

# Liquid phase catalytic transfer hydrogenation of aromatic nitro compounds on $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ perovskites prepared by microwave irradiation

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## Abstract

A series of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $x = 0.0$ – $1.0$ ) oxides were prepared to study the influence of A-site substitution in perovskite-type mixed oxides  $\text{LaFeO}_3$  ( $\text{ABO}_3$ -type perovskites) on the catalytic transfer hydrogenation of aromatic nitro compounds using propan-2-ol as hydrogen donor and KOH as promoter. The conventional method for the preparation of perovskites requires conductive heating for extended periods at elevated temperatures. We have used microwave irradiation method for the rapid synthesis of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $x = 0.0, 0.2, 1.0$ ) perovskites and the catalytic activity of these samples has been tested for the reduction of nitrobenzene. Kinetic studies have also been performed for nitrobenzene reduction.

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**Keywords:** Perovskites; Catalytic transfer hydrogenation; Microwave irradiation and Nitroarenes.

## 1. Introduction

Catalytic hydrogenation of aromatic nitro compounds to amino derivatives is an industrially important reaction. Aromatic amines are important starting materials and intermediates for the manufacture of variety of chemicals such as dyestuffs, pharmaceutical products, agricultural chemicals, surfactants and polymers. The oldest and industrially practiced method is the Bechamp reduction, which involves use of stoichiometric amounts of finely divided iron metal and water in the presence of small amounts of acid. But it has a distinct disadvantage of formation of iron sludges that are difficult to filter and always contain adsorbed reaction products and hence lead to disposal problems [1]. The sulfide reduction has a broader selectivity than Bechamp reduction and enables chemoselective reduction of nitro compounds in the

presence of C=C, azo and other nitro compounds. The major disadvantages are toxicity, odor of most reducing agents and sulfur containing organic side products and formation of elemental sulfur [2]. Hydrogenation using molecular hydrogen is non-polluting, but presents considerable hazards, since hydrogen is a gas of low molecular weight and gets easily ignited. An ecofriendly alternative to these commonly practiced reductions is catalytic transfer hydrogenation, which is a simple and safe operation.

A wide variety of homogenous metals have been reported for the catalytic transfer hydrogenation processes and most of them involve metal-catalyzed hydrogenations, complex hydrides. However, it has been observed that controlling the reduction rates is difficult with these active catalysts [3]. On the other hand, the use of heterogeneous catalysts offers several advantages over homogenous systems with respect to easy recovery and recycling of catalysts as well as minimization of undesired toxic wastes. However, these processes, requires moisture sensitive reagents or catalysts such

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as Raney-Ni, Pd/C, PtO<sub>2</sub>, etc [4,5]. Among these, Raney-Ni catalyst has been frequently used with hydrazine hydrate or propan-2-ol for catalytic transfer hydrogenation reactions. Although catalytic transfer hydrogenation reactions are facile over these catalysts, they are, however, not selective towards functional groups such as –CO, –CX and –NO<sub>2</sub> and almost all labile functional groups undergo reduction under the reaction conditions. Furthermore, Raney-Ni catalyst is flammable and presents considerable hazards during handling. Catalytic transfer hydrogenation using propan-2-ol and KOH on oxides has been widely reported [6]. Attention has been focused on catalysts like Mg–Fe hydrotalcite precursor, SnO–La<sub>2</sub>O<sub>3</sub> and nickel-based catalysts [7–9]. However, the activity of these catalysts decreases with subsequent recycling. With this background, there is a strong need to develop a new heterogeneous catalyst that can be reusable and efficient under the reaction conditions.

Although, perovskite type mixed oxides have been used for a gamut of reactions like NO<sub>x</sub> decomposition [10], oxidation of CO [11] and NH<sub>3</sub> [12], their application for catalytic transfer hydrogenation is still unexplored.

Perovskite-type mixed oxides have the general formula ABO<sub>3</sub> where A can be an alkali, alkaline earth or lanthanide ion and B a transition metal ion have interesting physico-chemical and catalytic properties. Studies have shown that increasing strontium content actually *increases* the catalytic activity for CO oxidation not only in the La<sub>1-x</sub>Sr<sub>x</sub>MO<sub>3</sub> (M = Co, Cr, Fe, Mn; x = substitution on cation site) perovskite system [13–15] but also in La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> systems [16].

The conventional method for synthesis of perovskites requires conductive heating for extended periods at elevated temperatures with intermittent grindings. In order to circumvent this limitation, there is increasing demand for new preparation methods. Microwave assisted synthesis of inorganic compounds is an active area of research in recent years [17,18]. If one or several of the components in a chemical reaction system strongly absorb microwaves, the resultant heat generated can be used to drive a reaction with other components. The most compelling features of microwave irradiation are dramatically accelerated reaction rates, shorter reaction times and easy workup. In the present investigation, we have achieved considerable reduction in time required for the preparation of perovskites of La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3</sub> (x = 0.0, 0.2, 1.0) using this methodology and compared the activity of these catalysts with those prepared by conventional methods for transfer hydrogenation reaction.

## 2. Experimental

### 2.1. Preparation of perovskites by microwave irradiation

La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3</sub> (x = 0.0, 0.2, 1.0) perovskites were prepared by microwave irradiation method. Stoichiometric quantities of respective nitrates were thoroughly ground and mixed. The mixture was placed in an open quartz tube, on a

bed of graphite. This assembly was mounted in a domestic microwave oven operating at a frequency of 2.45 GHz and irradiated for 5 min at a full power setting. Microwave source was then switched off and the sample was left to cool inside the oven. The sample was ground again and irradiated for 10 min in 2 cycles of 5 min each. Decomposition of nitrates results in the formation of reactive oxides, which can easily combine to form the mixed oxides. The perovskite phase was formed only when the nitrates were microwave irradiated. The oxides themselves did not absorb effectively even in the presence of an external absorber (graphite). The perovskite phase was also not formed when the nitrates were irradiated in the absence of graphite.

### 2.2. Preparation of perovskites by conventional method

La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3</sub> (x = 0.0–1.0) catalysts were prepared by the reported procedure [19]. Stoichiometric quantities of respective nitrates were mixed and co-precipitated using *n*-butylamine. The pH of the solution was adjusted between 9.0 and 9.5. The precipitates were then washed, dried, ground with a pestle and mortar and heated at 300 °C for 3 h. The powder so obtained was then calcined at 850 °C for 10 h.

### 2.3. Catalyst characterization

The catalysts prepared by both the methods were characterized by X-ray diffraction patterns recorded on a JEOL JDX-8030 X-ray diffractometer using Cu K $\alpha$  radiation.

### 2.4. Catalytic activity

All the reactions were carried out in a two-necked 100 ml round bottom flask under continuous stirring fitted with a reflux condenser. In a typical run, 100 mg of the catalyst was dispersed in a solution containing nitrobenzene (20 mmol), KOH pellets (20 mmol) and propan-2-ol (20 ml). The mixture was stirred and heated under reflux for 2–6 h in an oil bath. The products were analyzed at the regular intervals on the basis of their retention times using a Gas Chromatograph fitted with OV-1 Column (Eshita, Model-Eshika).

## 3. Results and discussion

### 3.1. XRD analysis

Fig. 1 shows the XRD patterns of the perovskites prepared by microwave irradiation. All the perovskites synthesized are essentially pure phases, as evidenced by their XRD. No unreacted precursor material was detectable.

### 3.2. Catalytic activity

Once the materials were characterized as regards structure, they were tested as catalysts for the reduction of nitrobenzene

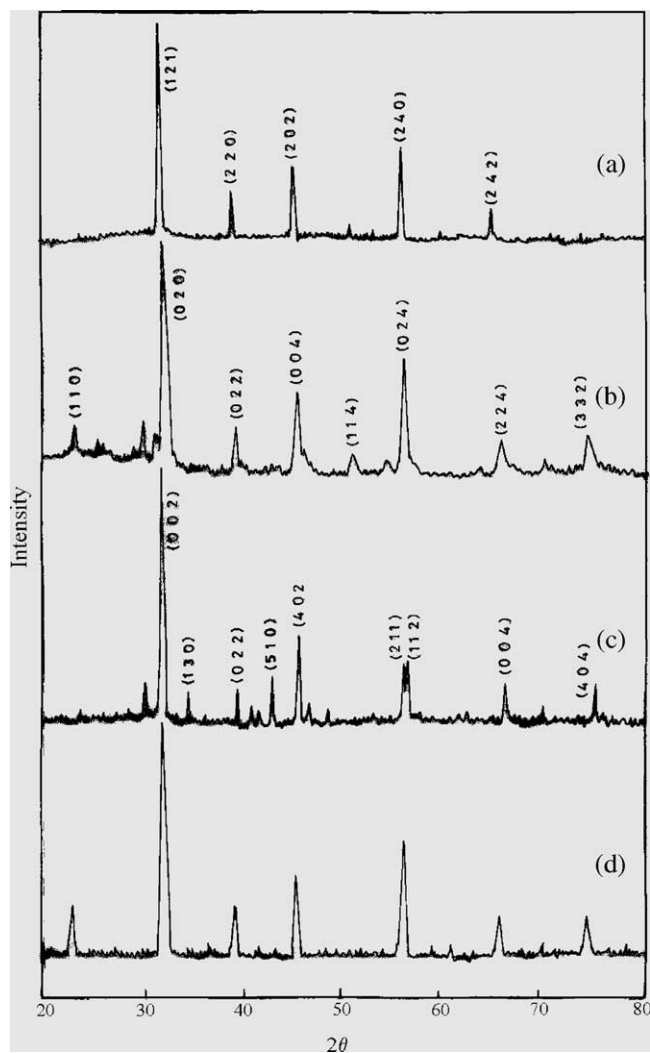
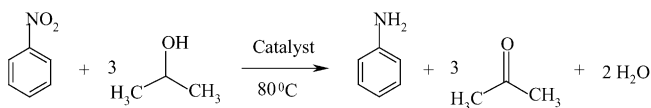


Fig. 1. The XRD patterns of perovskites (a) LaFeO<sub>3</sub>, (b) La<sub>0.8</sub>Sr<sub>0.2</sub>FeO<sub>3</sub> (c) SrFeO<sub>3</sub> (d) spent La<sub>0.8</sub>Sr<sub>0.2</sub>FeO<sub>3</sub>.

to aniline with propan-2-ol. Scheme 1 depicts a typical catalytic transfer hydrogenation. During the course of the reaction, alcohol is oxidized to ketone and nitrobenzene is reduced to aniline. Aniline was the only product obtained under these conditions. In the absence of either catalyst or KOH, there was no reaction. The activity of perovskites prepared by both the methods was found to be comparable and La<sub>0.8</sub>Sr<sub>0.2</sub>FeO<sub>3</sub> was the most active catalyst among the series (Table 1). Catalysts with strontium >20% are not as active as La<sub>0.8</sub>Sr<sub>0.2</sub>FeO<sub>3</sub> though their activities are still higher than that of LaFeO<sub>3</sub> and SrFeO<sub>3</sub> (Fig. 2).

Since the reduction of nitrobenzene to aniline was maximum on La<sub>0.8</sub>Sr<sub>0.2</sub>FeO<sub>3</sub> reduction of several other nitro aro-



Scheme 1.

Table 1  
Reduction of nitrobenzene to aniline over various catalysts prepared by both methods

| $x$ in La <sub>1-x</sub> Sr <sub>x</sub> FeO <sub>3</sub> | Method of preparation |           |
|---|-----------------------|-----------|
|   | Conventional          | Microwave |
| 0   | 67                    | 69        |
| 0.1   | 86                    | –         |
| 0.2   | 92                    | 91        |
| 0.4   | 87                    | –         |
| 0.5   | 86                    | –         |
| 0.6   | 81                    | –         |
| 0.8   | 83                    | –         |
| 0.9   | 80                    | –         |
| 1.0   | 81                    | 80        |

Nitrobenzene (20 mmol); KOH pellets (20 mmol); catalyst (100 mg); propan-2-ol (20 ml); Time 3 h.

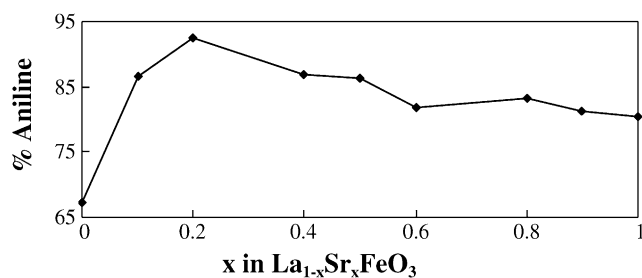


Fig. 2. Graph of yield % of aniline vs.  $x$  in La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3</sub>.

omatics was carried out on this catalyst (Table 2). It can be seen that *ortho*-substituted compounds give comparatively less yields as compared to *para*-substituted compounds, which may be attributed to steric hindrance. In case of 1,3-dinitrobenzene, selectively one nitro group was reduced leading to formation of 3-nitroaniline.

### 3.3. Catalyst reusability

For the study of reusability, La<sub>0.8</sub>Sr<sub>0.2</sub>FeO<sub>3</sub> was chosen. The catalyst could be reused up to five times without any loss in the activity. Also the XRD of the spent catalyst revealed no structural changes. The XRD of the spent catalyst is shown in Fig. 1(d).

Table 2  
Reduction of various nitro aromatics to anilines on La<sub>0.8</sub>Sr<sub>0.2</sub>FeO<sub>3</sub> catalyst

| Substrate            | Product              | Yield (%) | Time (h) |
|----------------------|----------------------|-----------|----------|
| Nitrobenzene         | Aniline              | 92        | 3        |
| 2-Nitrotoluene       | 2-Toluidine          | 89        | 4        |
| 4-Nitrotoluene       | 4-Toluidine          | 94        | 4        |
| 2-Chloronitrobenzene | 2-Chloroaniline      | 85        | 6        |
| 4-Chloronitrobenzene | 4-Chloroaniline      | 96        | 2        |
| 2-Nitroanisole       | 2-Methoxyaniline     | 84        | 6        |
| 4-Nitroanisole       | 4-Methoxyaniline     | 92        | 5        |
| 2-Nitroaniline       | 1,2-phenylenediamine | 92        | 4        |
| 1,3-Dinitrobenzene   | 3-Nitroaniline       | 80        | 6        |

Nitrobenzene (20 mmol); KOH pellets (20 mmol); catalyst (100 mg); propan-2-ol (20 ml).

### 3.4. Reaction kinetics

Kinetic studies were carried out for the reduction of nitrobenzene on  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $x = 0.0, 0.2, 1.0$ ) catalysts. The reaction was found to follow pseudo-first-order kinetics. The values of activation energy for  $\text{LaFeO}_3$ ,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$  and  $\text{SrFeO}_3$  are 88.9, 73.9 and 84.4 kJ/mol, respectively which are found to follow the order  $\text{LaFeO}_3 > \text{SrFeO}_3 > \text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ . The catalytic properties of perovskites for nitrobenzene reduction shows that lower the activation energy, the higher is the catalytic activity.

### 4. Conclusions

The results obtained in this work allow us to conclude that preparation of perovskites by microwave irradiation method have activity similar to those prepared by conventional methods. The method is simple and does not involve intermittent grindings and calcinations at elevated temperatures. Thus we have achieved considerable reduction in time required for preparation of perovskites. These perovskites have excellent catalytic activity for catalytic transfer hydrogenation in liquid phase. The activity of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$  was particularly significant giving quantitative conversion of nitrobenzene to aniline. The catalyst was recyclable without any significant loss in activity.

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