Fabrication and Characterization of Perovskite-Type Oxide $\text{LaFe}_{0.9}\text{Co}_{0.1}\text{O}_3$ Nanoparticles and Its Performance in Aerobic Oxidation of Thiols to Disulfide

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Abstract: $\text{LaFe}_{0.9}\text{Co}_{0.1}\text{O}_3$ (LFCO) perovskite nanoparticles were prepared using a sol-gel method. The physical and chemical properties of the catalyst were determined using X-ray diffraction (XRD), transmission electron microscopy, scanning electron microscopy, scanning tunneling microscopy, energy dispersive X-ray spectroscopy, thermogravimetric analysis, and Fourier transform infrared spectroscopy. The catalytic activity of the sample was evaluated using aerobic oxidation of thiols to disulfides. The XRD results indicated that the LFCO had a good crystalline phase at 750 °C. The experimental data revealed that the LFCO particles were nano-sized. LFCO nanoparticles can catalyze the oxidation of various thiols, including aromatic and aliphatic thiols. The effects of reaction parameters such as temperature, solvent, and the amount of catalyst on the oxidation of 4-chlorothiophenol were investigated. In comparison with reactions using the corresponding neat complexes, i.e., $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, higher yields were obtained in the oxidation reaction catalyzed by LFCO nanoparticles.

Key words: perovskite-type oxide; nanopowder; oxidation of thiols; sol-gel method

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The vast majority of catalysts used in the modern chemical industry are based on mixed metal oxides. The preparation of specific tailor-made mixed oxides able to perform complex functions is one of the main topics of research in the field of heterogeneous catalysis. Achieving complex catalytic reactions requires a polyfunctional catalyst with appropriate solid-state, surface, and morphological properties. The extensive background knowledge in solid-state surface chemistry available from studies in the field of heterogeneous catalysis can be usefully applied to the design of catalysts and the engineering of new high-performance materials. A wide cross-fertilization bridges heterogeneous catalysis and materials science in the areas of physico-chemical characterization, solid-state chemistry, and synthetic routes [1–3]. Among mixed metal oxides, perovskite-type oxides are prominent. Perovskite oxides have the general formula ABO_3 (A is a larger cation than B). Many perovskite-related oxides show large variations in oxygen non-stoichiometry and defect concentrations, and they therefore have rich redox chemistries with variable oxidation states of the metal cations at the B-sites in the ABO_3 structure. Perovskites have many possible applications, e.g., as electrolytes, in membranes for gas separation, as catalysts, and in sensors [4], and the redox properties are important in most applications. A recent example is the use

of perovskite-related oxides as oxygen-carrier materials in power production based on chemical looping combustion [5–7]. Other examples are hydrogen production using membrane reactors or chemical looping reforming processes [5,8,9]. The conversion of thiols to the corresponding disulfides is an important reaction in biological and chemical processes [10]. Reagents such as cerium(IV) salts [11], transition-metal oxides [12], molecular oxygen [13], nitric oxide [14], halogens [15], sodium perborate [16], H_2O_2 [17], solvent-free permanganate [18], 2,6-dicarboxypyridinium chlorochromate [19], and 1,3-dibromo-5,5-dimethylhydantoin [20], among others, have been used for oxidation of thiols to disulfides [21,22]. However, in many reactions, perovskite-type catalysts have higher activities comparable stabilities, and lower costs than traditional catalysts based on noble metals [23,24]. In previous work, we presented $\text{LaFe}_{0.9}\text{Co}_{0.1}\text{O}_3$ nanoparticles (LCNO NPs) as nanophotocatalysts for efficient removal of reactive blue 5 [25]. In this paper, we report the fabrication of a heterogeneous perovskite catalyst, LFCO NPs, which shows excellent catalytic efficiency towards oxidation of thiols using air as the oxidant. The effects of different solvents on the oxidation reaction were also investigated. The catalytic efficiency of the catalyst was compared with those of the corresponding neat complexes, i.e., $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, under similar reaction conditions.

1 Experimental

1.1 Synthetic procedure

Appropriate amounts of starting materials, i.e., $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%), were dissolved in deionized water and La_2O_3 was dissolved in nitric acid to form lanthanum nitrate. Aqueous solutions of metal nitrates, in nominal atomic ratio of $\text{La}:\text{Fe}:\text{Co} = 1:0.9:0.1$, were mixed together in deionized water. Citric acid (CA) was then added slowly to the metal solution at room temperature under constant magnetic stirring (1000 r/min). The solution was concentrated by evaporation at approximately $50\text{ }^\circ\text{C}$ with stirring for 1 h to convert it to a stable complex. To make a gel, stirring was continued at $\sim 70\text{ }^\circ\text{C}$ for 3 h. A dry gel was obtained by placing the sol in an oven and heating slowly to $110\text{ }^\circ\text{C}$ and then maintaining the temperature for 8 h. The gel was ground in an agate mortar to give a powder. LFCO NPs were obtained by calcination of the precursors at $750\text{ }^\circ\text{C}$ for 10 h in air.

1.2 Typical procedure for oxidative coupling of thiols

In a 25 ml round-bottomed flask, a solution of thiol (1 mmol) in a solvent (2 ml) was prepared. LFCO NPs (0.01 g) were added to the solution and the reaction mixture was stirred at room temperature in air (Scheme 1).

Scheme 1. Oxidation of thiols.

The progress of the reaction was observed using thin-layer chromatography (eluent: *n*-hexane/ethyl acetate = 4:1). The unreacted thiol was estimated by titrating against a standard alcoholic iodine solution, using pyridine as a base. After completion of the reaction, the reaction mixture was filtered and the solid material was washed with 10 ml of the same solvent as that used during the reaction. Excess solvent was evaporated using a rotatory evaporator, and concentration to dryness gave the desired product. Recrystallization afforded the pure disulfides in 92%–98% yields. Comparisons of the melting points and ^1H NMR spectra (bis(4-methylphenyl) disulfide, mp: $44\text{--}45\text{ }^\circ\text{C}$; ^1H NMR 2.3 (s, 6H); 7.1 (d, 2H); 7.4 (d, 2H)) of the purified products with those of the authentic disulfides showed the purity of the disulfide products. All the genuine disulfides were prepared from the corresponding thiols according to the method described in the reference [26]. Analysis of the complete spectral and physical data showed that only disul-

fides were formed and no further oxidation occurred.

1.3 Instrumentation

Thermal gravimetric analysis (TGA) of the gel precursor dried at $110\text{ }^\circ\text{C}$ was performed using a Shimadzu TGA-50 Thermoanalyzer in the temperature range from 50 to $800\text{ }^\circ\text{C}$ ($10\text{ }^\circ\text{C}/\text{min}$) and a dynamic air atmosphere. For structural investigation of calcined powder at 650 and $750\text{ }^\circ\text{C}$, powder X-ray diffraction (XRD) measurements were carried out in the region of $2\theta = 20^\circ\text{--}70^\circ$ using $\text{Cu } K_\alpha$ radiation on a Rigaku D/MAX RB XRD diffractometer equipped with a curved graphite monochromator. The microstructure of powder was examined using a LEO 912AB transmission electron microscope (TEM) under a working voltage of 120 kV , while the morphology of the particles was investigated using a LEO 1450VP ($V = 30\text{ kV}$) scanning electron microscope (SEM). Elemental distribution on the surface was analyzed by energy dispersive X-ray spectroscopy (EDX-XPS, Inca 400, Oxford Instruments). The surface morphology was also studied using an SS1 scanning tunneling microscope (STM) and all images were recorded in the constant-current mode at room temperature using a Re-manium tip with a bias voltage of around 2 V in atmosphere. FT-IR spectra were taken by KBr disks on a thermo Nicolet Nexus 870 FT-IR spectrometer.

2 Results and discussion

2.1 FT-IR spectroscopy

Figure 1 shows the FT-IR spectra of the LFCO perovskite before and after calcination. Figure 1(1) shows two strong and well-defined absorption bands, at 1400 and 1600 cm^{-1} , attributed to the stretching and bending vibrations of the carbonyl group of CA, before calcination. The modes in the spectral range from 700 to 900 cm^{-1} represent the bending

Fig. 1. FT-IR spectra of LFCO before (a) and after (b) calcination at $750\text{ }^\circ\text{C}$.

and stretching internal vibrations of octahedral oxygen in the LFCO NPs. Figure 1(2) shows that organic compounds and carboxylate impurities were removed completely when the gel was annealed at 750 °C. This indicates the possibility of metal carboxylate dissociation and conversion to metal oxides during the calcination process.

2.2 XRD analysis

Figure 2 shows the X-ray powder diffraction (XRD) pattern of the sample prepared by the sol-gel method. The product exhibited sharp peaks, indicating a high degree of crystallinity after calcination. The XRD results revealed the existence of perovskite-type LFCO NPs after calcination at 750 °C. The diffraction peaks at 2θ angles of 16°, 23°, 33°, 40°, 47°, 58°, and 69.77° can be assigned to scattering from the (010), (100), (110), (111), (200), (210), and (211) planes, respectively, of the LFCO NPs perovskite-type crystal lattice. The XRD data show that LFCO crystallized in the rhombohedral system. The crystallite sizes were calculated from the XRD peak broadening of the (110) peak using Scherrer's formula: $D_{hkl} = 0.9\lambda/\beta_{hkl}\cos\theta_{hkl}$, where D_{hkl} (nm) is the particle size perpendicular to the normal line of the (*hkl*) plane, β_{hkl} is the full width at half maximum, θ_{hkl} (rad) is the Bragg angle of the (*hkl*) peak, and λ (nm) is the X-ray wavelength. The calculated size of LFCO NPs calcined at 750 °C was about 10 nm.

Fig. 2. XRD pattern of LFCO NPs calcined at 750 °C.

2.3 TG analysis

Figure 3 shows the TG analysis and differential thermal gravimetric (DTG) curves for the thermal decomposition of LFCO NPs. The total mass loss of the xerogel was approximately 67% and the decomposition process can be divided into three distinct steps. The first mass loss occurred during the heating step from room temperature to 180 °C (24%), resulting from the dehydration and decomposition of nitrates. This is confirmed by the corresponding weight loss differential peak (149.21 °C) in the DTG curve. From 180

Fig. 3. TGA-DTG curves of LFCO xerogel from room temperature to 800 °C in air.

to about 350 °C, a mass loss of about 13% was observed, which was attributed to the decomposition of chemically bound groups. The third step, from 350 to 650 °C (30%), is the result of oxidation or combustion of the chelate complex along with formation of metal oxides, corresponding to the strongest weight loss differential peak (358.85 °C) in the DTG curve. No mass loss above 650 °C was detected on the TG curve, which indicates the formation of nanocrystalline LFCO as the decomposition product. It is therefore plausible to conclude that the optimum calcination temperature is about 720 °C.

2.4 SEM and EDX analyses

Scanning electron microscopy (SEM) analysis was carried out in order to determine the morphology of the sample. Figure 4 shows the micrograph of a sample synthesized by the sol-gel method and calcined at 750 °C. The SEM image shows that the surface is porous and the particles have grown to a uniform size. The pore size varies from 0.5 to 4 μm. It should be mentioned that large catalytic pores are more suitable for use in liquid-phase oxidation reactions because it is easy to separate solids from liquids, and there-

Fig. 4. SEM image of calcined xerogel of LFCO NPs.

fore the catalysts are easier to handle.

The surface looks scaly and is almost completely covered with particles that have grown on it. It can also be seen from the SEM results that in addition to large particles, there are also small particles on the surface. However, large particles on the surface are predominant. The aggregation of the smaller particles (in the nanometer range) may result in large LFCO NPs on the surface.

EDX analysis was performed to further confirm the composition of the obtained product. Figure 5 shows the EDX spectrum, which indicates the existence of La, Fe, Co, and O elements in the NPs.

Fig. 5. EDX spectrum of LFCO NPs.

2.5 TEM analysis

Transmission electron microscopy (TEM) image of LFCO NPs calcined at 750 °C is shown in Fig. 6. In the catalyst, the grains are homogeneous in size. The image shows that the particle size is about 8 nm. The obtained

Fig. 6. TEM image of LFCO NPs.

value is in agreement with the results achieved using XRD data.

2.6 STM analysis

Figure 7 shows scanning tunneling microscopy (STM) images of LFCO NPs. These can be used to determine the particle size and height. In Fig. 7(a), the bright spots are higher than the dark ones, and the distribution of particles on the surface is clearly mapped. Five particles were selected for quantitative measurements and the results showed that their average size and height were around 8 and 4.6 nm, respectively (Fig. 7(b)). The catalytic activity correlates with the particle size of the composite. It is deduced that the presence of more sites will increase the catalytic activity of the LFCO NPs.

Fig. 7. STM images (a) of LFCO NPs for an area of 300 nm × 300 nm and height profile along the white line (b).

2.7 Catalytic reaction

The oxidation of thiols to their corresponding products occurred in the presence of the LFCO NPs as a catalyst. All the products were obtained in high yields. 4-Chlorolthiophenol was chosen as a model substrate for optimization of thiol oxidation. Among the solvents used, methanol was the most effective for the oxidation reaction because of the relatively good solubility of the starting materials in methanol (Table 1, Entries 1–7). The reaction was also studied at different temperatures, and the results showed that the conversion rate decreased at 0 °C. The

Table 1 Optimization of reaction conditions for oxidation of 4-methylthiophenol in methanol at room temperature under air bubbling

Entry	Solvent	Catalyst (g)	Time (min)	Conversion (%)	Disulfide selectivity (%)
1	methanol	0.01	15	100	100
2	dichloromethane	0.01	60	10	90
3	ethanol	0.01	60	60	100
4	toluene	0.01	60	10	90
5	tetrahydrofuran	0.01	60	20	90
6	acetonitril	0.01	50	40	95
7	DMF	0.01	30	100	100
8 ^b	methanol	0.01	100	20	100
9 ^c	methanol	0.01	5	100	80
10 ^d	methanol	0.01	3	100	50
11	methanol	0.005	25	100	100
12	methanol	0.02	10	100	100
13	methanol	0.03	8	100	100
14	methanol	0.04	5	100	100
15	methanol	0.06	5	100	100
16	methanol	none	360	0	—
17	methanol	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	360	0	—
18	methanol	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	360	0	—
19 ^e	methanol	0.01	13	100	100
20 ^f	methanol	0.01	10	100	0
21 ^g	methanol	0.01	15	100	100
22 ^h	methanol	0.01	15	100	100
23 ⁱ	methanol	0.01	15	100	100
24 ^j	methanol	0.01	15	100	100
25 ^k	methanol	0.01	18	100	100

^aIsolated yield on the basis of the mass of the pure product obtained.

^bCarried out at 0 °C over LFCO NPs.

^cCarried out at 50 °C over LFCO NPs.

^dCarried out at 75 °C over LFCO NPs.

^eCarried out in the presence of O_2 as oxidant.

^fCarried out in the presence of H_2O_2 as oxidant.

^gCarried out with the first recycled LFCO NPs.

^hCarried out with the second recycled LFCO NPs.

ⁱCarried out with the third recycled LFCO NPs.

^jCarried out with the fourth recycled LFCO NPs.

^kCarried out with the fifth recycled LFCO NPs.

conversion rate increased at higher temperatures, but the selectivity decreased (Table 1, Entries 8–10). The oxidative coupling reaction of 4-chlorolthiophenol was also achieved using different amounts of catalyst. The conversion rate of the oxidative coupling reaction increased with a high amount of catalyst (0.05 g), but with lower amounts of catalyst, the conversion rate decreased, and no conversion was detected in the absence of a catalyst (Table 1, Entries 11–16). The reaction was also studied using the corresponding neat complexes, i.e., $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, under similar reaction conditions, but no conversion was detected (Table 1, Entries 17 and 18). The oxidation reaction was also performed in the presence of molecular oxygen as the oxidant; the reaction rate and catalyst selectivity were similar to those using air as the oxidant (Table 1, Entry 19). The catalyst selectively provided disulfide only, instead of the usual products (disulfide and sulfonic acid) in thiol oxidation. In addition, when the oxidation reaction was performed with hydrogen peroxide as the oxidant, the conversion rate increased, but the selectivity decreased significantly (Table 1, Entry 20). The reusability of the catalyst was investigated under the optimum conditions; the reaction occurred five times over LFCO NPs as the catalyst, with excellent yields (Table 1, Entries 21–25).

Oxidations of different thiols in methanol, in the presence of LFCO NPs as the catalyst, using air as the oxidant, were performed (Table 2). As can be seen from Table 2, a variety of aromatic (Table 2, Entries 1–9) and aliphatic (Table 2, Entries 10–12) thiols were easily converted to the corresponding disulfides in very short times and in excellent yields. Moreover, it is clear from the data in the third column of Table 2 that aromatic thiols react faster than aliphatic thiols. The experimental results suggest that oxygen held weakly on the surfaces of the LFCO NPs is valuable in the oxidation reaction. A proposed mechanism for the oxidation of thiols by air over the LFCO NPs catalyst is as follows:

3 Conclusions

Nanocrystalline LFCO NPs were synthesized by a sol-gel method using CA, and subsequent calcination. A study of the structural, morphological, and catalytic properties of the LFCO NPs was performed using various analytical techniques. XRD and microscopic analyses indicated that the LFCO NPs prepared by calcining the gel precursor at 750 °C had suitable crystallinity, with the rhombohedral perovskite structure. In addition, the present investigation

Table 2 Oxidative coupling of thiols to disulfides catalyzed by LFCO NPs

Entry	Substrate	Time (min)	Yield (%)	Selectivity (%)	Melting point (°C)	
					Found	Refs. [27,28]
1		10	98	100	61–62	59–60
2		15	95	100	72–73	73–74
3		15	96	100	74–76	75–76
4		20	96	100	90–93	91–93
5		12	98	100	44–45	45–46
6		15	98	100	42–44	43–44
7		8	92	100	74–76	75
8		20	94	100	111–113	112–115
9		10	92	100	141–144	142–145
10		35	92	100	243–244	242
11		42	94	100	—	—
12	$C_8H_{17}SH$	34	92	100	—	—

Reactions conditions: 1 mmol substrate in 2 ml of methanol, room temperature, 0.01 g LFCO NPs, bubbling of air into the solution.

showed that the synthesized LFCO NPs can be used for selective oxidation of thiols to the corresponding disulfides for a wide range of aromatic and aliphatic thiols. The processing parameters such as amount of catalyst, effects of different solvents, temperature, and different oxidants all affect the coupling reactions of thiols. The results show that the prepared powders effectively oxidized thiols to disulfides in high yields. The percentage removal of thiol in 5–42 min of stirring was 92%–98% using 0.01 g/2 ml of catalyst. Moreover, this catalytic oxidation system is clean, safe, and operationally simple, and the yields of the products are high. This oxidation method therefore meets the needs of contemporary green chemistry and is suitable for practical syntheses.

Supplementary materials

1H NMR spectra of bis(4-chlorophenyl) disulfide, difurfuryl disulfide, and *p*-tolyl disulfide are available as supplementary data.

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