1).[a]

Entry	Solvent	Substrate/ $NaBH_4$/ Catalyst (mole ratio)	Time/ min	Temperature (ºC)	Yield/%[b]
1	MeOH	1: 20: 0.1	20	25	92
2	EtOH	1: 20: 0.1	180	25	65
3	*i*-PrOH	1: 20: 0.1	12 h	25	trace
4	*t*-BuOH	1: 20: 0.1	12 h	25	trace
5	H_2O	1: 20: 0.1	12 h	25	35
6	MeOH	1: 20: 0	12 h	25	trace
7	MeOH	1: 10: 0.1	25	25	91
8	MeOH	1: 5: 0.1	30	25	90
9	MeOH	1: 2: 0.1	40	25	90
10	MeOH	1: 1: 0.1	180	25	53
11	MeOH	1: 2: 0.05	25	25	90
12	MeOH	1: 2: 0.025	35	25	89
13	MeOH	1: 2: 0.001	45	25	87
14	MeOH	1: 2: 0.0005	180	25	46
15	MeOH	1: 2: 0.001	180	0	52
16	MeOH	1: 2: 0.001	45	40	92
17	MeOH	1: 2: 0.001	25	60	94

[a] Reaction conditions: (1c; R = 4-Cl-C_6H_4) (1.0 mmol) was treated under various conditions in solvent (5 ml).

[b] Isolated yields.

The reduction of aromatic nitriles containing the functional groups -F, -Cl and -Br were completed within 40-45 min and the corresponding sec-amines were isolated in relatively high yields (entries 2-4). 4-Me-, 3-Me- and 2-Me-benzonitrile were also successfully reduced under the optimized reaction conditions in good yields after 90-120 min (entries 5-7). The reduction of aromatic nitriles containing the electro-donating groups -OMe, and -OEt were also performed in moderate yields (entries 8-10). However, these reactions required more time than the reduction of nitriles bearing electron-withdrawing groups. The reduction of the substrates containing heterocyclic aromatic compounds afforded the corresponding sec-amines in good yields (entry 11-14). All compounds were charaterized, as appropriate, by IR, ^{1}H NMR and ^{13}C NMR spectra.

A plausible mechanism of the reduction of nitriles with nano-sized $La_{0.5}Ca_{0.5}CoO_3$-$NaBH_4$ system has been suggested to involve the followed steps: reduction of a nitrile to the corresponding imine following the nucleophilic addition of it to another nitrile. The latter intermediate is further reduces to amine as well as formation of the corresponding imines as the result of the removing of NH_3. The latter intermediate was eventually reduced to the corresponding sec-amine due to the treatment with reducing agent. According to the similar literature,[44] it seems all reactions were conducted on the surface of the nano catalyst (**Fig. 8**).

Table 2. Yields of various bis(benzyl)amines **2a-n** formed by the reduction of aryl nitriles **1a-n** by $NaBH_4$ in MeOH (5 ml) in the presence of nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite (Scheme 1).[a]

Entry	Product No.	Time (min)	Product $(RCH_2)_2NH$, R =	Yield (%)[b]	TOF (h^{-1})[c]	mp (ºC)	mp (ºC)[lit.][d]
1	**2a**	60	C_6H_5	85	850	oil	[40]
2	**2b**	40	4-F-C_6H_4	80	1200	oil	[40]
3	**2c**	45	4-Cl-C_6H_4	92	1227	oil	[40]
4	**2d**	45	4-Br-C_6H_4	90	1200	47-49	46-48 [41]
5	**2e**	90	4-CH_3-C_6H_4	82	547	34-35	34-36 [41]
6	**2f**	90	3-CH_3-C_6H_4	80	533	oil	[42]
7	**2g**	120	2-CH_3-C_6H_4	75	375	oil	[42]
8	**2h**	150	4-CH_3O-C_6H_4	72	300	35-36	34 [41]
9	**2i**	150	4-CH_3CH_2O-C_6H_4	70	280	oil	[40]
10	**2j**	160	3,5-di-CH_3O-C_6H_4	65	244	oil	[42]
11	**2k**	20	pyrid-4-yl	92	2760	oil	[40]
12	**2l**	30	pyrid-3-yl	90	1800	oil	[40]
13	**2m**	35	pyrid-2-yl	85	1457	oil	[40]
14	**2n**	90	thiophen-2-yl	80	533	oil	[43]

[a] Reaction conditions: $NaBH_4$ (2.0 mmol) was added to a stirred solution of **1a-n** (1.0 mmol) in MeOH (5 ml) at 40 ºC in the presence of 1mol% nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite.

[b] Isolated yields.

[c] Turnover frequencies (TOFs) defined as mmoles of products reacted per mmoles of catalyst per hour.

[d] The products are also characterized by comparing their spectral data with literature.

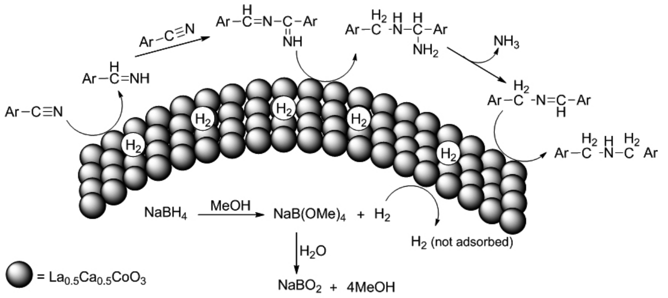

Fig. 8 A plausible mechanism for the reduction of nitiles to *sec*-amines.

One of the special features of nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite catalyst is its insolubility in organic solvents which makes its recovery very convenient. Therefore, the reusability of the catalyst was examined under the optimized reaction conditions with 4-chlorobenzonitrile as a model reaction. For each of the repeated reactions, the catalyst was recovered, washed with ethylacetate, consecutively and dried before being used for the next reductive hydrogenation reaction. The catalyst was reused four times without any significant loss of activity, the yields of product being, respectively, 97, 95, 91 and 90%.

A literature assay for the comparison of this method with some other previously reported ones including $NaBH_4$ reductive hydrogenation of benzonitriles demonstrates the efficiency of nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite catalyst for the preparation of sec-amines as shown in Table 3.

Table 3. A comparison of some other catalyst systems with nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite/$NaBH_4$ for the chemoselective reduction of aryl nitriles **1** to bis-(benzyl)amines **2** (Scheme 1).

Entry	Reaction conditions	Temperature (ºC)	Time	solvent	Yield (%)	[Lit.]
1	Rh (5 mol%) /HOAc /H_2 (1 atm)	rt	20-30 h	HOAc	70-95	45
2	Nickel(II) (1 mmol)/ $NaBH_4$ (3 mmol)	rt	15 min	$EtOH_{(dry)}$	3-11	16
3	$La_{0.5}Ca_{0.5}CoO_3$ nano particles (1 mol %)/ $NaBH_4$ (2 mmol)	40	20-160 (min)	MeOH	65-92	-[a]

[a]this work.

Furthermore, this methodology avoids the formation of primary amines which often occurs in the reduction of nitriles by catalytic hydrogenation. The many advantages of this method include high isolated yields, good chemoselectivity, easy work-up and also the stability of the catalyst towards air and moisture, allowing the reaction to be carried out in simple, readily available laboratory equipment in a protic solvent in the open laboratory.

EXPERIMENTAL

Thermogravimetric analysis (TGA) of the gel precursor dried at 110 ˚C was studied using NETZSCH-402EP thermoanalyzer at 20 to 1000 ˚C (5 ˚C/min) within a dynamic air atmosphere. X-ray diffraction (XRD) measurements were carried out for structural investigation of calcinated powder at 650 ˚C in the region of (2θ = 20 to 70˚) using CuK_α radiation on a Rigaku D/MAX RB XRD diffractometer equipped with a curved graphite monochromator. The microstructure of the powder was examined using LEO 912AB TEM under a working voltage of 120 kV. The SEM of the type LEO 1450 VP (V = 30 kV) was equipped with an EDX spectrometer on an Inca 400 Oxford Instruments. Differential thermal analysis (DTA) was recorded on an apparatus manufactured by STA 503 (Germany).

$La(NO_3)_3.9H_2O$, $Ca(NO_3)_2.4H_2O$ and $Co(NO_3)_3.6H_2O$ were obtained from Merck, Germany; citric acid was purchased from Aldrich, USA. All the reagents were analytical grade and thus used as received. Deionized water was used throughout the experiments.

Preparation and characterization of nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite

To a solution of $La(NO_3)_3.6H_2O$ (3 mmol, 1.29 g), $Ca(NO_3)_2.4H_2O$ (3 mmol, 0.71 g) and $Co(NO_3)_2.6H_2O$ (6 mmol, 1.75 g) in deionized water (30 ml), tartaric acid (12 mmol, 2.52 g) was added slowly at room temperature under constant magnetic stirring (1000 r/min). First, the solution was refluxed for 2 h and then, stirring was continued at 70 ˚C for 3 h. The obtained sol was placed in an oven and heated slowly at 110 ˚C for 12 h. The gel was ground in an agate mortar and then, nanoparticles of $La_{0.5}Ca_{0.5}CoO_3$ were obtained by calcinations of the powders at 700 ˚C for 10 h. The annealing of the amorphous precursor allows removing most of the residual carbon and the orthorhombic perovskite phase was obtained.

$La_{0.5}Ca_{0.5}CoO_3$ of the type perovskite oxide was fabricated by sol–gel method. Different techniques were employed to analyze and validate the synthesized nano catalyst $La_{0.5}Ca_{0.5}CoO_3$.

General procedure for the reduction of nitriles into their corresponding sec-amines.

To a stirring mixture of the appropriate nitrile (1 mmol) and nano-sized $La_{0.5}Ca_{0.5}CoO_3$ perovskite (1 mol%, 1.9 mg) in MeOH (5 ml) at 40 ˚C, $NaBH_4$ (2 mmol, 0.08 g) was added portion wise. After the completion of the reaction which was monitored by TLC using $CHCl_3$: MeOH (30:1) as eluent, the catalyst was centrifuged off and the solvent was evaporated under reduced pressure. To the resulting oily liquid, water (20 ml) was added and the mixture was extracted with CH_2Cl_2 (2 × 20 ml). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to afford the pure products.

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