

Methane CO₂ Reforming Using Perovskite Type Oxide as a Catalyst

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Abstract. LaNi_{0.4}Co_{0.6}O₃ perovskite oxide was prepared with the Pechini method and used as a promising catalyst in methane CO₂ reforming. X-ray Diffraction (XRD), Branauer-Emmett-Teller (BET) nitrogen adsorption technique, and Fourier Transform Infrared Spectroscopy (FTIR) were conducted to investigate the catalyst sample. The results showed that a single perovskite phase was formed in the synthesized sample and the conversion of methane in methane CO₂ reforming reached 0.96.

Keywords: Perovskite oxide, Methane CO₂ reforming, Characterization

1. Introduction

Perovskite -type oxides are an important class of catalytic materials and have been widely studied for their application in heterogeneous catalysts [1-4]. A general formula has been used for this type of material which is as follows: ABO₃ (A: alkali, alkali earth, rare earth and some large ions and B: some transition metals). Perovskite type catalysts have higher activity, comparable stability and lower cost than traditional catalysts based on noble metals in many reactions, but their low surface area is a disadvantage [5-6]. One of the most important of the reactions using perovskite oxides as a catalyst is methane CO₂ reforming to produce syngas (H₂+CO). This reaction has attracted much attention from both industrial and environmental aspects [7-8]. Since the methane CO₂ reforming is a highly endothermic reaction, Eq. (1), it has to be carried out at low pressure and high temperature to gain maximum conversions.



In the present work, LaNi_{0.4}Co_{0.6}O₃ perovskite oxide sample was prepared with the pechini method. The synthesized sample was characterized by Fourier transform infrared spectroscopy (FTIR), Branauer-Emmett-Teller (BET) nitrogen adsorption technique, and X-ray diffraction (XRD). Finally the the catalyst sample was tested in the methane CO₂ reforming (MCR) at 800 °C, under atmospheric pressure in a micro reactor.

2. Experimental

2.1. Catalyst Preparation

LaNi_{0.4}Co_{0.6}O₃ perovskite sample was prepared with the pechini method (Fig.1). La(NO₃)₃.6H₂O, Ni(NO₃)₂.6H₂O, and Co(NO₃)₂.6H₂O were used as the sources of Lanthanum, Nickel, and Cobalt respectively.

Heat treatment of the sample was as follows:

Drying: 90°C for 12 h

Calcination: 500°C for 5h and 800°C for 4h

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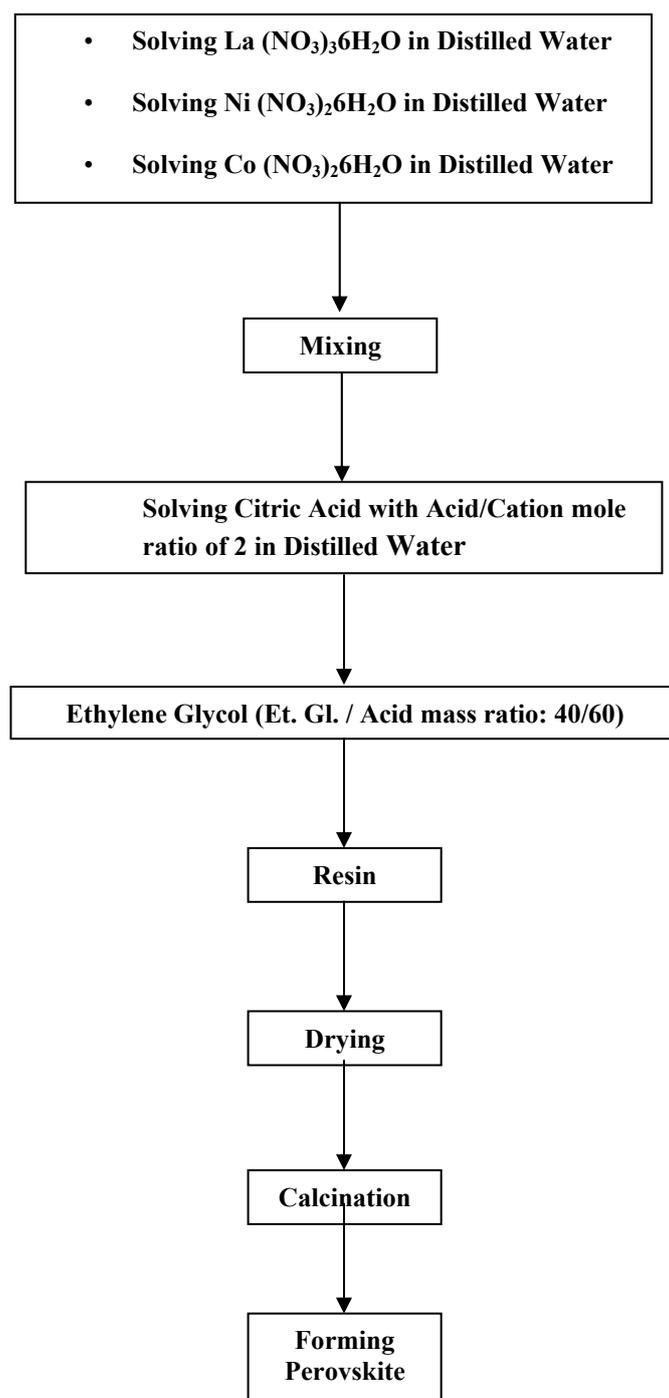


Fig. 1: Formation of perovskite phase by the Pechini method

2.2. Catalyst Characterization

X-ray diffraction (XRD) patterns were collected on a Philips PW1800 diffractometer using Cu K α radiation. FT-IR spectra were recorded on a Shimadzu FT-IR instrument (model IRsolution 8400S) by diluting with KBr in a pellet. The specific surface areas of the samples (S_{BET}) were carried out in a Quantachrome Nova 2000 apparatus. Prior to the adsorption, the supports were outgassed at 300 °C for 3 h.

2.3. Catalyst Evaluation

The catalyst performance in methane CO₂ reforming was evaluated in a fixed bed quartz tubular microreactor (9 mm o.d. and 6.6 mm i.d.), containing 0.2 g of the sample. The activity test was carried out at 800 °C, under atmospheric pressure with a feed composition of CH₄:CO₂ = 1:1 and a total flow of 50 mL min⁻¹. To activate the catalyst, it was previously reduced in situ under hydrogen flow (80 mL min⁻¹). A heat

rate of 5 °C min⁻¹ was used and the gaseous effluent was analyzed on line using a Varian model GC-380 gas chromatograph.

3. Results and Discussions

The XRD pattern of LaNi_{0.4}Co_{0.6}O₃ perovskite sample is shown in Fig. 2. As indicated in this figure, the pure perovskite structure has been formed. The perovskite structure could be indexed to a pseudo-cubic symmetry of the ABO₃ type. It can be concluded that the pechini method was an effective method for preparing a single perfect perovskite oxide.

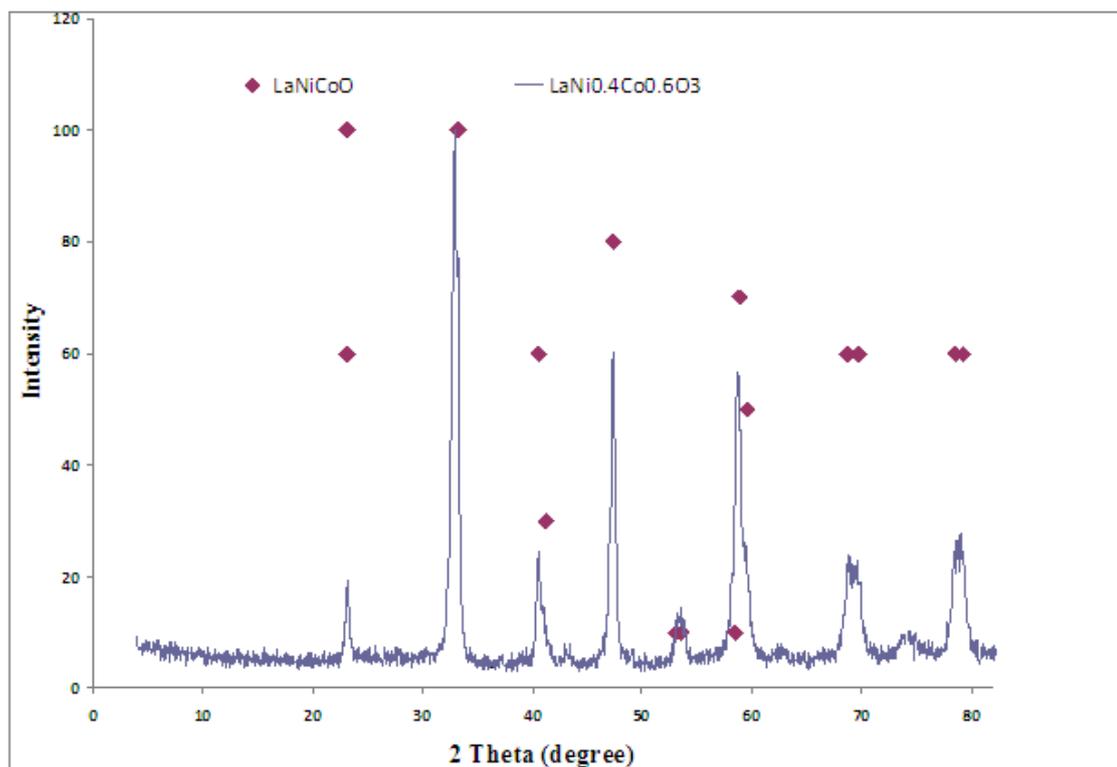


Fig. 2: XRD pattern of the catalyst sample

The FT-IR spectrum of the catalyst sample dried at 90 °C is shown in Fig. 3. A broad band around 3400 cm⁻¹ characteristic of a hydroxyl group can be observed in this figure. There were sharp absorption bands in the vicinity of 1740 and around 1187 cm⁻¹, which can be attributed to the monodentate ligand of a metal ion with carbonyl groups (COO⁻) [9-10].

The specific surface area of the sample was 16 m² g⁻¹. The conversion of methane was defined as the converted amount of methane per total amount of methane in the reactor feed, respectively, as shown in equation (2). The methane conversion of this sample in methane CO₂ reforming at 800 °C was 0.96.

$$X_{\text{CH}_4} = (F_{\text{CH}_4, \text{in}} - F_{\text{CH}_4, \text{out}}) / F_{\text{CH}_4, \text{in}} \quad (2)$$

4. References

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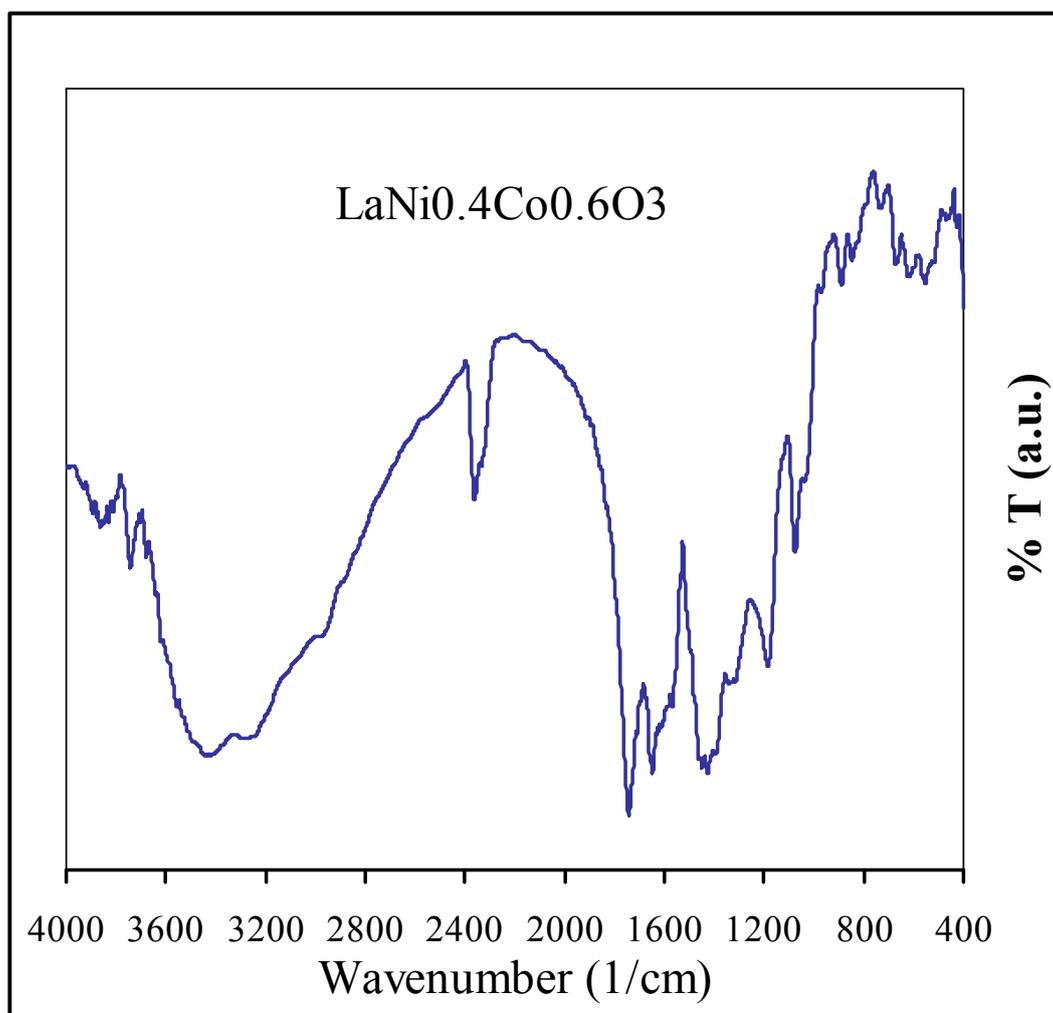


Fig. 3: FT-IR pattern of the catalyst perovskite sample